1951

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Paul Edward Porter
Iowa State College

Recommended Citation

Porter, Paul Edward, "Conductances, transference numbers, and activity coefficients of chlorides of some low atomic number rare earths in aqueous solution " (1951). *Retrospective Theses and Dissertations*. 12980.
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CONDUCTANCES, TRANSFERENCE NUMBERS, AND ACTIVITY COEFFICIENTS OF CHLORIDES OF SOME LOW ATOMIC NUMBER RARE EARTHS IN AQUEOUS SOLUTION

by

Paul Edward Porter

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College

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INTRODUCTION

Modern theories of electrolytic solutions have achieved great success in explaining the deviations from ideal behavior observed in extremely dilute solutions. At the present time, however, the extension of the theories into the region of higher concentrations is not entirely satisfactory. There is a great need for additional experimental evidence of all kinds in order to correlate the various properties of solutions and their dependence upon concentration. The discovery of empirical relationships often points the way to new theoretical treatments, and a fund of experimental data is essential to indicate the directions in which the existing theories must be modified.

The valencies of the ions of an electrolyte play a particularly prominent role in determining the extent of deviations from the laws of ideal solutions. The ions of higher valence type not only show greater deviations from ideal behavior, but are also observed to depart from the theoretical limiting laws at lower concentrations. It follows that a study of the properties of solutions of polyvalent electrolytes should provide the most sensitive indications of desirable modifications of the theories; however, comparatively few experimental data have been obtained for such solutions. In fact, the activity coefficients for only one 3-1 electrolyte have been studied in sufficiently dilute solutions to permit a satisfactory extrapolation of the data to infinite dilution.

The lack of data on polyvalent electrolytes results from the fact that the common polyvalent cations are weakly basic, so that their aqueous solutions are not only subject to hydrolysis but also to undesirable complexing reactions. These difficulties are avoided in using salts of the rare earth elements since they are strongly basic and show little tendency to hydrolyze or to complex with strongly acid anions if reasonable care is taken in the preparation of their solutions.

The rare earth elements, together with yttrium and scandium, are particularly valuable for studies in physical chemistry for another reason. In the series of rare earth elements the inner 4f shell of electrons is being filled, while the external shells of electrons are practically constant for the whole group. Since the characterisitics of the outermost electrons give rise to the observed chemical properties of an element, the rare earth elements are remarkably similar. The only major changes observed through the series are a decreasing atomic radius brought about by the increasing nuclear charge and the corresponding changes in properties resulting from the decrease in radius. Thus, the set of elements from lanthanum through lutetium provides an opportunity for studying the effects of shrinking ionic or atomic radius virtually independently of other factors. At the same time, the inclusion of scandium and yttrium allows a comparison of the effects of removing whole shells of electrons; thus two methods are available for studying the differences in properties brought about by changes in the effective nuclear field strength in the valence shell.

Another feature of several of the rare earths is the existence of absorption spectra in the visible and ultraviolet which result from electronic transitions in the inner shells. These spectra are sensitive to the symmetries of the fields produced by surrounding ions and molecules, but, as a first approximation, are otherwise unaffected by chemical reactions. The bands observed are very narrow and are resolved into sharp lines at low temperatures so that quantitative measurements of the energy levels of the ions are possible. The inner electrons of the rare earth elements are frequently unpaired, and thus give rise to paramagnetic properties which are also sensitive to the symmetries and magnitudes of surrounding fields. These paramagnetic properties can also be used for quantitative studies of the ionic energy levels in crystals and in solutions. The information provided by the absorption spectra and magnetic susceptibilities can be used to study directly the short range forces which surround the ion which largely determine the deviations from ideal behavior in solutions.

The principal deterrent to the use of rare earth salts has been their unavailability; however, they have recently become available through the development in the Iowa State College laboratories (1, 2, 3, 4) of an excellent technique for the separation of the rare earths. The new separation method involves the use of columns of ion-exchange resin, and has been used to produce multi-gram amounts of nearly all of the rare earths in a highly pure form.

The purpose of this thesis is to extend the knowledge of the electrochemical properties of 3-1 electrolytes by studying solutions of the chlorides of some rare earths of low atomic number. It is hoped thereby to supply data from which some conclusions may be drawn in regard to the range of the validity of modern theories and the directions in which modifications may be required. It is realized that similar data must be available for the whole rare earth series, and cross-checks must be possible with such information as heats of solution and dilution, partial molal volumes, dielectric constants, etc., before a complete study can be made. The properties chosen for the present study were conductances, transference numbers, and activity coefficients; these properties were chosen because there are well established limiting laws for them whose extension into the range of higher concentration would be highly desirable. In addition, the conductances, transference numbers, and activity coefficients are of considerable practical use in dealing with ionic equilibria.

CONDUCTANCE

Introduction

The conductances of solutions of electrolytes have played a very significant part in the development of present day theories of ionic solutions. The factors leading to changes in the mobilities of the ions, as a function of their concentration in extremely dilute solutions, have been expressed in the Onsager equation (5) which correctly predicts the limiting behavior of electrolytes at infinite dilution. This equation, however, contains an empirical constant, $\underline{\Delta_0}$, which has not yet been successfully computed theoretically; the equation is also incapable of expressing the experimental data except for the most dilute solutions. The complete solution of the conductance problem is a very worthwhile goal, but the problem can only be attacked when a large amount of information is available. The present work supplies such information for only a limited number of 3-1 electrolytes. It is hoped that the general equation for conductance will become apparent when the conductances of a number of salts have been obtained for the whole rare earth series, and when other electrochemical and thermal properties have been measured.

Theory

When two electrodes are immersed in a solution of an electrolyte and a voltage is impressed across them, a current is observed to flow through the solution. This current under the proper conditions obeys Ohm's law so that it is possible to measure the specific resistance and conductance of the solution. The specific resistance is defined as the resistance of a centimeter cube, and the specific conductance is defined as the reciprocal of the specific resistance.

The conductance of an electrolytic solution may also be expressed in terms of the equivalent conductance or molar conductance. The above quantities can be computed from the measured specific conductances by the equations:

$$\Lambda_e = 1000\,\frac{L}{C_e} \quad \text{and} \quad \Lambda_m = 1000\,\frac{L}{C_m} \qquad (1)$$

in which Λ_e, Λ_m are equivalent and molar conductances, respectively;

L is the specific conductance;

C_e is the concentration of electrolyte in equivalents per liter; and

C_m is the concentration of the electrolyte in moles per liter.

The molar conductance of an electrolyte depends upon the number of ions into which it dissociates, the charges on the ions, and the velocities attained by the ions in an electrical field. The general equation expressing this relationship is:

$$\Lambda_m = n_1 U_1 Z_1 \epsilon + n_2 U_2 Z_2 \epsilon + ---- \qquad (2)$$

in which n_1, n_2, ---- are the numbers of ions of kinds 1, 2, ---- which result from the dissociation of 1 mole of electrolyte;

U_1, U_2, ---- are the ionic mobilities, or the velocities of the ions per volt per cm;

Z_1, Z_2, ---- are the numbers of electronic charges on the ions; and

ϵ is the electronic charge.

For a substance $A_{\nu_+} B_{\nu_-}$ having a degree of dissociation, a, the expression for Λ_m becomes

$$\Lambda_m = N \epsilon \alpha \, (\nu_+ Z_+ U_+ + \nu_- Z_- U_-) \qquad (3)$$

in which N is the Avogadro constant.

The theoretical treatment of electrolytic conductance has been very extensive, and adequate reviews are available of the history and the development of the modern theories of electrolytic solutions (6, 7, 8). While the problem of the theoretical treatment of conductance is by no means solved, the limiting law of Onsager (5) seems to be essentially correct at high dilutions and serves as an excellent extrapolation law for conductivity data; a number of attempts have been made to extend it into a higher concentration range, but very little success has been realized.

The recognition of the basic factors which influence the motion of ions in dilute solutions occurred very soon after the dissociation theory of Arrhenius had become generally accepted. From the beginning it had been realized that the class of strong electrolytes did not obey the Ostwald dilution law or the law of mass action. In addition, for all electrolytes, the simple hypothesis of Arrhenius with regard to conductance, which assumed the mobilities of the ions to be independent of concentration, was not in agreement with the observed dependence of transference numbers upon concentration. The explanation of this apparent anomaly was first advanced by J. J. van Laar (9) who pointed out that if ions exist in solution coulomb forces must also exist among them and must produce an effect on the osmotic pressure, conductance, and other properties. In 1904, Noyes (10) showed that the optical behavior of solutions of colored strong electrolytes indicated that they were completely dissociated even at high concentrations; this observation was confirmed by a number of other investigators using optical properties and other physical properties of the solutions. Sutherland (11), in 1907, made the first attempt to calculate the magnitude of the effects of the ionic interactions on conductance. His calculations were only very approximate, but they showed that the coulomb forces could produce all of the observed conductance decrease with concentration observed for strong electrolytes. Later, Milner (12) developed a mathematical theory for the effects of inter-ionic attraction which was correct, but which employed statistical methods and graphical solutions. Although his theory was too cumbersome for practical use, he was able to show that at low concentrations the deviations from ideal behavior should be proportional to the square root of the concentration. Debye and Hückel (13) found a mathematical device by which they could effect an integration of Milner's equations leading to a highly useful expression for describing the effects of inter-ionic attraction. They assumed that all of the deviations from ideal behavior observed in solutions of electrolytes resulted from coulomb interactions of the ions with one another and with the molecules of the solvent. These coulomb interactions lead to the formation of an "ionic atmosphere" around each ion in a solution such that there will be a slight preponderance of positive ions in the vicinity of each negative ion and vice versa.

Debye and Hückel made the assumption that the time average charge distribution in this ionic atmosphere could be expressed by the Boltzman distribution. Upon this basis they effected an approximate solution of the Poisson equation for the system of ions by expanding the Boltzman exponential expression in series and by disregarding higher terms. This relation provided an expression for the electrostatic potential at the site of an ion, produced by its "ionic atmosphere". This potential could then be used for calculation of the deviations of the solution from ideal behavior as a result of the charge interactions. The fundamental assumptions involved in their theory can be summarized as follows: (1) if the electrical charges were removed from the ions, the solutions would show ideal behavior; (2) the medium in which the ions are immersed is continuous, with no variation of the dielectric constant in the vicinities of the ions; (3) the Boltzman relation correctly expresses the distribution of ions in the "ionic atmosphere"; (4) the Poisson equation is valid for the system of ionic charges and solvent; (5) the net electrostatic potential in the atmosphere of any ion is small enough so that higher terms in the expansion of the exponential expression of the Boltzman distribution may be ignored. These five assumptions are more closely met as the solution becomes more dilute; thus, the Debye-Hückel expression becomes more and more valid as infinite dilution is approached.

Debye and Hückel, using their "ionic atmosphere" concept, developed a preliminary theory of conductance. This theory was later corrected and extended by L. Onsager (5), whose final equation is now generally accepted as the correct limiting law. According to the Onsager treatment, the "ionic atmosphere" of Debye and Hückel affects the mobilities of the ions in two ways, which are usually called "the time of relaxation effect" and "the electrophoretic effect". The "electrophoretic effect" results from the fact that the ions of the "atmosphere" tend to drag solvent molecules with them in a direction opposite to the motion of the central ion when an electrostatic field is impressed upon the system. This phenomenon gives rise to a flow of solvent past any ion which reduces its net velocity. In the Onsager theory all of the effects which produce a frictional drag upon an ion at infinite dilution, or in the absence of other ions, are accounted for in the empirical constant, λ_o, for the ion. Thus the effect of water dragged by the central ion itself is considered in the Λ_o value for a salt, and only the frictional resistance caused by motion of the solvent produced by other ions must be corrected for. The "time of relaxation effect" results from the fact that in an electrostatic field the "ionic atmosphere" moves in a direction opposite to the motion of the central ion. Since it requires a finite time for the "atmosphere" to return to a random condition after it leaves the ion, the effect of the electrical field is to separate the ion and its "atmosphere" into a dipole. The electrostatic attraction of the "atmosphere" end of this dipole upon the central ion results in the partial cancellation of the impressed external field, with a consequent reduction in its mobility.

The Onsager equation has not been solved for the general case and is extremely complicated; however, certain approximations can be made and a simple relationship can be derived as the solutions become dilute. For a binary electrolyte, which is completely dissociated, this simplified "limiting law" can be written:

$$\Lambda = \Lambda_o - S_{(\Lambda)} \Gamma^{\frac{1}{2}} \qquad (4)$$

in which

Λ_o is the equivalent conductance at infinite dilution;

Γ is the ional concentration or $C_1Z_1^2 + C_2Z_2^2$; and

$$S_{(\Lambda)} = \frac{1.970 \times 10^6}{(DT)^{3/2}} \frac{q^*}{1 + \sqrt{q^*}} |Z_1Z_2| \Lambda_o + \frac{28.98(|Z_1| + |Z_2|)}{\eta (DT)^{1/2}}$$

in which

D is the dielectric constant of the medium;

T is the absolute temperature;

η is the viscosity of the solution; and

$$q^* = \frac{|Z_1Z_2|}{(|Z_1| + |Z_2|)} \quad \frac{\Lambda_o}{(|Z_2| \lambda_1^\circ + |Z_1| \lambda_2^\circ)}$$

in which

$\underline{\lambda_1^\circ}$ and $\underline{\lambda_2^\circ}$ are the equivalent ionic conductances at infinite dilution for ions 1 and 2.

In the expression for $\underline{S_{(\Lambda)}}$, the first term represents the "time of relaxation" effect, and the second term is the "electrophoretic effect". It must be remembered that this expression does not include effects of incomplete dissociation. This effect must be separately considered if the degree of dissociation of the electrolyte changes upon dilution. The Onsager law is the best means of extrapolating experimental data to infinite dilution, since it increases in validity as the concentration approaches zero; this is not true of empirical equations which are sometimes applied. The use of the Onsager equation for making the extrapolation will be further described in the experimental section.

History of Conductance Measurements

The literature on the measurement of conductance of solutions is very extensive. Since the subject has been adequately covered by others (14, 15, 16) it will not be reviewed in detail in this thesis; however, some of the more important developments will be mentioned.

Accurate measurements of electrolytic conductances began in 1868 when F. Kohlrausch (17) introduced the use of an alternating current bridge to avoid polarization effects. Kohlrausch developed the method of measurement to such a high degree of precision that his results are still some of the best available. In 1916, Taylor and Acree (18) made a thorough study of the factors entering into precision measurements. They studied various oscillators for producing the current, and concluded that the Vreeland oscillator was much superior to other devices. They also studied bridge and cell design and the preparation of solutions and were able to attain a reproducibility of 0.001 per cent in their measurements. Washburn (19) investigated the design of cells and the characteristics of the telephone receivers used as null indicators; his work effected considerable improvement. Hall and Adams (20) devised a suitable amplifier to be used with the detector, thus improving sensitivity.

H. C. Parker (21) found that the cell constant for conductance cells in use at that time varied with the resistance measured. This important effect was attributed by him to adsorption, but was later shown by Shedlovsky (22) and by Jones and Bollinger (23) to result from capacitance effects in the cell. The latter investigators designed cells which avoid this effect.

Morgan and Lammert (24), in 1926, discussed the problems of measuring electrolytic conductance upon the basis of all data available at that time. They also studied the design and shielding of the bridge, and paid particular attention to the characteristics of the oscillator. Jones and Josephs (25), in 1928, made a classic study of the conductance bridge and accessories which is still used as the basis for bridge design. T. Shedlovsky (26) devised a bridge arrangement capable of high accuracy, which differed only in the manner of shielding from the recommendations of Jones and Josephs.

In recent years the work of Jones and his associates has brought the measurement of conductance to a very high degree of accuracy. Jones and Bollinger (23) and Jones and Christian (27) studied design and use of conductivity cells; their work was so carefully performed that this paper has become the guide for the proper construction of conductance cells.

A most important factor in the measurement of conductances is the calibration of the conductance cells. By definition, the specific conductance of a solution is the reciprocal of the resistance of a centimeter cube of solution. Thus, if the electrodes of a conductance cell have an area <u>A</u>, and if they are separated by a distance <u>s</u>, the relation between the specific conductance and the measured resistance will be:

$$L = \frac{s}{RA} \; . \qquad (5)$$

In principle, each of the quantities s, A, and R can be measured in order to compute L; however, it is much simpler in practice to set up a secondary standard solution of known L value, and to evaluate s/A for the cell by measurement of the cell resistance when filled with the secondary standard. The quantity s/A is called the cell constant for the given cell. F. Kohlrausch (28) first set up a secondary standard by measuring the resistances of potassium chloride solutions in a number of conductance cells whose s/A values were measured very precisely. These specific conductance values were used until 1924, when the improvements in measuring techniques required a more careful specification of the method of preparing the potassium chloride solutions. The conductances were re-determined by Parker and Parker (29), but their data have been superseded by those of Jones and Bradshaw (30) and Jones and Prendergast (31). Jones and Bradshaw used a direct comparison of the conductances of the solutions employing mercury as the primary standard. This was accomplished by using a series of conductance cells of gradually decreasing values of cell constant. In the cell having the highest constant, the calibration was made by measuring the resistance when filled with pure mercury at 0°C. Since mercury at the above temperature is the primary standard for resistance, the cell constant so obtained is better than could be obtained by measuring cell dimensions. The specific conductance of a strong solution of sulfuric acid was measured in the calibrated cell, and this value was used as a secondary standard in calibrating the next cell in the series. The latter cell was satisfactory for the measurement of a 1 demal potassium chloride solution (one gram-molecular weight of electrolyte per 1000 grams of solution). The 1 demal potassium chloride was used to calibrate the next cell, which was then employed in standardizing a 0.1 demal solution. In this manner measurements of potassium chloride solutions were obtained for use as standards. After the entire set of measurements had been made at 0°C, they were extended to other temperatures; for these temperatures, the coefficients of thermal expansion for the various parts of the cells were used in calculating the cell constants. Jones and Prendergast (31) used the above procedure, but attempted to reproduce the solutions and temperatures initially used by Kohlrausch. Their data agree almost exactly with those of Kohlrausch, thus attesting to the high degree of accuracy attained by him with his relatively primitive apparatus.

Experimental

Preparation of solutions

The lanthanum oxide was obtained from the Lindsay Light and Chemical Corporation. The cerium oxide was prepared from a sample of cerium ammonium nitrate purchased from the G. Frederick Smith Chemical Company. The praseodymium and neodymium oxides were prepared by the rare earth group of the Ames Laboratory under the direction of Dr. F. H. Spedding. The purities of the oxides are given in Table 1. In all cases these oxides were further purified by two precipitations with doubly recrystallized oxalic acid in solutions approximately one normal in hydrochloric acid. The final oxalate precipitate was ignited in platinum.

The freshly ignited oxides were dissolved in an excess of redistilled hydrochloric acid. Chlorine was bubbled through the solution which was boiled vigorously to remove any possible bromine contamination and finally was evaporated to a thick syrup on a hot plate. Further drying was accomplished by placing the syrup in a pyrex tube, and heating under vacuum on a water bath until the remaining chloride crystals appeared flaky in composition. The final drying was accomplished by heating slowly in a hydrogen chloride atmosphere to a final temperature of 300-400°C. The hydrogen chloride, generated by dropping concentrated sulfuric acid into concentrated hydrochloric acid, was dried by passing the gas in succession through a bubbler filled with concentrated sulfuric acid; a dry ice-acetone cold trap; and a calcium chloride drying tube immersed in dry ice-acetone mixture. In the final drying step it was found to

TABLE 1

Purities of Rare Earths.

Element	Purity[*]
Lanthanum	No other rare earths or thorium detected by emission spectrography. Trace of calcium detected prior to two precipitations of oxalate from acid solution.
Cerium	No other rare earths, thorium, or common elements detected by emission spectrography.
Praseodymium	No other rare earths or thorium detected by emission spectrography. Faint traces of magnesium and calcium detected prior to two precipitations of oxalate from acid solution.
Neodymium	No other rare earths or thorium detected by emission spectrography. Faint trace of magnesium detected prior to two precipitations of oxalate from acid solution.

[*] The limit of detection of rare earths was about 0.02 to 0.03 per cent. That for common elements was about 0.01 per cent.

be essential to halt the temperature at several points to prevent melting of the crystals; oxychloride was formed, which was not re-converted to chloride upon further heating if the crystals were allowed to melt at any stage. Since the hexahydrates melt at about 80°C, the first halt was made below this temperature and the heating was continued until no water was evolved in the hydrochloric acid stream. The next halt was made in the vicinity of 100°C, and the final halt at about 160°C. The furnace could then be rapidly heated to the final temperature after water had ceased to be evolved at the last temperature. After the drying had been completed, the apparatus was flushed with helium until no hydrogen could be detected in the exit gas; the sample was then cooled and bottled in a previously weighed weighing bottle. The sample weight was obtained by re-weighing the bottle and contents.

To prepare the solutions, the lid of the weighing bottle was carefully removed and placed in a small beaker. The weighing bottle was inserted into a special glass apparatus which allowed the chloride to be slowly added to conductance water in a calibrated two-liter volumetric flask with the whole system closed. This precaution was observed because some investigators (32) have found that rare earth chlorides tend to expel hydrochloric acid on dissolving in water. After the transfer had been completed, the weighing bottle and attachment, as well as the lid and the beaker, were rinsed and the washings added to the flask. Finally, the solution was diluted to volume at 25°C.

The resulting solutions were completely clear and no residues were observed. The pH values, measured with a Beckman model G pH meter, were from 6.4 to 6.6. The normalities were calculated from the weights of the chloride added. They were checked by precipitation of aliquots with oxalic acid and weighing as oxalate; the analyses agreed within 0.1 per cent with the chloride weights in all cases. Test solutions were prepared by dilution of the stock solutions using calibrated volumetric ware. The water employed in all cases was conductance water having a specific conductance from 0.7 to 1.2 x 10^{-6} mho/cm.

Apparatus

The conductivity bridge was built by Leeds and Northrup Company in accordance with the recommendations of G. Jones (27); it is completely described by P. H. Dike (33). The oscillator and amplifier were also purchased from Leeds and Northrup (catalog numbers 9842 and 9847) and also conform to the high standards set by Jones. A Dumont type 208B five-inch cathode ray oscilloscope was used as a null-point detector, and was found to be a substantial improvement over the earphones normally employed.

The conductivity cells were commercially available types (Leeds and Northrup catalog numbers 4911, 4914, and 4915). They were platinized before use by the procedure recommended by Jones and Bollinger (34). The cells were found to have a slight Parker effect so that they were calibrated at a number of points; plots of cell constant against observed conductance were used to determine those constants applicable to the conductivity range to be studied. These plots are shown in Figure 1; no plot is shown for the high-concentration cell since no Parker effect was observed in this case. The potassium chloride used for calibration was prepared by twice recrystallizing reagent grade material and fusing in nitrogen. The calibrating solutions were made up to known normalities and the equivalent conductances listed by Shedlovsky (35) were used as standards.

The constant temperature bath maintained the temperature within 0.02°C as determined by a thermometer marked in 0.01° divisions and calibrated by the National Bureau of Standards. This bath was adequate for an accuracy within 0.1 per cent; for an accuracy of 0.001 per cent, a bath having a constancy of 0.001°C would be required.

Results

The data obtained for solutions of lanthanum, cerium, praseodymium, and neodymium chlorides are given in Tables 2, 3, 4 and 5, and are plotted in Figure 2. The ordinates

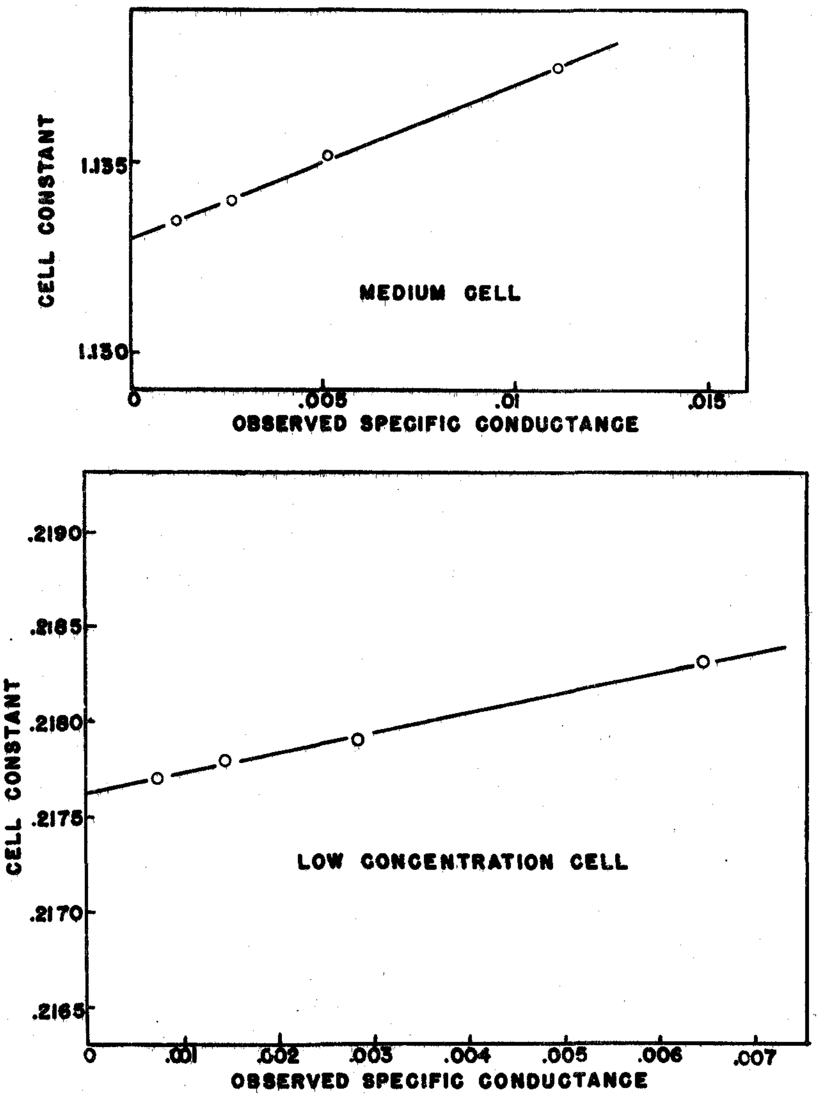


Figure 1. Calibration Data for Conductivity Cells.

TABLE 2

Equivalent Conductances of Lanthanum Chloride at 25°C.

Normality	Equivalent conductance
0.00000	(146.1)
0.0004967	140.0
0.002483	132.4
0.006209	126.0
0.009030	123.0
0.01242	120.1
0.01806	116.5
0.02483	113.3
0.04967	106.4
0.09933	99.1

TABLE 3

Equivalent Conductances of
Cerium Chloride at 25°C.

Normality	Equivalent conductance
0.00000	(146.2)
0.0004605	140.9
0.001535	135.3
0.004605	128.3
0.007675	124.4
0.01075	121.4
0.01535	118.0
0.04605	107.2
0.07675	101.9
0.1075	98.5

TABLE 4

Equivalent Conductances of Praseodymium Chloride at 25°C.

Normality	Equivalent conductance
0.00000	(146.0)
0.0008972	137.6
0.001794	134.5
0.003589	130.1
0.007177	124.9
0.01077	121.3
0.01794	116.5
0.05383	105.6
0.07177	102.2
0.1077	98.1

TABLE 5

Equivalent Conductances of

Neodymium Chloride at 25°C.

Normality	Equivalent conductance
0.00000	(146.6)
0.0004521	140.7
0.002621	133.4
0.004521	129.1
0.007642	124.5
0.01274	119.9
0.02547	113.3
0.05095	106.3
0.07642	102.0
0.1274	96.6

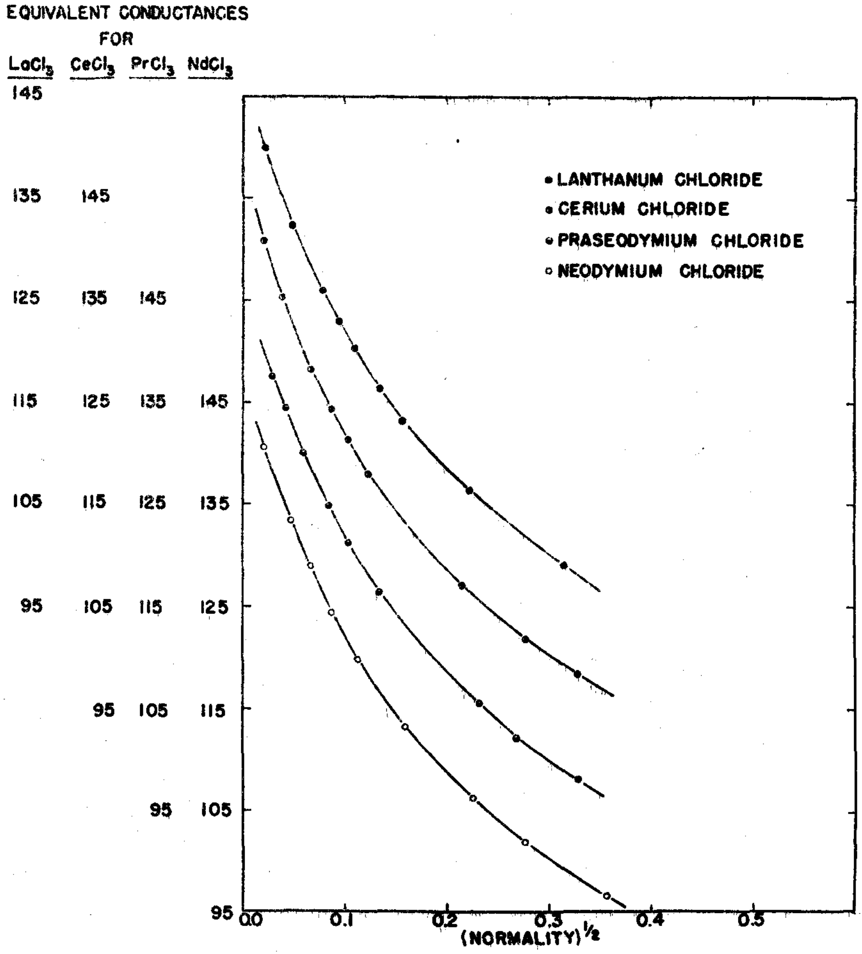


Figure 2. Equivalent Conductances of Rare Earth Chloride Solutions.

in this figure are staggered in order to separate the four curves.

Values of the equivalent conductance at infinite dilution were obtained by extrapolation using the Onsager limiting law, which for the special case of 3-1 electrolytes has the form:

$$\Lambda = \Lambda_0 - (3.3158\, Y\Lambda_0 + 170.25)\sqrt{C} \qquad (6)$$

in which

$$Y = \frac{0.75\Lambda_0/\Lambda_0 + 2\lambda_-^0}{1+\sqrt{0.75\Lambda_0/\Lambda_0 + 2\lambda_-^0}}$$

The limiting ionic conductance, λ_-^0, for the chloride ion is known to be 76.34 as calculated from the transference number and conductance data for hydrochloric acid, lithium chloride, sodium chloride, and potassium chloride; it follows that Λ_0 can be expressed as a function of Λ and C/Λ in the above equation. Thus, a Λ_0 value can be calculated for every experimentally determined Λ value given in Tables 2 through 5. These calculated Λ_0 values are distinguished from the true values of Λ_0 by the use of a prime. Since the Onsager equation becomes valid as the concentration is reduced, a plot of Λ_0' against C should asymtotically approach the true value of Λ_0 as C approaches zero. The true Λ_0 value is a constant for the salt and would plot as a straight line parallel to the concentration axis; the limiting slope of the plot must be zero since the plot of $\underline{\Lambda_0'}$ against concentration approaches this line as the solution becomes more dilute. This fact is an aid in making the extrapolation since the curve through the experimental points must be so drawn that it enters the axis of zero concentration with zero slope. The data for the four rare earths are plotted in Figure 3. The resulting values of $\underline{\Lambda_0}$ are listed in Tables 2 through 5 at zero concentrations.

Discussion of Results

The conductances of lanthanum chloride in aqueous solutions at 250°C have been previously determined with high precision by Jones and Bickford (36) and by Longsworth and MacInnes (37). The measurements were repeated in this investigation as a check on the preparation of solutions and the measuring technique. The satisfactory agreement of the data of Table 2 with those of the above investigators is shown in Figure 4.

The extent to which the Onsager limiting law is obeyed by solutions of the rare earth chlorides is indicated by the plots of $\underline{\Lambda - \Lambda_0}$ against $\underline{\sqrt{C}}$ shown in Figure 5. Good agreement is observed up to about 0.002N. The convergences with the expected slopes are excellent confirmations of the validity of the limiting law.

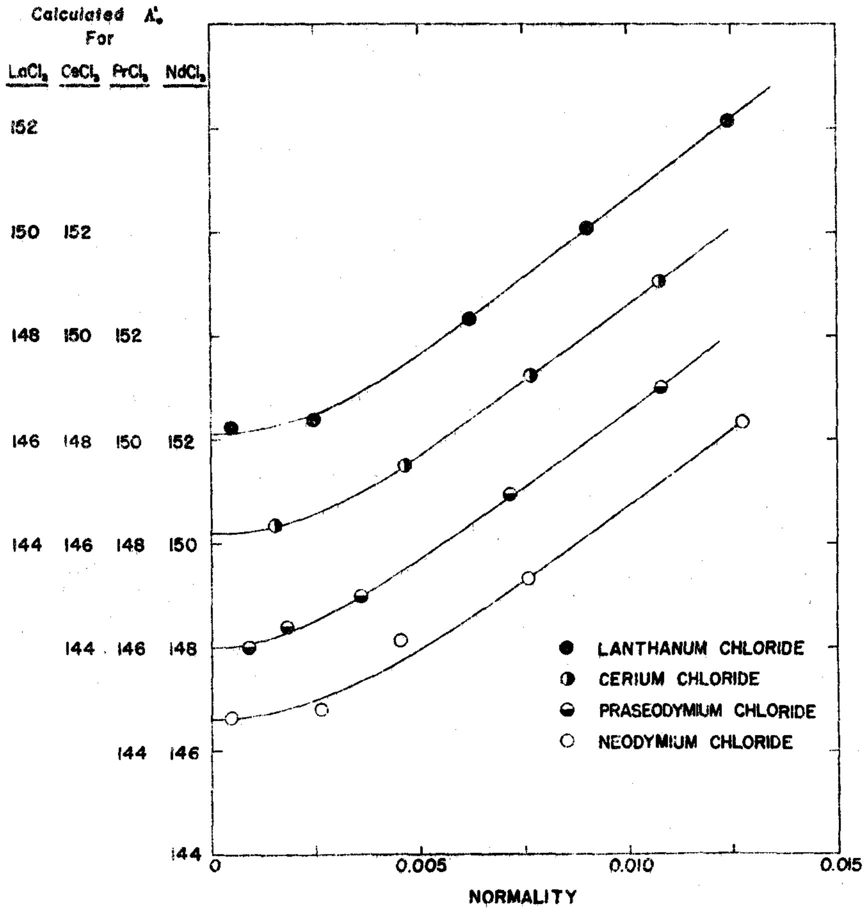


Figure 3. Extrapolation of Conductance Data to Infinite Dilution.

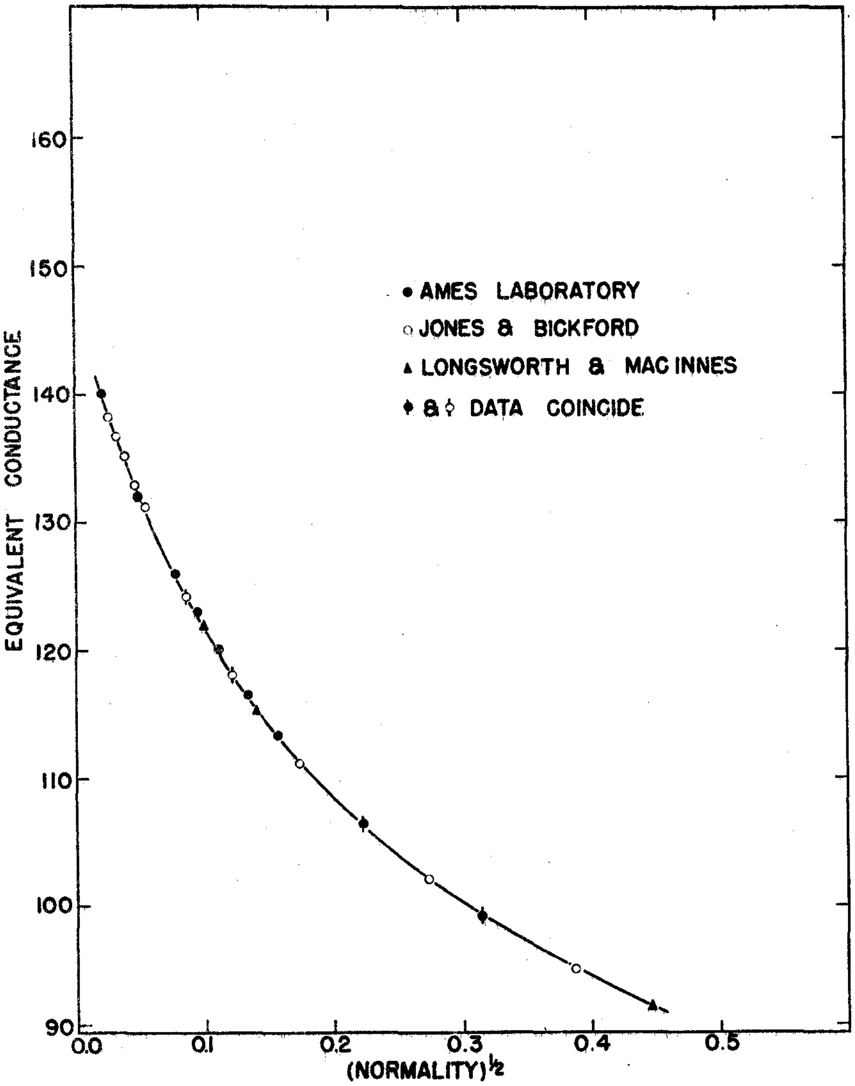


Figure 4. Comparison of Conductances of Lanthanum Chloride Solutions Obtained by Various Investigators.

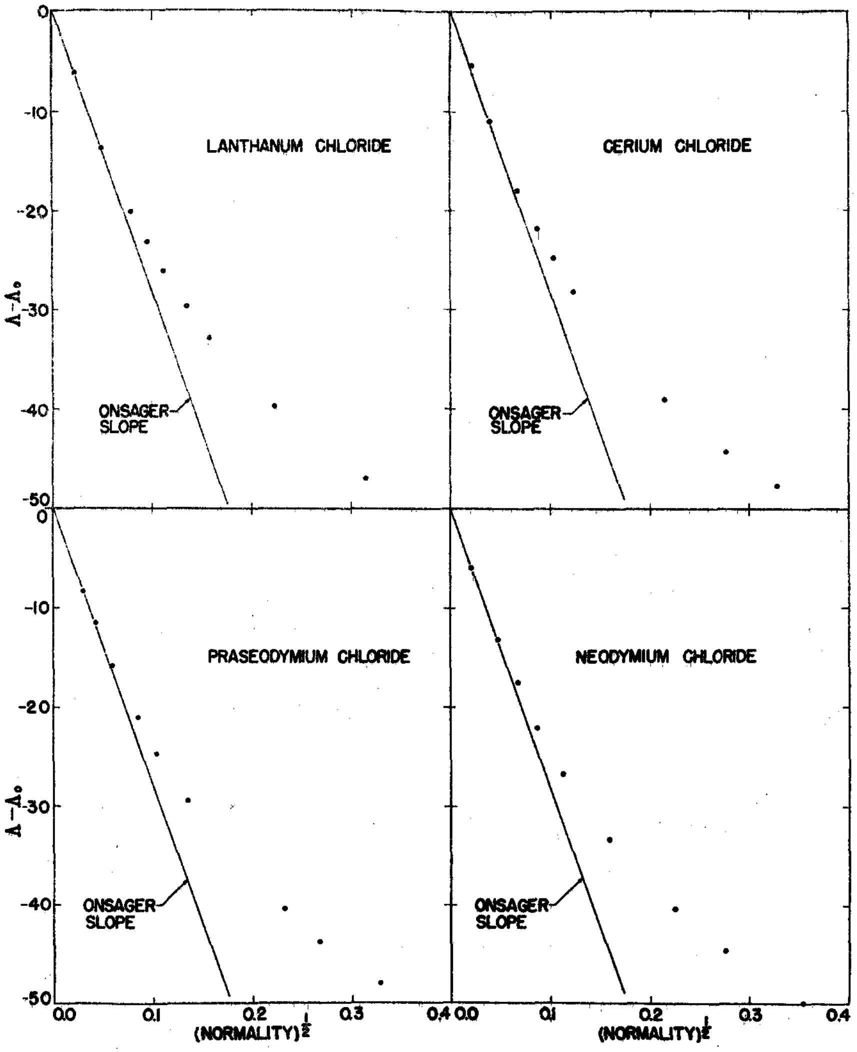


Figure 5. The Agreement of the Conductances of Rare Earth Chloride Solutions with the Onsager Limiting Law.

The conductances of the solutions of the chlorides of samarium, europium and ytterbium have recently been determined in the Iowa State College laboratories (38); a comparison of these data with those reported in the present thesis is given in Figure 6. The differences are more clearly evident in the combined plot of $\underline{\Lambda'_o}$ against normality in Figure 7. The rare earths, beginning with neodymium, show a progressive decrease in conductance with atomic number in spite of the fact that there is a progressive decrease in the crystallographic ionic radius for these elements. This fact suggests that the hydration of the ions plays a predominant role in determining the limiting mobility. The lack of a regular decrease in conductance for the first four elements is somewhat anomalous, since the rare earth series would be expected to show a regular change in properties over the whole series. A possible explanation, in view of the apparent importance of the hydration of the ions, is that as the ion becomes larger with lower atomic number a second coordination number may become possible, so that an equilibrium may be set up between two kinds of hydrated ions having different coordination numbers. A change of this type would undoubtedly give rise to a change in the effective radius of the hydrated ion and in the amount of water dragged with the ion in motion. Crystallographic evidence indicates that a change in the hydration

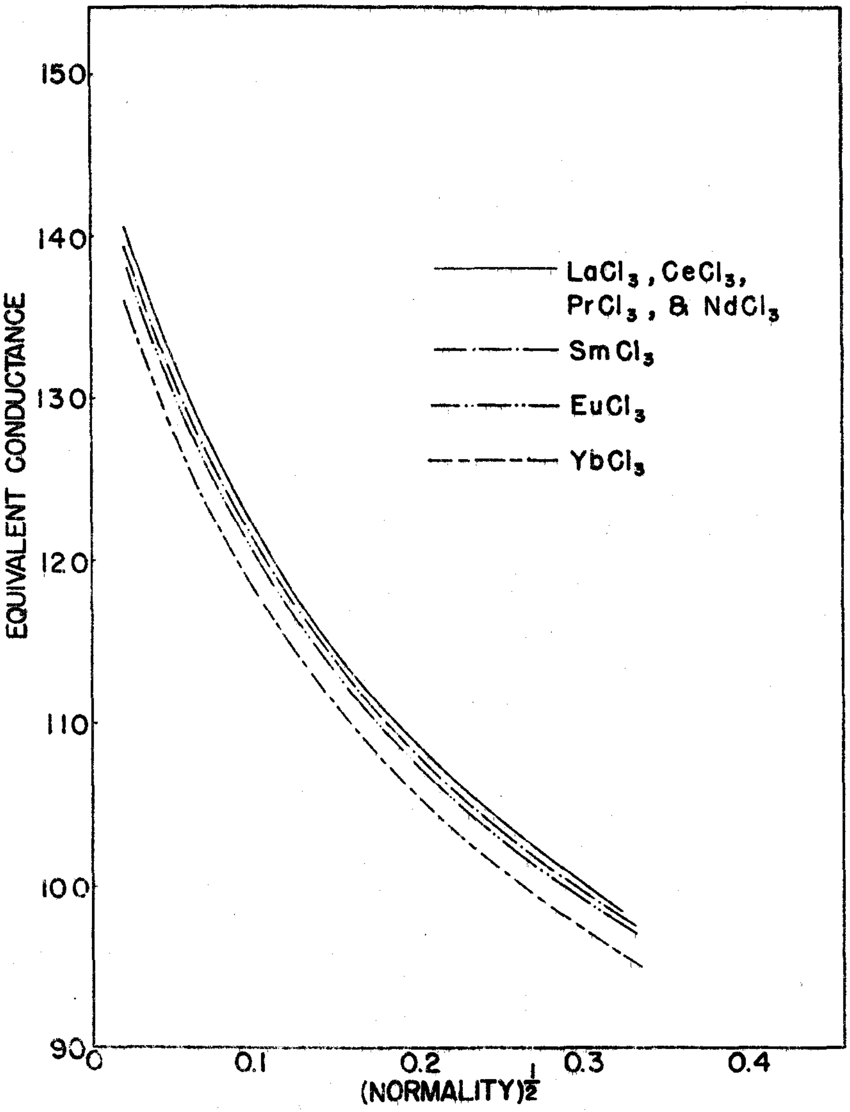


Figure 6. Comparison of the Equivalent Conductances of Rare Earth Chloride Solutions.

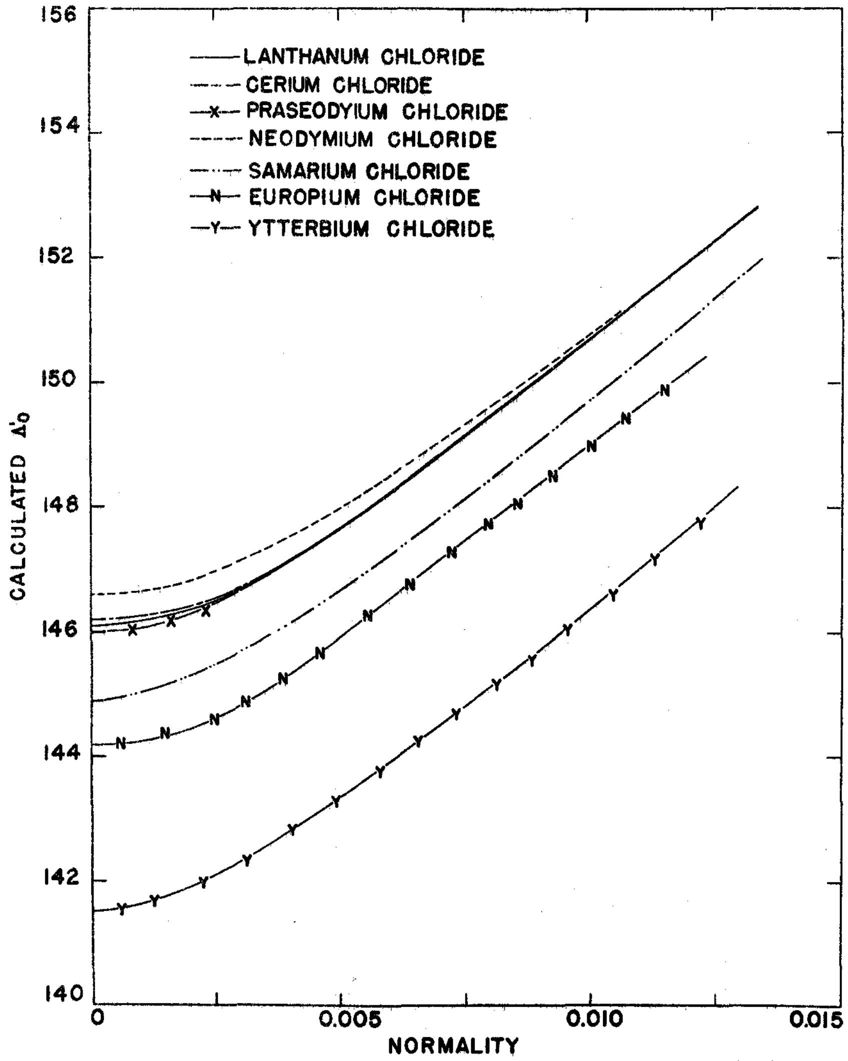


Figure 7. Comparison of the Limiting Conductances of Rare Earth Chloride Solutions.

of rare earth salts, in crystal form, occurs in the neighborhood of neodymium; in addition, x-ray measurements on lanthanum sulfate enneahydrate show that two different coordination numbers exist for the lanthanum ions in the same crystal. At the present time there are insufficient data for definite conclusions to be made; more crystallographic data should be obtained for the hydrated salts, and conductance measurements should be extended to higher concentrations.

The limits of error in the conductance determinations presented in this thesis were set by the accuracy of preparation of the solutions. The errors in measuring the resistances of the cells, as well as those resulting from calibration of the cells were estimated to be below 0.05 per cent, and the uncertainties in the molarities of the rare earth chloride solutions were less than 0.1 per cent.

TRANSFERENCE NUMBERS

Introduction

The transference number of an ion in solution is the ratio of the migration velocity of the ion to the sum of the velocities of the other ions in the solution. Values of the transference number of the ions and of the conductance of the solution, permits the calculation of absolute ionic mobilities and furnishes a means for studying the Onsager limiting law for the individual ions. A knowledge of the individual ionic mobilities of the rare earth series should be of particular interest, since variations in their ionic conductances can then be compared with such quantities as ionic radius and coordination number without making any arbitrary assumptions relative to the contribution of the chloride ion.

Measurements of the transference numbers of a salt can be made in three ways: (1) the Hittorf method, (2) the moving-boundary method, and (3) the electromotive force method. These three methods will be described in detail in following sections of this thesis. The first method involves an analytical procedure which is very time-consuming and is now of historical interest only. The third method requires the use of electrodes reversible to both ions of an electrolyte, and thus cannot be applied to the study of rare earth salts until suitable reversible rare earth electrodes can be found. The moving-boundary method was used in the present work since it is applicable to the rare earth salts and is convenient and accurate.

Theory

The different kinds of ions in an electrolytic solution do not migrate with the same velocities in an electrical field, but each species possesses a characteristic mobility of its own. As a result, the ions do not transport equal amounts of electric current during electrolysis. The fraction of the total current which is carried by a particular species of ion is called the transference number of that ion.

Thus:

$$\mathcal{T}_i = q_i/Q = \frac{C_i\ Z_i\ U_i}{\sum\limits_s C_s Z_s U_s} \tag{7}$$

in which

$\mathcal{T}_i$ is the transference number of the ith ion;

C_s is the equivalent concentration of ion species s; and

U_s is the velocity of the ion species, s, in an electrical field of given strength.

For a binary electrolyte the equation becomes:

$$\tau_+ = \frac{C_+Z_+U_+}{C_+Z_+U_+ + C_-Z_-U_-} \qquad (8)$$

or, since for a binary electrolyte $C_+Z_+ = C_-Z_-$,

$$\tau_+ = \frac{U_+}{U_+ + U_-} \quad . \qquad (9)$$

There are three kinds of transference numbers, depending upon the standard relative to which the velocities of the ions are measured. The most useful type is the Hittorf number which measures the velocities relative to the solvent. Another type is the Nernst number which is sometimes called the "true" transference number; it is a measure of velocities relative to molecules of inert solute present in the solution which are supposedly not influenced by the electrical field. The third type measures the velocities relative to fixed points on the walls of the containing vessels; this type of transference number is not a true physical property of an electrolytic solution, but combines the characteristics of the ionic motions with the structural characteristics of the apparatus. Therefore, when transference numbers of the third type are measured, as in the uncorrected moving-boundary method, they are always corrected to one of the other types. The differences among the three kinds of transference numbers result from the fact that different amounts of solvent are transported by the positive and negative ions owing to differences in their solvation and in their velocities. There is thus a net transport of solvent in the direction of one of the electrodes, which produces a motion of the solution as a whole. The resulting motion of the solution is dependent upon the shape, size, and other characteristics of the electrolysis vessel; this motion can be corrected for in either of two ways. In the Hittorf method the net motion of <u>solvent</u> during the electrolysis is either calculated or obtained in an analysis of the solutions; the correction is made so that the velocities of the ions relative to the solvent are obtained. In the Nernst method an inert solute, such as raffinose, is added to the solution and the motion of the <u>solution</u> is observed by analyzing the contents of various parts of the cell for the inert solute after electrolysis; the velocities of the ions are obtained relative to the inert solute molecules. There is a small numerical difference between the two methods which, in general, becomes larger for higher concentrations. Either the Hittorf or the Nernst numbers can be used in thermodynamic equations; however, the Hittorf number is more convenient for this purpose because its use avoids any correction for solvent transfer. When calculations are made using the Hittorf number the solvent is considered to be stationary.

The theory of transference numbers is closely associated with the theory of electrolytic conductance, since both phenomena depend upon the migration velocities of the ions. Since the ionic conductances are proportional to the ionic velocities:

$$\tau_+ = \frac{\lambda_+}{\lambda_+ + \lambda_-} = \frac{\lambda_+}{\Lambda} \qquad (10)$$

The Onsager theory of conductance can be used to express both $\underline{\lambda_+}$ and $\underline{\Lambda}$ as functions of concentration, and thus the concentration dependence of the transference number can be expressed. The resulting expression is very complex, but at low concentrations it becomes:

$$\tau_+ = \tau_+^{\circ} + S_{(\tau)} \sqrt{C} \qquad (11)$$

in which

$$\underline{S_{(\tau)}} = \left(\frac{\tau_+^{\circ} \left(|Z_+| + |Z_-| \right) - |Z_+|}{\left(|Z_+| + |Z_-| \right) \Lambda_o} \right) \beta^*$$

in which

$$\underline{\beta^*} = \frac{28.98 \left(|Z_+| + |Z_-| \right)^{3/2}}{\eta \, (DT)^{1/2}}$$

in which

$\underline{\eta}$ is the absolute viscosity of the solution;

$\underline{D}$ is the dielectric constant; and

$\underline{T}$ is the absolute temperature.

The above expression has been found to fit the experimental data quite well for uni-univalent electrolytes, but it is not very satisfactory for ions of higher valence. It is possible that this is due to the formation of ion-pairs; however, if this were the case, greater deviations would be expected from the limiting law in the case of conductance than are actually observed.

History of the Method

The first evidence for the fact that the positive and negative ions of an electrolyte do not transport the same amount of charge during electrolysis was obtained by Daniell (39). He electrolyzed a number of acids, bases and salts in a three compartment apparatus in which the compartments were separated by diaphragms of bladder. After electrolysis, he analyzed the contents of the anode compartment and cathode compartment, and found that the concentration changes in the two solutions were different. This phenomenon was not explainable on the basis of the old theory of conductance propounded by Grotthuss, but it could be explained on the basis of unequal transport of current by the cations and anions.

In 1853, Hittorf (40) began his more quantitative studies on ion migrations using the same type of apparatus, but under more carefully controlled conditions. He confirmed the earlier observations and, over the period of years from 1853 to 1903, collected a large number of data on the transference numbers of electrolytes. Unfortunately, although his methods were constantly improved and his researches laid the groundwork for the study of transference, his data never reached a degree of accuracy which would render them useful today. In spite of this fact, the work of Hittorf was of fundamental importance in the development of the law of independent ion migration advanced by Kohlrausch in 1876 and the dissociation theory proposed by Arrhenius in 1884.

Accurate studies on transference numbers began when the dissociation theory had been placed upon a firm foundation and the essential features of the mechanism of electrolytic conductance were known. Many methods of determination were tried; however, only three of them were capable of sufficient accuracy to warrant attention: (1) the Hittorf method, (2) the moving-boundary method, and (3) the electromotive force method. The first two will be discussed in the present section; the third will be discussed in the section on activity coefficients.

The Hittorf method, or analytical method, for determining transference numbers has remained essentially unchanged since the initial measurements. The many improvements in technique which have been made consist of improvements in analytical methods; devices for measuring the current; and in the arrangement of the three compartments of the electrolysis vessel. The most recent applications of this method by MacInnes and Dole (41) and by Jones and Bradshaw (42) have reached a high degree of accuracy; however, the painstaking care required and the amount of time needed for such measurements have caused it to fall into disfavor. Since the Hittorf method is now of historical interest only, its development will not be further considered here. A full treatment of the details of the method is given by MacInnes (6).

The moving-boundary method was originated by O. Lodge (43) who set up an apparatus for the study of absolute ionic velocity. The apparatus consisted of two cups joined by a horizontal tube filled with gelatin gel containing an electrolyte having a different ion from that to be measured; it also contained a very small amount of indicator or precipitant whose reaction with the ion to be studied would indicate depth of penetration of the ion into the gel. The cups were filled with a solution containing the ion whose mobility was under study; the electrodes were inserted; a voltage was impressed across the cell; and the rate at which the ion passed through the gel was measured.

In 1893, W. C. D. Whetham (44) showed that Lodge had not correctly estimated the voltage gradient in his tube. He pointed out that Ohm's law, together with the specific resistance of the electrolyte solution in which the ion moved, should be used in evaluating the gradient. Whetham carried out experiments using an apparatus in which a liquid junction could be formed in a narrow-bore tube between two solutions of electrolyte having one ion in common. The salts were always chosen so that the ions not common to both were different in color so that the boundary was visible. When a current was passed first in one direction, and then in the other, the motion of the boundary was observed and the velocities of the ions in the field were obtained. The two solutions were always selected in such a way that the specific resistances were nearly equal, in order that the potential drop should be uniform throughout the tube.

In 1897, the first theoretical treatment of the concentration changes and the motion of concentration gradients during electrolysis was published by Kohlrausch (45). This theory was merely an application of the equation of continuity, familiar to physicists, to the problem of ionic migrations in an electric field. Although Kohlrausch was well aware of the facts that the ionic mobilities varied with concentration and that the charges on the ions themselves would cause some variations in the mobilities, he chose to ignore these factors since insufficient information about their magnitudes was available. He considered his theory to be a limiting law which could be used to predict the factors which might enter into electrolysis experiments. Kohlrausch applied his equation of continuity to the case in which three species of ions are present; he used boundary conditions for solving the equation appropriate to the moving-boundary experiment. He found that, for a stable moving-boundary to be formed, the slower ion should follow the faster and that the concentrations of the electrolytes leading and following the boundary should be adjusted to the so-called "Kohlrausch ratio", $T/C = T'/C'$, in which the unprimed values are those for the leading ion and the primed values are those for the following ion. The Kohlrausch equations show that the migration velocity of a boundary between solutions not adjusted to the proper ratio is not constant, but that the following and leading solutions automatically adjust themselves to the Kohlrausch ratio by the action of the electrical current so that the motion of the boundary soon becomes constant. Masson (46), in 1899, arrived at essentially the same conclusions by experiment independently of Kohlrausch, and thus demonstrated the essential validity of the above approach.

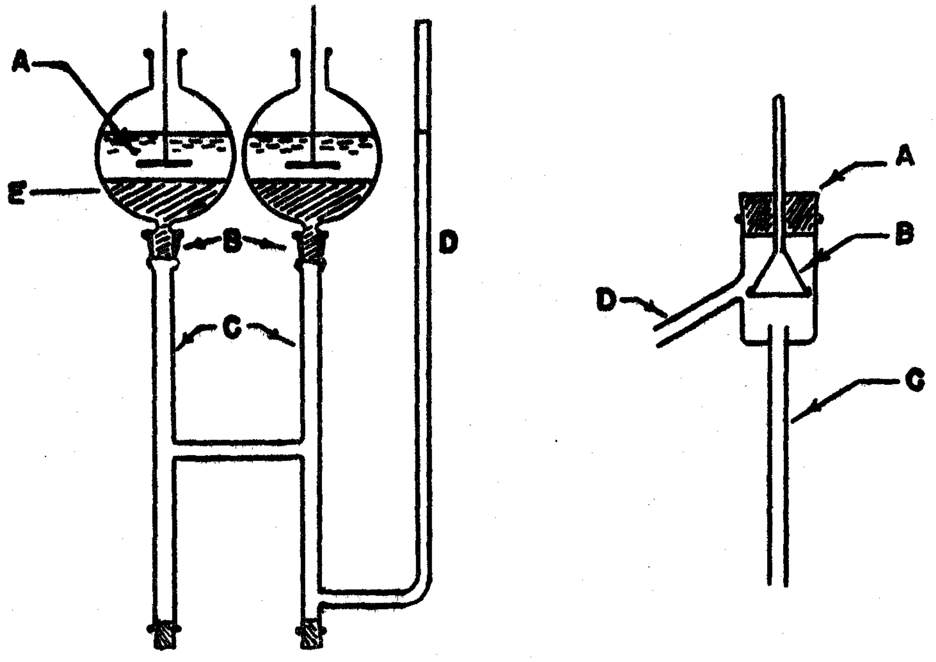
Weber (47), Nernst (48), and Planck (49) improved the details of the Kohlrausch theory, principally through the introduction of the effects of diffusion. So far as the determination of transference numbers were concerned, however, the additional features were of little importance since little was known of the diffusion laws and of factors involved in deviations from ideality.

Masson (46) formed two boundaries within the same tube thereby allowing simultaneous observation of the motion of both anion and cation and making the observation free of the necessity for accurate current measurement. In a typical experiment Masson used a gelatin gel containing potassium chloride in a cylindrical tube connecting two electrode compartments. In one electrode compartment he placed potassium dichromate and in the other cupric chloride. On electrolysis the cupric ion followed potassium at one end of the gel; the dichromate ion followed chloride ion at the other end. The boundaries could be easily located by color; the transference number of potassium was obtained from the expression:

$$t_K = \frac{\text{vel. of Cu-K boundary}}{\text{vel. of Cu-K boundary} + \text{vel. of Cl-Cr}_2\text{O}_7} \qquad (12)$$

As a result of his experiments, Masson concluded that a good boundary results only if the leading and following electrolytes conform to the Kohlrausch ratio; the following ion must have a lower mobility than the leading ion; the indicator ion must not react chemically with the solutions to be examined; and no rapidly moving ions should be produced at the electrodes in such a way that they enter the gel.

A considerable advance in technique was made by B. D. Steele (50), in 1901, who arranged his apparatus so that the boundary traveled in aqueous solution and not in a gel. A diagram of his apparatus is shown in Figure 8A. The electrode compartments A, provided with a ground joint at the bottom, were filled, as shown at E, with a gel containing indicator solution of appropriate concentration. They were then inserted into the joints, B, of the measuring tubes, C, which were full of the solution to be tested. Excess liquid was displaced into D. The current was started by filling the region immediately around the electrodes with indicator solution and boundaries immediately appeared in the measuring tubes C. As soon as the boundaries were well away from the gelatin it had no further effect upon them and their velocities were measured in the same manner as in Masson's experiments. Steele was the first experimenter to use refractive index differences as a means of observing the boundary, although Lenz (51) and Bein (52) had previously noted this possibility. This method of observation permitted the use of ions having no color and considerably broadened the scope of the moving-boundary method. Steele reported that, owing to the difference in refractive index of the indicator and leading solutions, the boundary in virtually all cases was easily visible to the unaided eye. He followed its progress with a



(A) (B)

Figure 8. Transference Number Apparatus of B. D. Steele.

telescope cathetometer. Steele was a careful worker and investigated the various factors leading to error. He noted that the stability of the boundary is greatly affected by convection currents produced by the electrical heating; to avoid this effect, he recommended using low current densities and an indicator solution of as high conductance as possible. He confirmed again the necessity for close approximation to the Kohlrausch ratio; however, he pointed out that if he allowed the boundaries to diffuse away by turning off the current, he could restore them within 10 minutes by again passing the current. From these observations it was evident that the law of Kohlrausch was essentially correct. Steele used his apparatus with modified electrode compartments to observe rising boundaries as well as falling boundaries, and he noted that the latter were the more successful. The indicator solution is always of lower conductance than the leading solutions and hence its resistance is greater. This causes more heat to be generated by the current in the indicator solution and consequently more convection is produced. These convection currents cause less trouble if the indicator solution is on top.

In 1903, Denison (53) improved the method of Steele by correcting the results for electroendosmosis through the gelatin plugs. He found that, with such corrections, good agreement with the Hittorf method was realized.

In 1904, Franklin and Cady (54) applied the moving-boundary technique to the measurement of ionic mobilities in liquid ammonia solutions. Their apparatus is schematically shown in Figure 9. The tube in which the boundary moved, A, has its lower end just below the surface of a pool of mercury which acts as one electrode. The other end protrudes into vessel, B, containing a platinum electrode D. To observe a cation boundary the tubes B and A were filled with the solution to be tested and the current was turned on. The electrode reaction, $Hg \longrightarrow Hg^{++} + 2e$, taking place at the lower electrode, gave rise to an indicator solution which automatically adjusted itself to the Kohlrausch ratio behind the boundary. The boundary so formed rose through the measuring tube, A, and was readily visible. Since the metallic electrode produces the indicator solution directly, this type of boundary is known as "autogenic". To observe an anion boundary the tubes B and A were filled as before, then the indicator solution was prepared in the region C. To form a boundary, the mercury level was lowered by means of E, and indicator was allowed to flow under the tube A. The current was then started and the boundary soon became sharp. Franklin and Cady checked their measurements for the cation boundary by using copper in place of mercury, and also by using ammonium ion indicator in the usual way. The results were identical, and indicated that the automatic

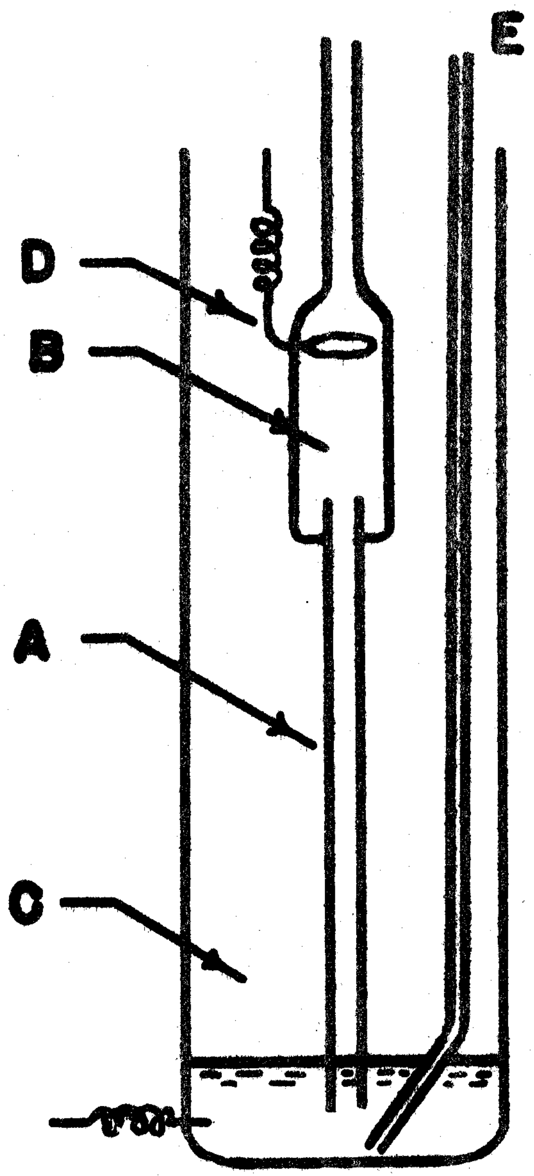


Figure 9. Moving Boundary Apparatus of E. C. Franklin and H. P. Cady.

adjustment was satisfactory. The main disadvantage they found in the use of the autogenic and non-autogenic rising boundaries was the tendency of the convection currents from the warmer indicator solution to destroy the boundary. As had been found by Steele, the indicator solution having the higher resistance preferably should be the top layer.

In 1906, Denison and Steele (55) devised an apparatus which eliminated the need for the gelatin plugs used in their first work. The essential feature was a parchment-covered cone closure for the ends of the measuring tubes. The device is pictured in Figure 8B. The parchment on cone B covered the top of the boundary tube, C, until the start of the experiment. When the current was turned on, it was found that there was sufficient leakage around the parchment so that the boundary started down the tube. When the boundary was away from the edges the funnel was cautiously drawn up. This apparatus gave excellent results and was used for both rising and falling boundaries. In all measurements both cation and anion boundaries were simultaneously observed.

The advantages of the moving-boundary method in precision and in ease of performance became obvious with the work of Denison and Steele; however, the relation between this method and that of Hittorf still was not settled. Slightly different results were obtained by the two methods;

it was suggested that the water dragged by the ions might be the cause (56). The true relation was elucidated by W. Lash Miller (57) and by G. N. Lewis (58). Miller pointed out that since it was an observed fact that a sharp boundary migrated down the tube, one could consider the moving-boundary method as a Hittorf experiment, with the concentration changes in the electrode compartments being determined by observing the penetration of the second electrolyte into one of the compartments. Using this idea, he showed that no assumptions such as absolute ionic motions are necessary to arrive at the same conclusions as those of Kohlrausch. If a sharp boundary between two electrolytes moves through a volume, V, then $Vc/1000\,F$ is the total charge carried by the ion leading the boundary out of the region left behind; F is one Faraday and c the equivalent concentration of the ion. If i represents the total current passed through the cell, and if the time, t, were required for the boundary movement, the transference number of the ion would be given by:

$$\tau = \frac{Vc/1000\,F}{i\,t} = \frac{Vc}{1000\,i\,t\,F} \qquad (13)$$

To form a stable boundary it is evident that the following ion must move at the same rate as the leading ion, so V, i, and t are the same for the following ion. For a stable boundary:

$$\mathcal{T}/\mathcal{T}' = \frac{\dfrac{Vc}{1000\ i\ t\ F}}{\dfrac{Vc'}{1000\ i\ t\ F}} = \frac{c}{c'} \qquad (14)$$

as required by Kohlrausch.

While Miller recognized that some correction should be necessary for the volume changes occurring around the electrodes during the electrolysis, Lewis (58) was the first to show how the correction should be made. He found that the volume correction becomes very large under the experimental conditions used by Steele and made a remarkably accurate approximation to the correction he should have used. The method of Lewis can be summarized as follows. The Hittorf transference number can be defined as the number of equivalents of an ion constituent which, on the passage of one Faraday of current, cross a boundary fixed with respect to the water of the solution. In a moving-boundary experiment, readings are made relative to the tube so that motion of the water relative to the tube must be known for the correction. In a properly designed experiment one of the electrode vessels is maintained closed and the other open. Suppose that one has the situation diagrammed in Figure 10. The boundary between LiCl and $LaCl_3$ is moving downwards, and during a certain interval moves from b-b to b$'$-b$'$. Simultaneously a reference point in the solution moves from a-a

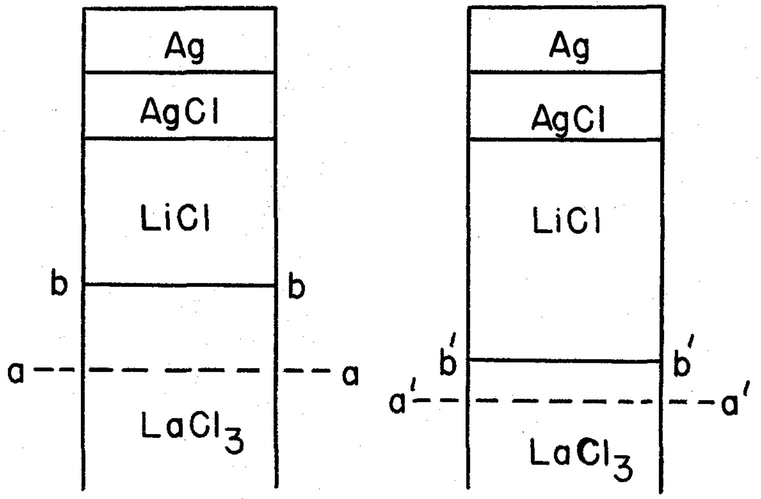


Figure 10. Illustration of Volume Changes During Electrolysis.

to a$'$-a$'$. The latter volume change represents the changes in volume due to electrode reactions and displacement of $LaCl_3$ by LiCl. During the passage of one Faraday of current the following volume changes must occur in the region above the reference plane a-a: (1) loss of 1 equivalent of Ag and gain of 1 equivalent of AgCl; (2) loss of 1 equivalent of Cl^- from the LiCl solution by deposition; (3) regain of 1 equivalent of Cl^- in the LiCl solution and loss of 1 equivalent in $LaCl_3$ solution owing to the motion of the boundary b-b; (4) loss of $\tau_{La^{+3}}$ equivalents of lanthanum ion by transfer through a-a, and gain of τ_{Cl^-} equivalents of chloride ion in $LaCl_3$ solution for the same reason. Thus the total volume change beneath a-a for one Faraday becomes:

$$\Delta V = -\bar{V}_{Ag} + \bar{V}_{AgCl} - \underset{(LiCl)}{\bar{V}_{Cl^-}} + \underset{(LiCl)}{\bar{V}_{Cl^-}} - \underset{(LaCl_3)}{\bar{V}_{Cl^-}}$$

$$-\frac{1}{3}\underset{(LaCl_3)}{\tau_{La^{+3}}\bar{V}_{La^{+3}}} + \underset{(LaCl_3)}{\tau_{Cl^-}\bar{V}_{Cl^-}} \qquad (15)$$

since:

$$-\underset{(LaCl_3)}{\bar{V}_{Cl^-}} + \underset{(LaCl_3)}{\tau_{Cl^-}\bar{V}_{Cl^-}} = -(1-\underset{(LaCl_3)}{\tau_{Cl^-})\bar{V}_{Cl^-}} = -\underset{(LaCl_3)}{\tau_{La^{+3}}V_{Cl^-}}$$

equation (15) becomes:

$$\Delta V = -\bar{V}_{Ag} + \bar{V}_{AgCl} - 1/3\,\tau_{La^{+3}}\bar{V}_{LaCl_3} \qquad (16)$$

If one Faraday of current is passed, the transference number can be computed from formula (13) as:

$$\tau_{La^{+3}} = \frac{(V - \Delta V)c}{1000}$$

or, since the uncorrected or observed number would be Vc/1000, this can be written:

$$\tau_{La^{+3}} = \underset{\text{Observed}}{\tau_{La^{+3}}} - \frac{\Delta V}{1000}c \qquad (17)$$

Two methods have been used to test the validity of the correction method introduced by Lewis. Smith (59) used an apparatus in which one electrode compartment could be detached and used as a pycnometer. He obtained excellent agreement with the Lewis formula by electrolyzing a potassium chloride solution employing a silver-silver chloride electrode. MacInnes and Longsworth (60) determined the transference numbers of potassium in very strong potassium chloride solutions using either a silver-silver chloride anode or a cadmium anode. The results for the two types of electrodes differed widely without correction but agreed exactly after correction with the Lewis formula.

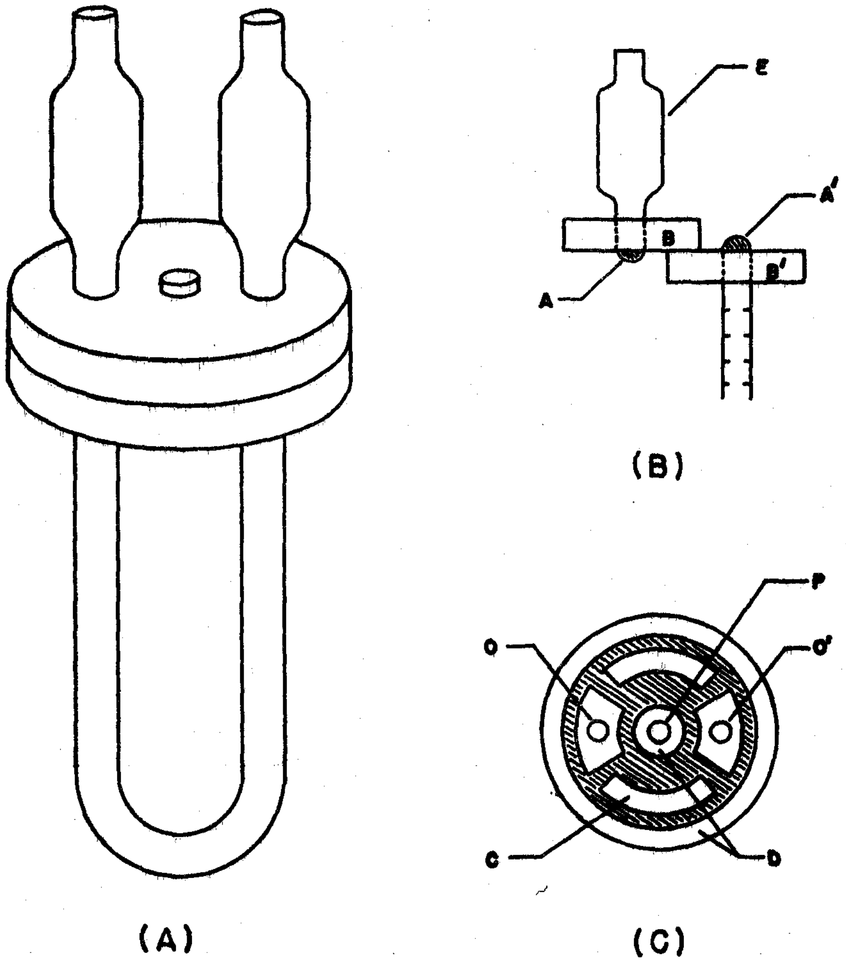
In 1915, M. von Laue (61) extended the Kohlrausch, Weber, Planck theory of the moving-boundary to include the effects of incomplete dissociation. He considered the mobilities of the ions to be independent of concentration but assumed the ionic concentration to vary as required by the Ostwald dilution law. Since the motion of a boundary consists of the motion of the whole electrolyte, owing to the rapid equilibrium between undissociated and dissociated particles, the true ionic mobility is much faster. If the Ostwald dilution law holds, and if appropriate constants are measured, the von Laue law can be used to calculate the true ionic mobilities. It is now recognized that his assumptions do not account for the observed variations in conductance so that the extension is now of little importance.

R. Lorenz and W. Neu (62) called attention to the fact that incomplete dissociation had never been considered either in calculating ionic mobilities or in applying the Kohlrausch theory. They pointed out that the von Laue treatment remedies this situation, and they obtained values for the absolute mobilities. However, their experimental technique was so inadequate that their conclusions are of interest only in so far as they recognized a need for further extensions of the theory.

In 1923, D. A. MacInnes and his associates began their studies of the moving-boundary method which advanced the technique to the present day level of accuracy. The work of these investigators is completely summarized in the review article on the subject by D. A. MacInnes and L. G. Longsworth (60). A brief summary follows.

Using the apparatus of Denison and Steele (55), but forming a single boundary only, MacInnes and Smith (63, 64, 65) made a study of the effect of the indicator solution upon the motion of the boundary, the effects of applied E.M.F., and the effects of tube size. They concluded that the indicator solution must be adjusted to the Kohlrausch ratio within about 3 per cent. If this adjustment were made, the magnitude of the applied E.M.F. had no effect, provided it was high enough to maintain a sharp boundary, and that it was below the value which would cause enough convection to destroy the boundary. They controlled the current to a constant value by hand regulation when using the standard size apparatus. This regulation led to difficulties so that they attempted to scale up the tube size in order to use a coulometer for current measurement. In the large size tube, however, convection was very great and the experiments gave results of poor accuracy. They concluded that an upper limit on tube diameter should be found by trial whenever moving-boundary experiments are performed.

In 1925, MacInnes and Brighton (66) described a new type of boundary-forming apparatus which gave a very much sharper initial boundary than did the plunger type. This apparatus is pictured schematically in Figure 11. The principle is demonstrated in Figure 11B. The electrode vessel and the measuring tube are fitted into glass plates B, B′ as shown. The electrode vessel is filled with indicator solution so that a drop hangs at A; the moving-boundary tube is filled with the leading electrolyte so that it protrudes at A. To establish a sharp junction the plates are slid together so that the tubes sealed through the plates coincide. The excesses of solution A and A′ are sheared off and a sharp boundary is formed. Diagrams A and C show the complete apparatus. Two plates of hard rubber or glass are formed as in Figure 11C. The shaded



(A)

(B)

(C)

Figure 11. Boundary Shearing Device of D. A. MacInnes and T. B. Brighton.

areas are etched to about 1/8" below the plane of the unshaded areas and the latter are ground flat. Two electrode vessels are fitted, as shown in Figure 11A, into the holes, o and o′, of one plate and a U-tube whose arms form the measuring tubes are fitted into similar holes in the other plate. The center holes, P, fit over a brass pin which keeps the two plates concentric. The raised parts of the plates are lightly greased, and the electrode compartments are filled with anion and cation indicator solutions so that a pendant drop hangs as illustrated by the drop at A in Figure 11B. The U-tube in the lower plate is filled with the solution under test until drops protrude as illustrated by the drop at A′ Figure 11B. The plates are then placed over the brass pin as shown in Figure 11A, but the upper plate is pressed onto the lower plate so that the line of centers of the holes, o and o′, is at right angles to that of the holes in the lower plate. This procedure leaves the surplus drops of solution hanging into or protruding into the hollows of the other plate. The raised portions, D, insulate the inner parts of the plates from the water bath and pin. When it is desired to form the boundaries, the two plates are rotated until holes o and o′ coincide with the holes in the lower plate and both boundaries are formed simultaneously.

In 1926, MacInnes, Cowperwaithe and Blanchard (67) devised an automatic current controller which maintained currents more constant than was possible with hand control. The instrument was improved by Longsworth and MacInnes (68) and in final form was capable of control to within 0.02 per cent. This machine allowed the use of single boundaries with better accuracies than were previously obtainable with the double boundaries.

In 1927, MacInnes, Cowperwaithe and Huang (69) made a number of improvements in the Brighton apparatus, and investigated more thoroughly the effects of tube size and limits of the Kohlrausch adjustments. Their results concur with those of earlier workers but set no reliable limits. Further modifications of the Brighton apparatus were made by Longsworth (70, 71, 72) who discovered the need for a solvent correction (71). Since the solvent conducts a part of the current through the tube it must be considered as a sort of shunt current in parallel with the current which causes the motion of the boundary. Therefore, it is necessary to employ the correction:

$$\tau_{corr.} = \tau_{obs.} \left(1 + \frac{K_{solvent}}{K_{solution}}\right) \qquad (18)$$

in which $\tau_{corr.}$ and $\tau_{obs.}$ are corrected and observed transference numbers; $K_{solvent}$ and $K_{solution}$ are the specific conductances of solvent and solution. This correction becomes especially important at high dilutions.

A modification of the moving-boundary technique, known as the "balanced boundary" method, was begun in 1928 by E. R. Smith (73) and developed further by Hartley and Collie (74). Smith used the Denison and Steele method of forming the boundary, but included a dropping funnel full of mercury as a part of the closed electrode compartment containing the indicator solution. The boundary was allowed to travel down the measuring tube to a scratch line. At this point a coulometer was connected, and the boundary was kept in the vicinity of the scratch by withdrawing mercury from the electrode compartment. After a substantial current had passed, enough mercury was withdrawn to bring the boundary above the scratch, and the coulometer was detached at the instant it again touched the scratch. The volume swept out by the boundary was measured by weighing the mercury withdrawn. This procedure eliminated the necessity for calibrating the boundary tube.

Hartley and Collie used the balanced boundary in a different way. They desired to know the transference numbers of some very heavy anions, and could find no suitable indicator solution. They therefore modified the technique of Smith in such a way that the Kohlrausch concentration of the following electrolyte could be determined.

The boundary was formed in the apparatus by the use of an air-lock; a system of three tubes was arranged so that an air bubble could be maintained between the two solutions until junction was desired, at which time the bubble could be withdrawn through the third tube. The boundary was allowed to move a short distance down the measuring tube, and was then rendered stationary by adding solution to the cathode compartment by means of a hypodermic syringe operated by clockwork. The solution effectively flowed through the boundary and was allowed to pass out the tube used previously to withdraw the air bubble. After a short time, the solution above the boundary attained the Kohlrausch regulating ratio by virtue of the automatic adjustment, and its concentration was determined conductometrically. Since the transference numbers of the leading solutions were known, those of the indicator electrolytes were easily determined from their concentrations. The results of the balanced boundary technique were excellent; the method of measuring the volumes of liquid withdrawn to maintain the boundary fixed was definitely more accurate than the measurement of concentration by conductance, but the latter is somewhat more rapid and requires no accurate control of the current.

Another feature introduced by Hartley (75) was the use of an electronic current control. A better unit was described by P. Bender and D. Lewis (76). The use of such a device greatly simplified the apparatus required for the moving-boundary method.

In 1931, E. R. Smith (77) measured the motion of a boundary between two different concentrations of the same salt. Such a boundary will move with uniform velocity according to the Kohlrausch equations, although diffusion will tend to blur it as it moves. By a material balance argument, of the type used by W. L. Miller (57), it can be shown (53) that for such a boundary:

$$\frac{\tau' - \tau''}{C' - C''} = \frac{vF}{q} \tag{19}$$

in which τ', τ'' are transference numbers, and C', C'' are concentrations of leading and following solutions, v is the volume passed through by the boundary for q coulombs of charge passed, and F is the Faraday of charge in coulombs.

While the results of Smith were not satisfactory, they served as a guide in later work by L. G. Longsworth (78) which reached a high degree of accuracy. Longsworth used the Schlieren scanning technique, well known to biophysicists and biochemists (79), to study both the motion and structure of the boundaries between two solutions of the same salt. Although the method has been shown to produce excellent results, it is not yet satisfactory for concentrations below 0.2 normal, and supplements rather than replaces the usual moving-boundary method.

In recent years little work has been done on the technique of measurement of transference numbers by the moving-boundary method. The only modifications worthy of note have been those of D. J. LeRoy and his associates at the University of Toronto (80, 81, 82, 83, 84). These workers employed an electronic current control and a novel apparatus for producing a sheared boundary. The essential feature was a special four-way stopcock which was arranged in such a manner that opposite pairs of its connecting tubes were joined with any setting. One of the stopcock outlets was connected to the measuring tube, and a stopcock outlet at right angles was connected to the anode compartment. The other two tubes were used for filling the cells. The stopcock was first set so that the measuring tube was joined to the other filling tube. The two sections were filled with the appropriate solutions, then the stopcock was given a quarter turn connecting the anode compartment and the measuring tube, thereby forming a sheared boundary at the bottom of the measuring tube. The device was exceedingly convenient for use for either rising or falling boundaries.

A completely new approach to the measurement of transference numbers was begun in 1942 by D. A. MacInnes (85).

This method utilizes the effects of gradients of centrifugal force upon the E.M.F. of simple galvanic cells. The following equation applies for a cell of the type: $\begin{Bmatrix} Pt \\ r_2 \end{Bmatrix}$: I_2, KI, I_2 : $\begin{Bmatrix} Pt \\ r_1 \end{Bmatrix}$, with the electrodes at radii, $\underline{r_1}$ and $\underline{r_2}$, in a centrifugal field:

$$EF = 2\pi^2 n^2 (r_2^2 - r_1^2)\left[\tau_K (M_{KI}\rho) - (M_I - \bar{V}_I\rho)\right] \quad (20)$$

in which

$\underline{E}$ is the E.M.F.;

$\underline{F}$ is the Faraday;

$\underline{n}$ is the number of revolutions per second;

$\underline{\tau_K}$ is the transference number of the cation;

$\underline{\rho}$ is the density of the solution.

Preliminary results (85, 86) indicate that the method has considerable promise. It is especially important for use with non-aqueous solutions where the Hittorf and moving-boundary methods encounter difficulties due to heating.

Experimental

Preparation of solutions

Solutions of the rare earth chlorides were prepared as described under the section dealing with the theory and measurement of conductances.

Lithium chloride was used as the indicator electrolyte for all measurements. A stock solution of this salt was prepared by dissolving c.p. lithium carbonate in redistilled hydrochloric acid, and flushing out carbon dioxide with nitrogen until the pH of the solution reached exactly 6.6 as recommended by Scatchard and Prentiss (87). The normality of this stock solution was determined by taking aliquots, adding sulfuric acid, evaporating to dryness, igniting to 800°C, and weighing as sulfate. Solutions to be used as indicators were prepared from the stock solution by dilution. Conductance water was used as the solvent.

Apparatus

A modification of the apparatus of MacInnes and Longsworth (60) was used for measuring the transference measurements. This technique was selected because it is highly precise and convenient, and also because the above investigators (88) have applied their method to the determination of the transference numbers of lanthanum chloride with excellent results. In place of the glass disc shearing assembly of MacInnes and Longsworth, a high vacuum hollow bore stopcock was used to produce the boundary. This device was more conveniently constructed and operated than was the glass disc apparatus; the use of a stopcock in an analogous manner had been shown to be entirely satisfactory by D. J. LeRoy (82) and his associates. An electronic constant current unit was employed in place of the mechanical current supply used by Longsworth and MacInnes. This substitution seems to be preferred by the more recent investigators (75, 76, 80, 81, 82, 83, 84) and it is much more compact and less fragile. The other details of construction and operation were the same as those recommended by Longsworth and MacInnes.

The electrolysis vessel, shown in Figures 12 and 13, consisted of a large two-way hollow-bore stopcock connected at the end-opening to the anode compartment and at the center-opening to the measuring tube. The cathode compartment was joined to the other end of the measuring tube by a large bore U-tube. Two sizes of measuring tubes were employed, one of 0.2 cm^2 area and one of 0.1 cm^2 area. These tubes were prepared and calibrated as recommended by Longsworth (71). Graduations were made by coating the tube with wax; mounting it in a lathe; cutting the wax at opposite sides of the tube so that the graduation circle would be interrupted at the front and back; and finally etching the glass by one minute immersion in dilute hydrofluoric acid. The volumes between marks were determined by sealing a stopcock to one end of the tube, and calibrating with mercury by the customary burette calibration procedure.

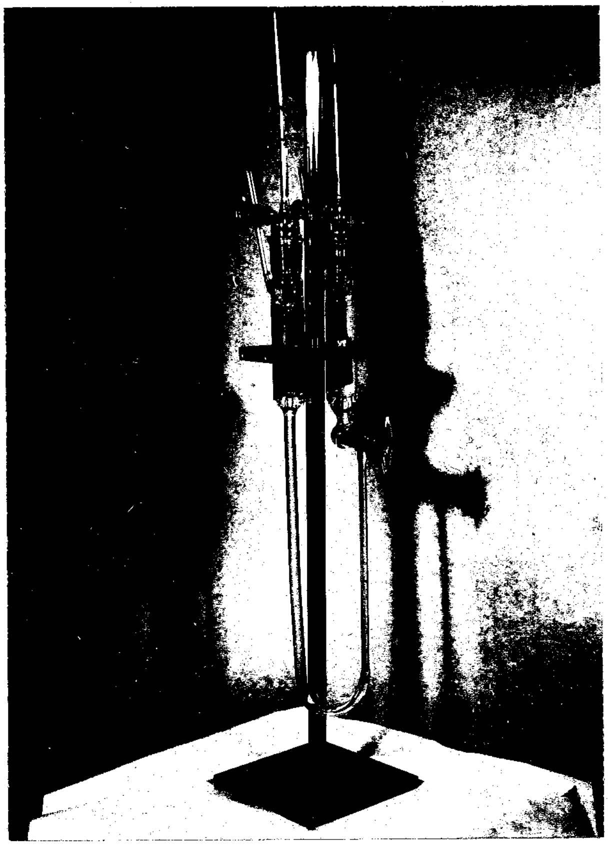


Figure 12. Assembled Apparatus for Determination of Transference Numbers.

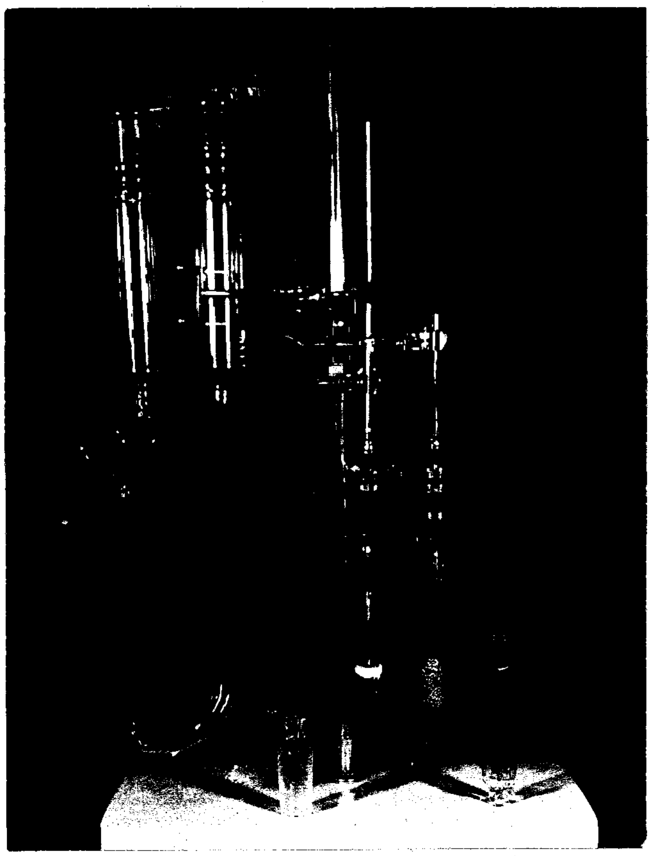


Figure 13. Component Parts of the Apparatus for Determination of Transference Numbers.

A cadmium anode and a silver-silver chloride cathode were used. The silver-silver chloride electrode was purchased from the Klett Manufacturing Company. It consisted of a silver sheet wound in a spiral, with the successive layers separated by a currugated silver sheet. The silver chloride was deposited electrolytically from a 1 N. solution of hydrochloric acid. The cadmium anode was made by melting c.p. cadmium metal in a pyrex test tube in an atmosphere of helium, and then allowing it to solidify around the end of a pyrex tube containing a copper wire for an external connection. The two electrodes were sealed into hollow standard taper stoppers as shown in the figures.

The electrode compartments were made from 30 mm glass tubing, and were fitted at the top with standard taper joints to accommodate the electrodes. A capillary stopcock just under the ground joint, provided an escape valve for solution displaced when the electrodes were seated in the joints. Pyrex cups were provided in each compartment to prevent the heavy products of the electrode reactions from reaching the measuring tube.

To prepare the apparatus for use, the measuring tube and cathode compartment were rinsed with the rare earth chloride solution and then filled. The hollow-bore stopcock was turned to the closed position; the cathode compartment was then assembled and closed. The anode compartment and the stopcock bore were then thoroughly washed, rinsed with lithium chloride solution, and filled with the indicator solution. The anode was inserted, and this compartment was sealed. The whole unit was then placed in the water bath and the capillary stopcocks were opened to allow the solutions to expand. When temperature equilibrium had been established, the voltage was impressed across the terminals, the cadmium electrode compartment was closed, and the boundary was formed by opening the hollow-bore stopcock.

An electronic power supply was constructed from a design furnished by J. Palmer and A. Read of the Department of Physics of Iowa State College. A diagram is given in Figure 14. The load is placed in the plate circuit of a 6L6 beam power pentode tube equipped with a cathode follower circuit which adjusts the 6L6 control grid voltage in such a way that its cathode is sensitively maintained at 87 volts. Since the 6L6 cathode potential is dependent upon the voltage drop of the controlling resistor between the cathode and ground, the current through this resistor, and hence in the plate circuit of the tube is maintained at a very constant value. Under extreme conditions of use, the device was able to maintain the current constant within 0.05 per cent.

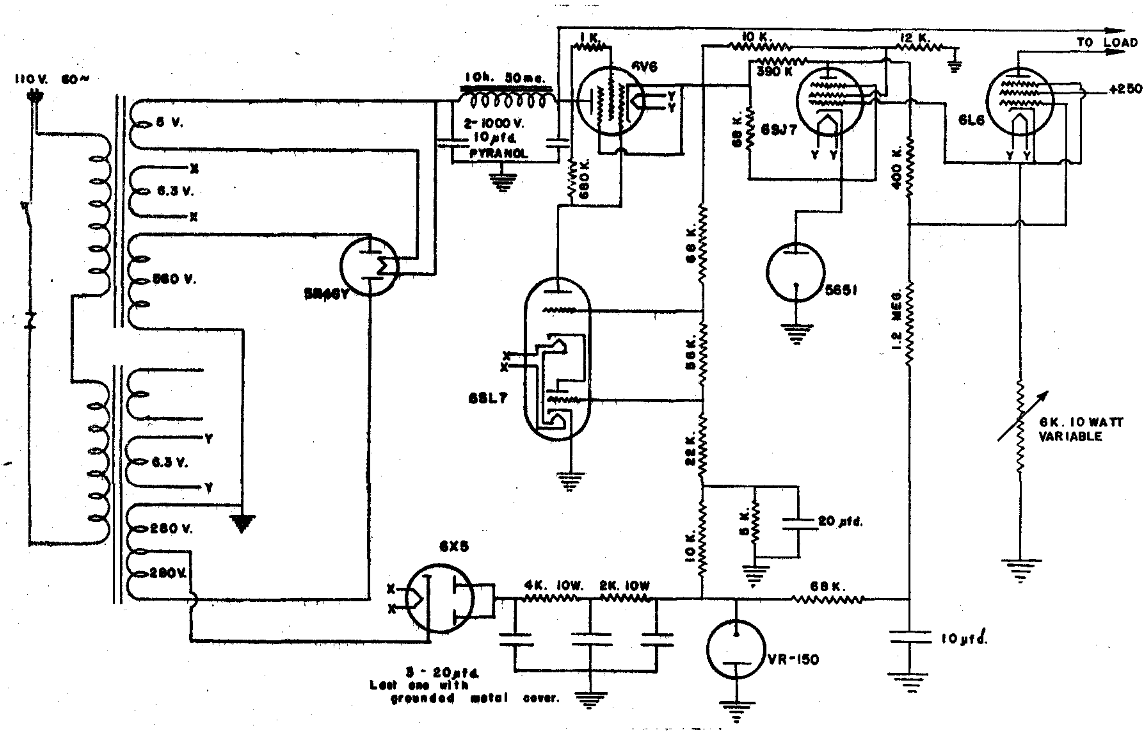


Figure 14. Constant Current Power Supply.

The current through the transference cell was measured by observing the voltage drop of a standard resistor in series with the cathode side of the cell. The standard resistor was wound with manganin wire and was calibrated by comparison with a Bureau of Standards certified resistor. The voltage drop was measured continuously by bucking out all but 8 to 10 millivolts with a Rubicon precision type B potentiometer, and reading the remainder on a Brown 0-12 mv full scale recorder. The measuring system was carefully tested to determine the current required for its operation; it was found that less than one microampere was diverted. This diverted current corresponded in the usual case to less than 0.02 per cent of the current measured, and in the worst case to 0.04 per cent.

The position of the boundary was observed by making use of the difference in refractive index between the indicator solution and the leading solution. Light striking the interface between the solutions was deviated in accordance with Snell's law; at a critical angle of incidence the deviated beam left the boundary tube parallel to the boundary surface; above this angle refraction no longer occurred and the beam was reflected. Therefore, if a narrow light source was placed so that all light falling upon the boundary came from below the boundary surface, there was a narrow angle on the opposite side of the tube into which no light was reflected or refracted. The upper limiting ray of this dark angle could be observed with a telescope, and the boundary position could thus be easily located.

The assembly of the apparatus used for observing the boundary is pictured in Figure 15. The elevator shown at the left contained a 110 volt 50-watt light bulb, which brightly illuminated a narrow frosted glass plate covering a 2 cm wide slit in the front of the box. This light source could be adjusted to any height by appropriate use of the two-way motor at the top of the shaft. The telescope at the right was focussed at the center of the measuring tube and the position of the light was varied until the boundary became visible. With proper adjustment, the boundary appeared as a well defined sharp line across the tube which was easily followed.

The time required for the boundary to move between marks on the measuring tube was determined by using two stop watches mounted in such a way that one was stopped at the instant the other was started. The device was triggered, with both watches set at zero, when the boundary passed the first mark. One watch was then stopped and reset to zero. When the boundary reached the next mark the device was pressed, stopping the moving watch, and

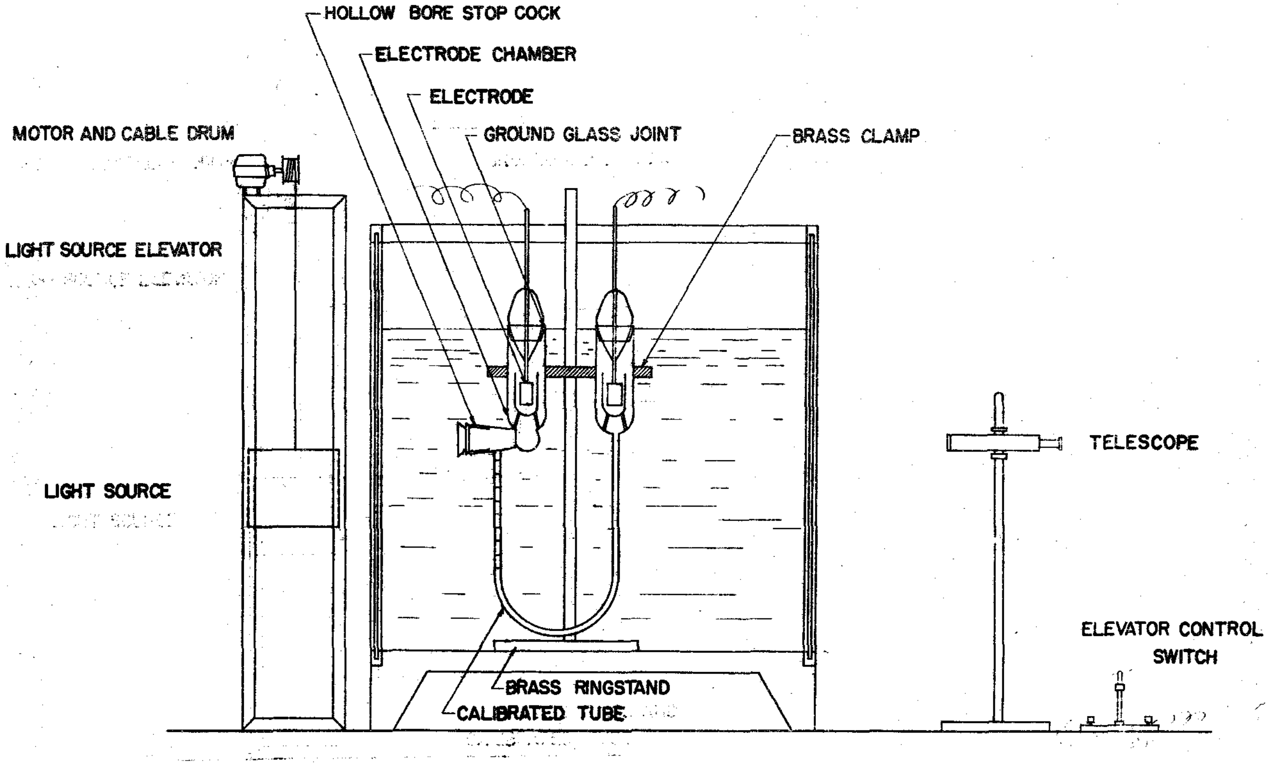


Figure 15. Apparatus for the Determination of Transference Numbers.

starting the other. The time recorded by the first watch was read, it was reset to zero, and the process was repeated at the next mark. The two watches were tested on a "Western Electric Time Rate Recorder" and were found to be accurate within 5 seconds in 24 hours.

Results

The Hittorf transference numbers of lanthanum, cerium, praseodymium and neodymium ions in chloride solutions were measured. The indicator solutions of lithium chloride were adjusted to the Kohlrausch regulating ratio using the transference number data of L. G. Longsworth (71). In all cases the concentration used was within the prescribed limits. The data are presented in Tables 6, 7, 8 and 9, and in Figure 16. The ordinates of Figure 16 are staggered in order to separate the various curves. The extrapolated values of transference numbers were obtained from the conductance data in the first section.

The volume corrections to obtain Hittorf transference numbers were made by the method of Lewis (58) described in the historical section. The molar volume of cadmium was taken as 13.0 ml (88), and the partial molal volume of $CdCl_2$ was taken as:

$$\overline{V}_{CdCl_2} = 23.24 + 8.82\ (\text{Molality})^{\frac{1}{2}}\ \text{(Reference 89)}$$

TABLE 6

Cation Transference Numbers for Lanthanum Chloride at 25°C

Normality	$\mathcal{T}_+$ (uncorrected)	$\mathcal{T}_+$ (average)	Volume correction	Solvent correction	$\mathcal{T}_+$ (corrected)
0.00000	-	-	-	-	0.4775 *
0.006209	0.4638	0.4638	0.0000	0.0007	0.4645
0.009030	0.4624	0.4624	0.0000	0.0005	0.4629
0.01242	0.4601 0.4604	0.4603	0.0000	0.0003	0.4606
0.02483	0.4558	0.4558	-0.0001	0.0002	0.4559
0.04967	0.4491 0.4491	0.4491	-0.0002	0.0001	0.4490
0.09933	0.4391 0.4391	0.4391	-0.0003	0.0001	0.4389

* Obtained from $\underline{\Lambda_o}$ value together with known $\underline{\lambda^o_-}$ value.

TABLE 7

Cation Transference Numbers for Cerium Chloride at 25°C

Normality	τ_+ (uncorrected)	τ_+ (average)	Volume correction	Solvent correction	τ_+ (corrected)
0.00000	-	-	-	-	0.4778 *
0.007675	0.4647	0.4647	0.0000	0.0003	0.4650
0.01075	0.4626 0.4628	0.4627	0.0000	0.0002	0.4629
0.01535	0.4599 0.4601	0.4600	0.0000	0.0002	0.4602
0.04605	0.4509 0.4500	0.4505	-0.0001	0.0001	0.4505
0.07675	0.4437 0.4432	0.4435	-0.0002	0.0000	0.4433
0.1075	0.4381 0.4380	0.4381	-0.0003	0.0000	0.4378

* Calculated from $\underline{\Delta_o}$ value together with known $\underline{\lambda^{o}_{-}}$ value.

TABLE 8

Cation Transference Numbers for Praseodymium Chloride at 25°C

Normality	τ_+ (uncorrected)	τ_+ (average)	Volume correction	Solvent correction	τ_+ (corrected)
0.00000	-	-	-	-	0.4772 *
0.007177	0.4646	0.4646	0.0000	0.0006	0.4652
0.01794	0.4594 0.4593	0.4594	-0.0001	0.0003	0.4596
0.05383	0.4495 0.4494	0.4495	-0.0002	0.0001	0.4494
0.07177	0.4449 0.4455	0.4452	-0.0003	0.0001	0.4450
0.1077	0.4384 0.4386	0.4385	-0.0004	0.0001	0.4382

* Calculated from $\underline{\Lambda_o}$ value together with known $\underline{\lambda^o_-}$ value.

TABLE 9

Cation Transference Numbers for Neodymium Chloride at 25°C

Normality	τ_+ (uncorrected)	τ_+ (average)	Volume correction	Solvent correction	τ_+ (corrected)
0.00000	-	-	-	-	0.4792 *
0.007642	0.4643 0.4637	0.4640	0.0000	0.0005	0.4645
0.01274	0.4610 0.4609	0.4610	0.0000	0.0003	0.4613
0.02547	0.4568 0.4565	0.4567	0.0000	0.0002	0.4569
0.05095	0.4501 0.4495	0.4498	-0.0001	0.0001	0.4498
0.07642	0.4440 0.4439	0.4440	-0.0002	0.0001	0.4439
0.1274	0.4340 0.4341	0.4341	-0.0003	0.0000	0.4338

* Calculated from $\underline{\Delta o}$ value together with known $\underline{\underline{\lambda^{o}}}$ value.

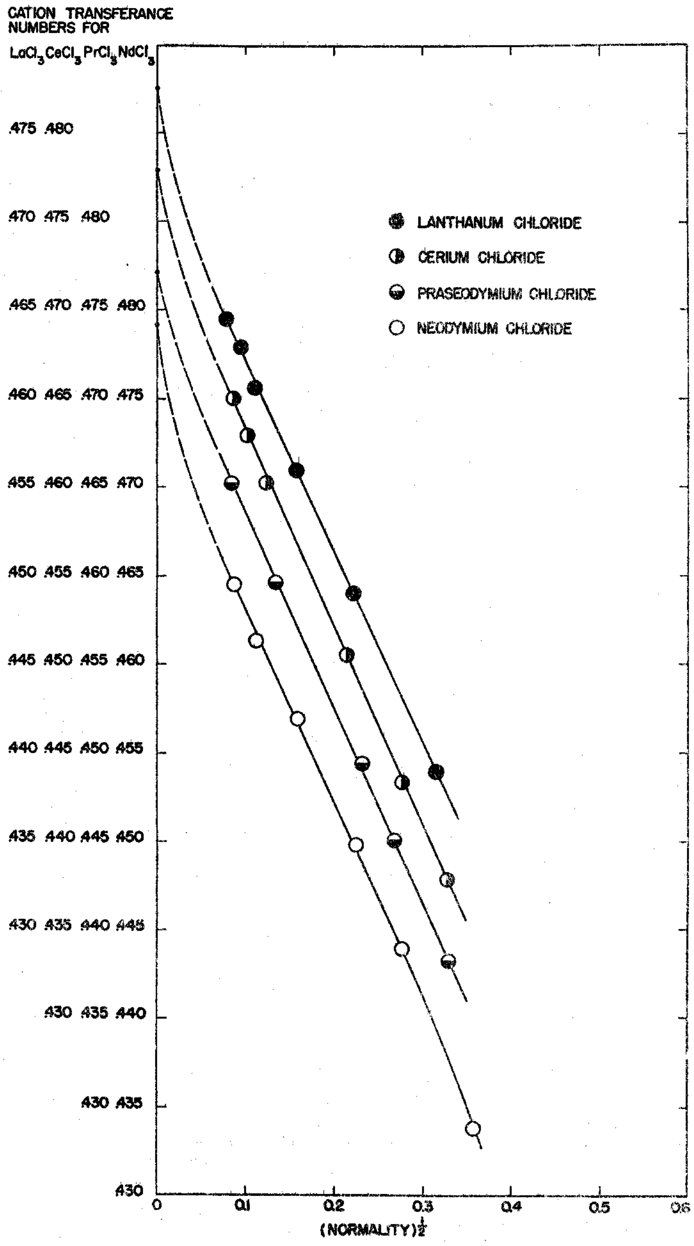


Figure 16. Transference Numbers of Rare Earth Ions in Aqueous Solutions of Their Chlorides.

The partial molal volume of lanthanum chloride was taken to be:

$$\overline{V}_{LaCl_3} = 16.02 + 10.28\ (\text{Normality})^{\frac{1}{2}}\ (\text{Reference } 90)$$

The densities of chloride solutions of cerium, praseodymium and neodymium at 25°C were determined up to 0.1 molar using a 50 ml pycnometer, and were found to fit the expressions:

$$\rho_{CeCl_3} = 0.99707 + 0.228\ C_m$$

$$\rho_{PrCl_3} = 0.99707 + 0.231\ C_m$$

$$\rho_{NdCl_3} = 0.99707 + 0.235\ C_m$$

These density data were used in computing the respective volume corrections.

The solvent corrections were made using the conductance data in the first section of this thesis together with the measured specific conductances of the water used to prepare the solutions.

A number of combinations of time and volume were used to compute transference numbers in each moving-boundary experiment. Each of these combinations involved a movement of the boundary of at least 8 cm to minimize time and volume errors. Table 10 shows a typical set of data obtained in one moving-boundary experiment; each result reported in Tables 6 through 9 is the average of a set of data of this type.

TABLE 10

Typical Moving-Boundary Experiment

Cerium Chloride 0.01535 N
Lithium Chloride 0.01100 N
Standard Resistance 250.38 ohms

Marks	Volume	Time	E.M.F.	$\tau_{Ce^{3+}}$ (uncorrected)
0 - 7	1.05868	2007.8	0.4254	0.4597
0 - 8	1.28012	2423.8	0.4253	0.4605
0 - 9	1.48983	2823.4	0.4253	0.4601
0 - 10	1.54404	2929.5	0.4253	0.4596
1 - 8	1.23059	2332.1	0.4253	0.4601
1 - 9	1.44030	2731.7	0.4253	0.4598
1 - 10	1.49451	2837.8	0.4253	0.4592
2 - 9	1.37916	2613.0	0.4253	0.4602
2 - 10	1.43337	2719.1	0.4253	0.4597
3 - 10	1.33451	2530.6	0.4253	0.4598
			Average	0.4599
			Av. deviation	0.0003
			Max. deviation	0.0007

Discussion of Results

The transference numbers of lanthanum chloride had been previously determined by L. G. Longsworth and D. A. MacInnes (87) using essentially the same procedure as that described in this thesis. A comparison of their data with those presented in this thesis is shown in Figure 17; the agreement is well within the experimental error. The limiting slope to be expected theoretically from the Onsager equation is indicated in Figure 17; it is evident that only at extremely high dilutions is there any tendency for the experimental data to merge with the limiting slope. This behavior is typical of the four rare earths studied, and is anomalous in view of the fact that the conductance data agree with the Onsager equation to a considerably greater extent than for transference numbers. It appears that some factor must be operative, which is compensated for in some manner in the case of conductance, but which causes a departure from the limiting law in the case of transference numbers.

The transference numbers of cerium, praseodymium, and neodymium ions are identical within the limits of experimental error, but are slightly higher than those for lanthanum. This order is not in agreement with the order of the conductances; this lack of agreement could be

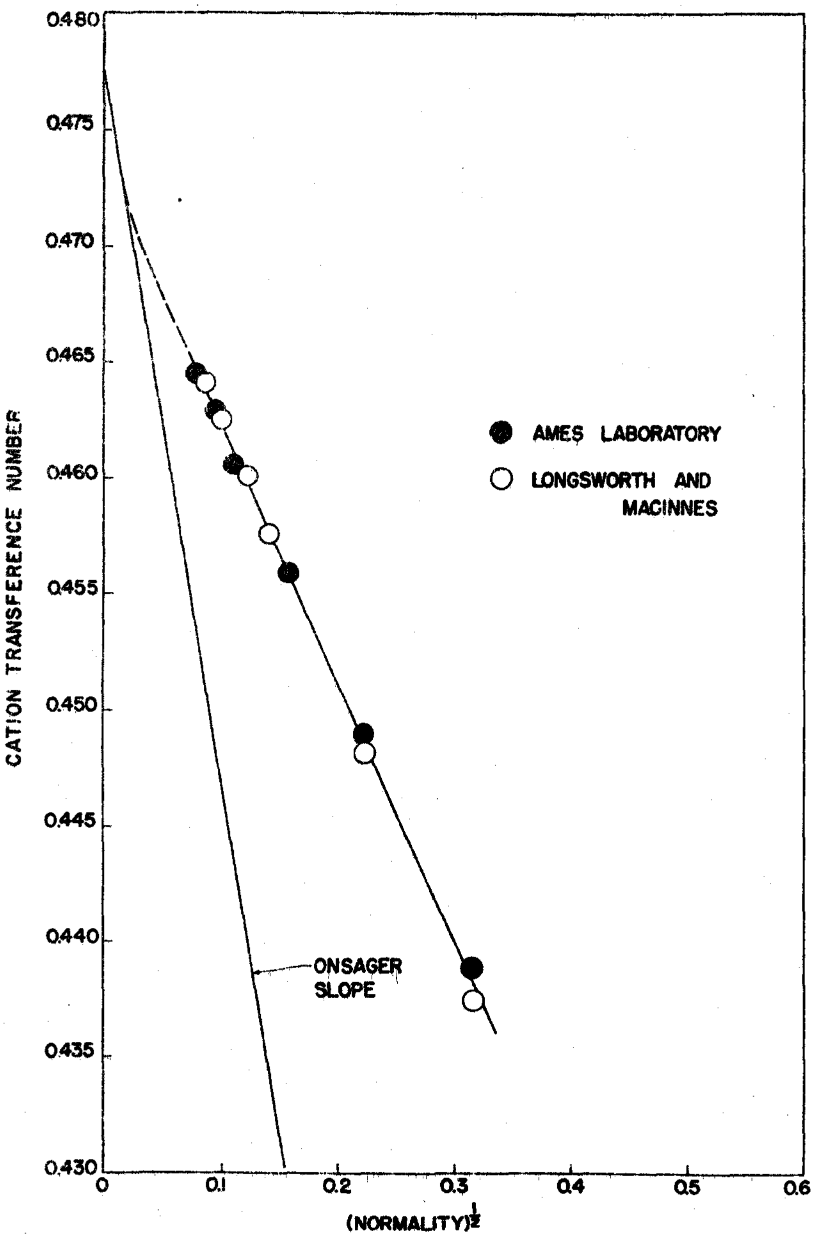


Figure 17. Cation Transference Numbers of Lanthanum Chloride Solutions.

attributed to the same effect which causes the deviation from the limiting law for transference numbers. The transference numbers of samarium, europium, and ytterbium ions, in solutions of their chlorides, have recently been determined (38); the data show a progressive decrease with increasing atomic number in agreement with the behavior of their conductances. As in the case of conductance measurements, a regular decrease of transference number with increase of atomic number seems to occur for the elements beginning with neodymium. This fact is a further indication of an anomalous behavior of the first four elements similar to that which appears in the crystal structures of the hydrated salts. It would be of considerable interest to investigate this behavior further as data for more rare earths are obtained.

The errors in transference number measurement are estimated to be less than 0.1 per cent. The set of transference data obtained within a single run have an average deviation of about 0.0003. This deviation is due to the errors in estimating the exact time at which the boundary has arrived at a mark, since the volume of the tube and the current are known to within 0.02 per cent. Duplicate runs agree within 0.1 per cent and the average difference between duplicate runs was 0.0003. The solution concentrations were known to better than 0.1 per cent.

ACTIVITY COEFFICIENTS

Introduction

When a substance is dissolved in a give solvent, its partial molal free energy is decreased. This decrease can be divided into two parts; the decrease in free energy which the substance would have undergone if it had formed an ideal solution and the decrease brought about by the non-ideal behavior of the solution. The activity coefficient of the substance in the given solution is defined in terms of the latter part of the free energy decrease; it represents a correction term which modifies the laws of an ideal solution so that they will apply to the case at hand. The generalization of the ideal solution laws, achieved in this manner, is extremely useful; consequently, the activity coefficients are of immense practical as well as theoretical importance.

The activities of a substance in its solutions are true thermodynamic properties of the substance. They are so inter-related with other thermodynamic properties that activity data can be cross-checked in a number of ways. The rate of change of the logarithm of the activity with temperature is related to the partial molal heat contents of the solute; its rate of change with pressure is related to the partial molal volumes and the solution densities; its second derivative with respect to temperature is related to heat capacities; its second derivative with respect to pressure is related to compressibilities; and its first derivative with respect to both temperature and pressure gives the thermal coefficient of expansion. It would be of considerable interest to accumulate experimental data for all of these properties for the rare earths and to compare them with observed variations of activities with temperature and pressure. The Debye-Hückel theory of electrolytic solutions yields an expression for the free energy decrease of a salt in solution due to the electrostatic interactions among the ions. At high dilutions this free energy decrease appears to account for the observed experimental data; however, in more concentrated solutions the Debye-Hückel expression is not satisfactory. The amounts by which the various thermodynamic properties deviate from the Debye-Hückel limiting laws should vary from property to property, since a breakdown in the validity of any of the assumptions of the limiting laws would not be expected to have the same effect upon all properties. Thus, a correlation among such properties as the activities, heats of solution and dilution, and densities, with emphasis upon the deviations from the limiting laws in more concentrated solutions, should make clear the nature of the factors which produce the deviations. A knowledge of these factors should then make it possible to alter the basic assumptions of the theories in such a manner that they can be made applicable to higher concentrations.

Activities can be measured in a variety of ways discussed in the following section; however, for solutions of strong electrolytes the galvanic cell methods are by far the most sensitive. The method involving cells with transference was employed in this thesis rather than that using cells without transference, because the latter requires the use of electrodes reversible to the rare earth ions. Such electrodes are not yet available.

Theory

The concept of activity was first introduced by G. N. Lewis (91), in 1907, to facilitate the application of the laws of thermodynamics to solutions. This concept has since assumed a fundamental role in the study of all thermodynamic systems and is of particular interest in connection with solutions of electrolytes. Before attempting to define the activity of a substance the basic thermodynamic principles will be briefly reviewed.

The consequences of the first and second laws of thermodynamics can be expressed in the form of a differential equation which is perfectly general for any system. This equation is:

$$dE = TdS - PdV + \sum_{i=1}^{k} \frac{\partial E}{\partial n_i} dn_i + \sum_{i=1}^{j} \frac{\partial E}{\partial \xi_i} d\,\xi_i \qquad (21)$$

in which

E is the energy of the system as defined by the first law of thermodynamics;

S is the entropy of the system as defined by the second law of thermodynamics;

P, V, T are the pressure, volume, and absolute temperature of the system;

n_i is the number of moles of a given component, i, present in the system;

ξ_i represents any other variable such as magnetic or electrical field strength required to define the state of the system.

The quantities represented by the term $(\partial E/\partial n_i)_{S,V,n_j,\xi_j}$ are extremely important, and are called the "chemical potentials" of the system; they are usually represented by the symbol μ_i.

It is often convenient to express the fundamental differential equation in terms of other functions which are defined in such a way as to facilitate the handling of special systems. These functions are:

Enthalpy = $H = E + PV$

Free Energy = F = E + PV - TS = H - TS

Work Function = A = E - TS

The above relations lead to the differential equations:

$$dH = VdP + TdS + \sum_{i=1}^{k} \mu_i \, dn_i$$

$$dF = VdP - SdT + \sum_{i=1}^{k} \mu_i \, dn_i \qquad (22)$$

$$dA = -PdV - SdT + \sum_{i=1}^{k} \mu_i \, dn_i$$

The quantities represented by $\underline{\xi_i}$ have been ignored, since they remain constant for the usual thermodynamic systems. Since $\underline{dH}$, $\underline{dF}$, and $\underline{dA}$ are perfect differentials by virtue of their definitions, it is evident that:

$$\mu_i = \left(\frac{\partial E}{\partial n_i}\right)_{S,V,n_j} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j} =$$

$$\left(\frac{\partial F}{\partial n_i}\right)_{P,T,n_j} = \left(\frac{\partial A}{\partial n_i}\right)_{V,T,n_j} \qquad (23)$$

The importance of the chemical potential, $\underline{\mu_i}$, to the chemist lies in the fact that it is an excellent measure of the "escaping tendency" of the component $\underline{i}$. In a manner analogous to electrical potential differences, differences in chemical potentials can be thought of as driving forces tending to the reversible isothermal transfer of component $\underline{i}$ from one state into another.

As an example, consider first a system of two phases each composed of *K* components. Suppose that $\underline{d\epsilon}$ moles of component *i* are transferred from phase 1 to phase 2. The changes in energy in the two phases will be:

$$dE_1 = T_1\ dS_1 - P_1 dV_1 - \mu_i^1\ d\epsilon \qquad (24)$$

$$dE_2 = T_2 dS_2 - P_2 dV_2 + \mu_i^2\ d\epsilon \qquad (25)$$

The total energy change will be:

$$q - w = dE = dE_1 + dE_2 = T_1 dS_1 + T_2 dS_2 - (P_1 dV_1 + P_2 dV_2) + (\mu_i^2 - \mu_i^1)\ d\epsilon \qquad (26)$$

If pressure-volume work were the only type of work done in the transfer, the pressure-volume terms cancel the term *W*, and, therefore, $q = T_1 dS_1 + T_2 dS_2 + (\mu_i^2 - \mu_i^1) d\epsilon$.

According to the second law of thermodynamics, for a reversible or equilibrium process, $q = T_1 dS_1 + T_2 dS_2$ while for a spontaneous process $q < T_1 dS_1 + T_2 dS_2$. Thus the condition for equilibrium, when pressure-volume work alone is done, is that $\mu_i^1 = \mu_i^2$. The condition of spontaneous transfer is that $\mu_i^2 < \mu_i^1$, thus material will spontaneously transfer from a region of higher to a region of lower chemical potential.

It is important to note that one could introduce a work term $\underline{w'}$ in addition to pressure-volume work. If this is done then the condition of equilibrium becomes $(\mu_i^2 - \mu_i^1) d\epsilon = w'$; use is made of this expression in deriving the voltages of reversible galvanic cells. In the example under discussion, if equilibrium were to be established by applying a voltage, E, to the system, it follows that $W' = -nFd\epsilon\ E$ so that $\mu_i^2 - \mu_i^1 = -nFE$. The integer, n, is the number of Faradays of charge transported by one mole of component i.

A further important example of the properties of the chemical potentials is their use in predicting the spontaneity of chemical reactions. Consider a system containing any number of constituents, among which a chemical reaction is possible such that:

$$aA + bB + \text{---} \longrightarrow mM + nN + \text{----} \tag{27}$$

If the reaction were allowed to proceed by an infinitesimal amount, the change in energy must conform to the relation:

$$dE = TdS - PdV + \sum_{i=1}^{k} \mu_i\, dn_i \tag{28}$$

If only pressure-volume work is done, and if the process is reversible, $q = TdS$ and $W = PdV$. Thus, for such a process:

$$\sum_{i=1}^{k} \mu_i\, dn_i = o \tag{29}$$

For a spontaneous reaction to occur, $q < TdS$ so that:

$$\sum_{i=1}^{k} \mu_i\, dn_i < o \tag{30}$$

If the reaction is allowed to proceed to an infinitesimal degree such that a $d\epsilon$ moles of A are consumed, then:

$$\sum_{i=1}^{k} \mu_i \, dn_i = (m\mu_M + n\mu_N + \text{--} \; - a\mu_A - b\mu_B \text{--})d\epsilon \qquad (31)$$

The condition of equilibrium is thus:

$$(m\mu_M + n\mu_N + \text{--} - a\mu_A - b\mu_B \text{--}) = 0 \qquad (32)$$

Although the chemical potential of a given component of a system is an excellent measure of the "escaping tendency" of that component, it is not a convenient quantity to use for chemical calculations. It was for this reason that G. N. Lewis (91) introduced the activity concept which is much better suited to the needs of the chemist. Lewis recognized that the great majority of chemical systems adhere fairly closely to simple laws relating their properties to compositions and pressures. For example, most solutions show little deviation from Raoult's law; at low concentrations Henry's law is obeyed; most chemical systems at equilibrium can be described by the mass action law of Guldberg and Waage. Lewis therefore considered that a solution which obeyed these laws exactly could be considered to be an ideal solution. For any actual solution the same laws were supposed to hold exactly provided that the concentrations were corrected by the introduction of an "activity coefficient". The product of the concentration and the appropriate coefficient was called the activity. Since most solutions follow the laws to a first approximation, the activities are very similar in value to concentrations and are thus more easily handled by the chemist than are chemical potentials.

The relationship between activities and chemical potentials can be deduced from any of the relations mentioned above. For example, according to the Guldberg and Waage law, one would have the following equation for the equilibrium system previously discussed in terms of chemical potential:

$$\frac{a_M^m \, a_N^n \, \cdots\cdots}{a_A^a \, a_B^b \, \cdots\cdots} = K \tag{33}$$

The expression for equilibrium in terms of chemical potential is:

$$m\mu_M + n\mu_N + \text{--} - a\mu_A - b\mu_B \text{--} = 0 \tag{34}$$

The only manner in which the linear expression can be expressed in the form of the equilibrium constant is to set the values of μ as some linear function of the logarithms of the activities. Thus, if one sets:

$$\mu_i = C_i + S \ln a_i \tag{35}$$

equation (34) can be written:

$$(mC_M + nC_N + \ldots - aC_A - bC_B \ldots\ldots) +$$

$$S \ln \frac{a_M^m a_N^n \ldots\ldots}{a_A^a a_B^b \ldots} = o \qquad (36)$$

Since the quantity in parentheses is a constant it is equivalent to the Guldberg and Waage form. The constants, $\underline{C_i}$, in equation (35) are perfectly arbitrary and can be set as desired. The constant, $\underline{S}$, can be evaluated by considering the application to a perfect gas, for which pressure is the appropriate representation of the concentration. The choice of $\underline{C_i}$ is arbitrary and it can be taken as equal to $\underline{\mu_i^o}$, the potential of the gas when its pressure is unity. Under this condition $\underline{a_i}$ has a value of unity for the gas at one atmosphere since $\underline{\ln a_i}$ will be zero. Now consider the change in chemical potential resulting from an isothermal compression to pressure, $\underline{p}$, from a pressure of unity.

$$\mu_{(p)} - \mu_{(1)} = S \ln \frac{a_{(p)}}{a_{(1)}} = S \ln a_{(p)} \qquad (37)$$

however:

$$\mu_i = \left(\frac{\partial F}{\partial N_i}\right)_{P,T,n_j} \qquad (38)$$

For one component:

$$F = \int_o^{n_1} \mu_1 \, dn_1 = \mu_1 n_1 = \mu_1$$

thus, for one mole:

$$\mu_{(p)} - \mu_{(1)} = \Delta F_{(compr.)} = \int_1^P VdP =$$

$$\int_1^P RTd\ln P = RT\ln P \qquad (39)$$

so that:

$$S \ln a_{(p)} = RT \ln P \qquad (40)$$

As expected, activity corresponds to the "concentration" in terms of P; and S is shown to be equal to RT. Thus the definition of the activity can be made as:

$$\mu_i = C_i + RT \ln a_i \qquad (41)$$

The constant, C_i, can be written as μ_i^o, and is the chemical potential in an arbitrary state chosen for convenience. By convention, the standard states are chosen in one of the following ways:

(1) $$\frac{a_i}{N_i} \rightarrow 1 \text{ as } N_i \rightarrow 1 \qquad (42)$$

in which N_i is the mole fraction of the component i. This choice is made for handling a solvent component, since the mole-fraction of solvent is usually close to unity.

(2) $$\frac{a_i}{N_i} \rightarrow 1 \text{ as } N_i \rightarrow o \qquad (43)$$

in which N_i is the mole fraction of the component i. This standard state is often used for discussing the solute in a solution. If Raoult's law is obeyed for a solution the activity is very nearly equal to the mole-fraction. For a perfect solution activity is exactly the mole-fraction.

$$(3) \quad \frac{a_i}{m_i} \rightarrow 1 \text{ as } m_i \rightarrow 0 \tag{44}$$

$$\text{or} \quad \frac{a_i}{C_i} \rightarrow 1 \text{ as } C_i \rightarrow 0 \tag{45}$$

in which m_i represents the molality of the component in solution and C_i the molarity of the component. One of these choices is often made for the treatment of dilute solutions. In such solutions Henry's law is approximately obeyed and the activities with the above convention are nearly equal to the molalities as well as molarities.

The usual practice in dealing with activities is to assume a perfect solution to be one for which the activity is always equal to the mole-fraction under convention (2). With this assumption, activity coefficients of perfect solutions under convention (3) are not unity, but are very close to it. If the activity coefficient for convention (2) is designated by f, that for the molality convention under (3) is designated by γ, and that for the molarity convention is designated by y, then the following relations exist among them:

$$\ln f = \ln \gamma + \ln (1 + mM_1/1000)$$

$$\ln f = \ln y + \ln\left[\frac{d}{do} + C\left(\frac{M_1 - M_2}{1000\ d_o}\right)\right] \quad (46)$$

$$\ln \gamma = \ln y + \ln\left[\frac{d}{do} - \frac{CM_2}{1000\ d_o}\right]$$

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

For solutions of electrolytes a further convention is employed. The standard states for the ions are chosen under either (2) or (3) as formulated above, and the standard state for the undissociated molecules is chosen in such a way that the dissociation constant is unity. This means that for a salt $M_{\nu_+} A_{\nu_-}$:

$$\mu_2^\circ = \nu_+ \mu_+^\circ + \nu_- \mu_-^\circ \quad (47)$$

in which μ_2° is the chemical potential of the undissociated salt in its standard state and μ_+°, μ_-° are the chemical potentials of the ions in their standard states.

In the case of electrolytes which are completely dissociated, the chemical potential of the solute as a whole is simply the sum of those of the constituent ions so that $\mu_2 = \nu_+ \mu_+ + \nu_- \mu_-$ and:

$$\mu_2^\circ + RT \ln a_2 = \nu_+ \mu_+^\circ + \nu_- \mu_-^\circ + RT \ln a_+^{\nu_+} a_-^{\nu_-} \quad (48)$$

Since μ_s^o is equal to $\nu_+\mu_+^o + \nu_-\mu_-^o$, it follows that:

$$a_s = a_+^{\nu_+} a_-^{\nu_-} \tag{49}$$

For convenience in dealing with electrolytes of the above type of mean ionic activity, $\underline{a_\pm}$, is defined such that:

$$a_\pm = \left(a_+^{\nu_+} a_-^{\nu_-}\right)^{1/\nu} \tag{50}$$

in which $\underline{\nu} = \nu_+ + \nu_-$. It follows that $a_s = a_\pm^{\nu}$.

The measurement of activities of solutes in solution falls into two general classifications: those in which the activities of the solute are calculated from the measured activities of the solvent, and those in which the activities of the solute are measured directly.

The first method includes measurements of freezing point depression, boiling point elevation, osmotic pressure, and other colligative properties of the solutions; the freezing point depression method is typical of these and is used below to illustrate their application.

Assume that, upon freezing a solution, the pure solid solvent separates from the liquid phase. Choose the standard state for the solvent in both phases as pure liquid solvent at one atmosphere and at the freezing point. For the pure solid solvent:

$$\left(\frac{\partial \ln a_s}{\partial T}\right)_P = -\frac{\Delta H(\text{solidification})}{RT^2} \tag{51}$$

Equation (51) can be integrated for a_s if ΔH has been measured and T is known. Since both the solvent in the solution and the solid solvent are referred to the same standard state, the value of a_s so obtained is the activity of the solvent in the solution at the freezing point. To obtain the activities of solvent, a_1, as a function of concentration at a given temperature, T, it is necessary to measure the relative heat contents of the solvent as a function of composition so that the equation:

$$\left(\frac{\partial \ln a_1}{\partial T}\right)_P = -\frac{\overline{L}}{RT^2} \tag{52}$$

can be applied.

After the activities, a_1, of the solvent have been determined, the Gibbs-Duhem equation can be used to evaluate the activities, a_2, of the solute. According to this equation:

$$\ln \frac{a_2}{N_2} = -\int_{N_2=0}^{N_2=N_2} N_1/N_2 \, d\ln a_1/N_1 \tag{53}$$

The value of the integral in Equation (53) can be computed graphically.

The second method, direct measurement of the solute activity, could utilize one of the procedures considered above for solvent activity; however, this is usually impractical owing to the relatively small contribution of the solute to the properties of dilute solutions. Measurement of solute activity can also be made for electrolytic solutions by employing electrochemical cells. These cells are of two general types, that is, cells without transference and cells with transference. In a cell without transference there is no contact between two phases which are miscible, whereas in a cell with transference such a contact occurs. For example, a typical cell with transference contains a junction between two solutions of different concentrations of an electrolyto; a cell without transference has no junction of this type, but is so arranged that all phase boundaries occur between immiscible phases. The cell without transference always requires the use of electrodes reversible to each ion of an electrolyte whose activity is to be measured; the cell with transference requires electrodes reversible to only one species of ion in the solutions.

An example of a cell without transference is afforded by the cell:

$$H_2\ (1\ \text{atm}) - Pt \mid HCl \mid AgCl - Ag$$

If an electrical current were allowed to flow through this cell so that electrons were passed from right to left outside the cell, then the electrode reactions are:

$$\tfrac{1}{2}\,H_2\ (1\ \text{atm.}) \longrightarrow H^+ + e$$

$$e + AgCl \longrightarrow Ag + Cl^-$$

and the overall reaction is:

$$\tfrac{1}{2}\,H_2\ (1\ \text{atm.}) + AgCl \longrightarrow H^+ + Ag + Cl^-$$

As indicated above, if an equilibrium were established in the system by impressing an external E.M.F. across the electrodes, the E.M.F. would be given by the relation:

$$\sum_i \mu_i\, dn_i = W' = -\,n\,FE\,d\epsilon \tag{54}$$

If the standard states of the solid phases and of hydrogen are chosen as their respective states in the cell, and if the standard state $a_i/m_i \longrightarrow 1$ as $m_i \longrightarrow o$ is chosen for the ions, then the above equation can be written:

$$-\,FE = \mu_{H+} + RT\ln a_{H+} + \mu^{o}_{Ag} + \mu^{o}_{Cl-} + RT\ln a_{Cl-} - \tfrac{1}{2}\mu^{o}_{H_2} - \mu^{o}_{AgCl}$$

$$E = \frac{\tfrac{1}{2}\mu^{o}_{H_2} + \mu^{o}_{AgCl} - \mu^{o}_{H+} - \mu^{o}_{Cl-} - \mu^{o}_{Ag}}{F} - \frac{RT}{F}\ln a_{H+}a_{Cl-}$$

$$E = E_o - \frac{2RT}{F}\ln a_{\pm\,HCl} \tag{55}$$

in which $\underline{E_o}$ represents the term into which the values of $\underline{\mu^{o}}$ are collected.

It is evident from this expression that $a_\pm$ values for salts can be determined from the potentials of such cells; however, they require an electrode reversible to each of the ions of the salt and these are often not available. For this reason the scope of the second class of cells which requires an electrode reversible to one of the ions alone is greater.

Cells with transference were used in the present work and will be discussed in terms of the arrangement used for lanthanum chloride. This cell can be written:

$$\mathrm{Ag - AgCl} \left| \begin{matrix} \mathrm{LaCl_3} \\ C_1 \end{matrix} \right| \begin{matrix} \mathrm{LaCl_3} \\ C_2 \end{matrix} \bigg| \mathrm{AgCl - Ag}$$

The changes occurring in the cell during the passage of current consist of electrode reactions together with ionic transport through the liquid junction. If the junction is initially sharp it will begin to disappear immediately owing to diffusion, so that a region of varying concentration is produced between the two solutions of composition C_1 and C_2. For this reason the contribution of each infinitesimal layer in this region of varying concentration must be computed and the total effect obtained by integration. Consider a plane in the boundary region having on the left an electrolyte of concentration C, and on the right a concentration $C + dC$. If one Faraday of electrons is passed from right to left within the cell then $\underline{\tau_+/3}$ g-ion of La^{+3} will be transported across the boundary from left to right, while $\underline{\tau_-}$ g-ion of chloride will move from right to left. $\underline{\tau_+}$ and $\underline{\tau_-}$ are the Hittorf transference numbers for the ions. The change in chemical potential of the lanthanum ions will be $\underline{d\mu_+}$ while that of the chlorides will be $\underline{-d\mu_-}$. The increment of E.M.F. required to bring the layer to equilibrium is:

$$-FdE = \frac{\tau_+}{3}\, d\mu_+ - \tau_-\, d\mu_-$$

The total E.M.F. required to bring equilibrium to the junction will thus be:

$$E_j = \int_{C_1}^{C_2} -\frac{\tau_+}{3F}\, d\mu_+ + \frac{\tau_-}{F}\, d\mu_- \qquad (56)$$

One equivalent of chloride is formed at the right electrode and one equivalent disappears at the left during the passage of one Faraday of current. It is evident that the net effect is the transfer of one equivalent of chloride from solution of concentration $\underline{C_1}$ to one of concentration $\underline{C_2}$. The E.M.F. required to balance this reaction is:

$$E_{\text{electrodes}} = \frac{-\mu_-(C_2) + \mu_-(C_1)}{F}$$

so that the overall E.M.F. for the cell will be:

$$E = E_j + E_{\text{electrodes}} = \frac{-\mu_-(C_2) + \mu_-(C_1)}{F}$$

$$+ \int_{C_1}^{C_2} \left[-\frac{\tau_+}{3F}\, d\mu_+ + \frac{\tau_-}{F}\, d\mu_- \right]$$

Writing the first term as an integral, the following relations are obtained:

$$E = \int_{C_1}^{C_2} \left[-\frac{d\mu_-}{F} - \frac{\tau_+}{3F}\, d\mu_+ + \frac{\tau_-}{F}\, d\mu_- \right]$$

$$E = -\int_{C_1}^{C_2} \frac{\tau_+}{F} \left[\frac{d\mu_+}{3} + d\mu_- \right]$$

$$E = -\int_{C_1}^{C_2} \frac{\tau_+}{F} \left[\frac{RT}{3}\, d\ln a_+ + RT\, d\ln a_- \right]$$

$$E = -\int_{C_1}^{C_2} \frac{\tau_+ RT}{F}\, d\ln\, (a_+ a_-^3)^{\frac{1}{3}}$$

$$E = -\int_{C_1}^{C_2} \frac{4RT}{3F}\, \tau_+\, d\ln a_\pm \tag{57}$$

Using the above relations, the activities can be calculated from the observed E.M.F. values of the cells. The transference numbers must be known as a function of concentration. Since the process by which the E.M.F. is computed is essentially the same as that taking place in a moving-boundary experiment, transference numbers obtained by the latter method are correct for this application. The details of the computation are given under the experimental section.

The appearance of the transference numbers in the equation (57) suggests that the transference numbers of an electrolyte can be measured using cells with transference if the activities of the salt have been measured by some other means. This method has been applied; it is the third of the methods mentioned in the section on transference numbers. The usual practice is to determine the activity coefficients for the electrolyte by using cells without transference, although any suitable procedure can be employed for this purpose. In general, this method for determining transference numbers has been avoided, since the measurement of activities by the use of concentration cells without transference or by the freezing point or boiling point methods is relatively difficult.

The theoretical treatment of the activity coefficients of strong electrolytes has been very extensive. Adequate reviews of the history and development of the modern theories are available (6, 92), and no attempt will be made here to repeat their contents. There is little doubt at the present time of the essential validity of the Debye and Hückel (13) treatment of electrolytic solutions at very high dilutions. Their limiting law has been found correct in innumerable situations for salts of 1-1, 2-1, and 1-2 valence types, and it can be used with confidence for extrapolation of data for such salts.

As indicated in the introduction, the free energy change experienced by an electrolyte, upon dissolving in a solvent, can be separated into a decrease due to ideal solution behavior and a decrease due to the non-ideal behavior. In 1923, Debye and Hückel (13) derived an expression for the non-ideal decrease upon the assumption that it was due entirely to the charge-charge interactions among the ions. Using the assumptions and method discussed in the theory part of the conductance section of this thesis, they arrived at a formula for the electrostatic potential at the site of any ion in a solution. From this potential it was possible to calculate the expected free energy decrease of the salt due to electrostatic interactions. The final expression for an ion of species _i_ is:

$$\frac{\Delta F_i(\text{non-ideal})}{RT} = \ln f_i = \frac{-AZ_i^2 \sqrt{\mu}}{1 + a_i^o B \sqrt{\mu}} \qquad (58)$$

in which:

$$\underline{A} = \frac{\epsilon^3}{(DkT)^{3/2}} \sqrt{\frac{2\pi N}{1000}};$$

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

$\underline{D}$ is the dielectric constant;

$\underline{k}$ is the Boltzman constant;

T is the absolute temperature;

Z_i is the number of charges on the *ith* ion;

N is Avogadro's number;

a_i^o is the effective ionic radius of the *ith* ion;

μ is the ionic strength of the solution; and

$B = \sqrt{\frac{8 \pi N \epsilon^2}{1000\ DkT}}$

For a binary electrolyte, Equation (58) may be used to compute the mean ionic rational activity coefficient, $f_\pm$, by the relation:

$$\ln f_\pm = \frac{-Z_+ Z_- A \sqrt{\mu}}{1 + a^o B \sqrt{\mu}} \qquad (59)$$

The quantity, a^o, represents the mean distance of closest approach of the centers of the ions; since the ions of like charge repel each other while those of unlike charge attract each other, the value of a^o should be very nearly the closest distance of approach of the positive and negative ions. It has been found that in many cases the value for a^o required for a satisfactory fit to experimental data is much smaller than the mean ionic diameter of the ions as measured crystallographically; in some cases, for large ions, a value of zero must be assumed. This indicates that the a^o may not actually be the average value of the ionic diameters, but might be a parameter which corrects for a whole variety of theoretical imperfections.

Various extensions of the Debye and Hückel theory have been proposed. Gronwall, LaMer, and Sandved (93), and LaMer, Gronwall, and Greiff (94) have successfully solved the Poisson equation for the case in which a few of the higher terms in the expanded Boltzman expression were retained. Bjerrum (95) has taken into consideration the formation of ion-pairs; the many proposed empirical extensions have been reviewed by Harned and Owen (7, Chapter 3). At the present time, however, it is evident that much more work must be done on the problem before an adequate theory for solutions of even moderate concentrations can be evolved. The present theories are useful only in the extremely dilute range and no convincing arguments have yet been applied to the higher ranges of concentrations.

History of the Method

Helmholtz (96), in 1877, was the first investigator to consider the nature of the E.M.F. of concentration cells with transference. In order to calculate the junction potential between two solutions of the same salt upon the basis of purely thermodynamic reasoning, he calculated the maximum work available from the transfer of salt from one concentration to the other by considering the work required to undo the transfer by vaporizing water from one solution; compressing it; and returning it to the other solution. His ideas were essentially correct although he considered the transference number to be independent of concentration.

The work of Helmholtz laid the foundation for the study of cells with transference and his ideas were soon roughly confirmed by the work of Moser (97) and Miesler (98) using silver nitrate cells and silver acetate cells. In 1889, Nernst (48) wrote a very thorough paper on concentration cells in which he derived an expression for the E.M.F. by a kinetic method. He assumed that the osmotic pressure of the solution acted upon the salt in the same manner as gas pressure acts upon the molecules of a gas, and he computed the junction potential from the differences in velocities to be expected from the rates of diffusion of the different ions. He considered the transference numbers of the salts to be independent of concentration; other than this his equation agreed with that of Helmholtz. Nernst performed a large number of experiments on concentration cells with transference and found fair agreement with his theory, even though he assumed osmotic pressures to be proportional to concentration, and he estimated ionic concentrations from conductance measurements. Jahn (99) made extensive measurements on cells with potassium chloride, or sodium chloride, or hydrochloric acid; his results showed reasonable agreement with the Nernst theory. He employed the degree of dissociation obtained from conductance to estimate the concentrations; thus effectively made a partial correction for activity effects. He noted that the conductance might not give a satisfactory estimate of concentrations above 0.01 normal.

In 1915, D. A. MacInnes and K. Parker (100) became interested in the possibility of measuring transference numbers from the E.M.F. values of cells with and without transference. In an extensive investigation on potassium chloride they showed that the use of Nernst's equation gave excellent checks with the known transference data. The above authors indicated, for apparently the first time, that activities should be employed in place of concentrations in the Nernst equation since the activities of the ions are proportional to osmotic pressures. MacInnes and Beatty (101) materially improved the technique for measuring potentials of concentration cells with transference, and they took into consideration the variation of the transference numbers with concentration. A method of successive approximations was used to evaluate cation transference numbers for lithium chloride.

Prior to 1927, some confusion remained concerning the true nature of the junction potential between two solutions of the same salt. This confusion was ended when P. B. Taylor (102) presented a thoroughly accurate treatment of the whole subject. Unfortunately he based his treatment on the "true" transference number in place of the Hittorf transference number, and thus introduced a correction for the transport of water which is unnecessary when the Hittorf number is used.

Prior to 1935, the concentration cell with transference had not been applied to the determination of activities of electrolytes, because the available transference number data were not sufficiently precise. The accumulation of good moving-boundary data, however, led MacInnes and Brown (103) to use such cells for that purpose. They and later experimenters used this method for determining activity coefficients with great success, and a large number of data have been accumulated for salts which could not have been studied in cells without transference.

The apparatus employed for determinations of the voltages of concentration cells with transference has remained essentially the same as that employed by the earliest workers and the method of forming the boundary is not critical as long as there is no diffusion into the electrode compartments. The most recent forms of cells are completely described by D. A. MacInnes (6).

The only recent contributions to the method have been by Hermans (104) and Koenig (105). The latter gave conclusive proof that the Hittorf transference number should be used to compute the junction potential, and that when this number is used no water corrections are required; he also extended the theory to cover the effects of gravitational, magnetic and electrical fields. The work of Hermans is of particular interest in connection with the theory of diffusion.

Experimental

Preparation of solutions

The method for preparing the solutions of rare earth chlorides was the same as that described in the conductance section of this thesis.

Apparatus

The cell assembly used for measurement of the concentration cell potentials is shown in Figure 18. It consisted of a hollow-bore two-way vacuum stopcock modified as shown and joined to the two electrode compartments. Each electrode compartment was equipped with two 10/30 standard taper ground-glass joints into which the electrodes could be inserted. The compartment which was used for the more

Figure 18. Concentration Cell with Transference.

dilute solution was connected to the central opening of the stopcock and was provided with a small trap as a safeguard against the entry of the stronger solution. To use the cell, it was first thoroughly cleaned, and the stopcock was seated, using a lubricant prepared by melting together beeswax and vaseline and leaching the mixture thoroughly by boiling several times in conductivity water. The compartment for the more dilute solution was filled first and the stopcock was turned to the closed position. The electrodes, prepared as described below, were then inserted. When the dilute compartment had been prepared, the bore of the stopcock and the other compartment were rinsed with at least 5 portions of the stronger solution, and finally filled with the stronger solution. The electrodes for this compartment were inserted, the stopper was placed in the stopcock plug, and the cell was placed in a bath at 25° ± 0.02°C. After a minimum of one hour, the stopcock was turned to the open position to establish the junction, and the potentials were read. It was found that the potentials remained constant within one or two microvolts for periods as long as 8 to 12 hours.

The preparation of the silver-silver chloride electrodes was found to require extreme care. The method used was the thermal-electrolytic method of H. S. Harned (106), in which silver is deposited upon platinum by coating it with silver oxide and igniting at 400°C. The chloridizing is done electrolytically from dilute hydrochloric acid. The details of the method of preparation of the electrodes are given below.

A dilute solution of c.p. sodium hydroxide in conductance water was slowly added to a dilute solution of reagent grade silver nitrate in conductance water to precipitate silver oxide. The resulting solution and suspension were boiled and allowed to settle. The supernatant liquor was decanted; the silver oxide was then washed thoroughly 35 times by boiling in a large volume of conductance water and filtering with a pyrex sintered glass filtering funnel. The electrodes were constructed by sealing platinum wires into the ends of short extensions attached to the ends of 10/30 standard taper male joints. These platinum wires extended about 5 cm outside of the glass and were rolled into small spirals. The platinum spirals were cleaned thoroughly by alternately heating to redness and plunging into concentrated nitric acid. They were then filled with silver oxide paste, dried in an oven at 150°C, and heated at 400°C for about 12 hours. The silver so produced was pure white and spongy; it was necessary to re-coat with silver oxide and re-ignite several times in order to completely cover the platinum spiral. When a good deposit of silver had been attained, mercury was added to the inside of the glass tubing to allow good electrical contact with the platinum wires, and the electrodes were chloridized by electrolyzing for 45 minutes at 8 milliamperes in a solution of 1 normal hydrochloric acid.

After preparation of each batch of about 30 electrodes, they were immersed in a solution of 0.1 normal KCl for 24 hours with all electrodes connected together electrically. The potassium chloride used for this purpose must be specially purified by the method of Pinching and Bates (107). After the 24-hour equilibration period the potentials of all the electrodes were compared, and any electrodes were rejected which differed from the mean by more than 0.02 millivolts. In using the electrodes for measurement, they were first rinsed with conductance water and then with the solution to be studied. They were then soaked in the test solution for at least an hour, the solution was changed, and they were soaked at least one more hour in fresh solution before they were introduced into the cell. To compensate for the differences of the order of 0.01 millivolts between electrodes, all measurements were repeated with the electrodes reversed and the average voltage was taken as the true cell voltage. Table 11 shows a typical set of readings taken for a concentration cell.

The potentiometer used to make the readings was a Rubicon type B precision potentiometer equipped with a

TABLE 11

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

(Cerium Chloride: 0.199 normal vs. 0.004794 normal)

Electrodes	E.M.F. millivolts	Average E.M.F. millivolts
1 vs. 2	40.811	
2 vs. 1	40.850	40.832
1 vs. 3	40.800	
3 vs. 1	40.872	40.836
2 vs. 4	40.852	
4 vs. 2	40.810	40.831
3 vs. 4	40.825	
4 vs. 3	40.845	40.835
	Average	40.833 mv.
	Average deviation	0.002 mv.
	Maximum deviation	0.003 mv.

special galvanometer having a sensitivity of 1.2×10^{-9} amp. per mm with an internal resistance of 16.4 ohms and a critical damping resistance of 8 ohms. Three standard cells recently calibrated by the National Bureau of Standards were used for standardization; these cells were in perfect agreement with one another.

Results

The data obtained are summarized in Tables 12, 13, 14 and 15, and in Figure 19. The detailed procedure for calculating the activity coefficients is given below.

The differential expression for the E.M.F. of a concentration cell with transference is:

$$dE = \frac{\nu RT}{\nu_+ Z_+ F} \tau_+ \, d \ln a_\pm \tag{60}$$

If a quantity $\delta = \frac{1}{\tau_+} - \frac{1}{\tau_+ \text{ (Ref. Sol'n.)}}$ is introduced into Equation (60) and the equation is integrated and rearranged, the following equation is obtained for 3-1 electrolytes:

$$\log \frac{y_\pm}{y_\pm \text{ (Ref.)}} = - \frac{3F}{(2.303)4RT} \int_0^E \delta \, dE - \frac{3FE}{(2.303)4RT \, \tau_+ \text{(Ref.)}} + \log \frac{C\text{(Ref.)}}{C} \tag{61}$$

TABLE 12

Activity Coefficients of Lanthanum Chloride Solutions.

Molarity	Molality	E.M.F.	E.M.F. (average)	$\log \frac{y_\pm}{y_\pm(\text{Ref.})}$	$y_\pm$ (observed)	$\gamma_\pm$ (observed)	$\gamma_\pm$ (Debye-Hückel)*
0.031077	0.031186	0.000	0.000	0.0000	0.4321	0.4319	0.4320
0.02486	0.02494	2.568					
		2.568					
		2.566					
		2.567	2.567	0.02318	0.4558	0.4556	0.4549
0.01243	0.01247	10.833					
		10.831					
		10.826					
		10.821	10.828	0.09024	0.5319	0.5318	0.5299
0.006215	0.006234	19.542					
		19.540					
		19.535					
		19.536	19.538	0.14850	0.6083	0.6082	0.6075
0.003108	0.003117	28.669					
		28.665					
		28.644					
		28.630	28.652	0.19840	0.6824	0.6824	0.6823
0.002486	0.002493	31.635					
		31.642					
		31.638					
		31.630	31.636	0.21360	0.7067	0.7067	0.7050

TABLE 12 (continued)

Molarity	Molality	E.M.F.	E.M.F. (average)	$\log \frac{y_\pm}{y_\pm(\text{Ref.})}$	$y_\pm$ (observed)	$\gamma_\pm$ (observed)	$\gamma_\pm$ (Debye-Hückel)*
0.001243	0.001248	41.405					
		41.394					
		41.375					
		41.395	41.392	0.24870	0.7661	0.7661	0.7700

* Calculated using $a^o = 5.75$ Å

TABLE 13

Activity Coefficients of Cerium Chloride Solutions.

Molarity	Molality	E.M.F.	E.M.F. (average)	$\log \frac{y_{\pm}}{y_{\pm}(\text{Ref.})}$	$y_{\pm}$ (observed)	$\gamma_{\pm}$ (observed)	$\gamma_{\pm}$ (Debye-Hückel)*
0.03995	0.04009	0.000	0.000	0.00000	0.4080	0.4078	0.4074
0.03196	0.03207	2.547					
		2.547					
		2.543					
		2.541	2.545	0.02316	0.4304	0.4302	0.4292
0.02397	0.02405	5.907					
		5.903					
		5.910					
		5.909	5.907	0.05162	0.4595	0.4594	0.4587
0.01598	0.01603	10.712					
		10.703					
		10.720					
		10.708	10.711	0.09147	0.5036	0.5035	0.5022
0.007991	0.008015	19.289					
		19.293					
		19.293					
		19.294	19.292	0.15247	0.5796	0.5795	0.5795
0.003196	0.003205	31.250					
		31.238					
		31.260					
		31.245	31.248	0.22109	0.6788	0.6788	0.6720

TABLE 13 (continued)

Molarity	Molality	E.M.F.	E.M.F. (average)	$\log \frac{y_\pm}{y_\pm(\text{Ref.})}$	$y_\pm$ (observed)	$\gamma_\pm$ (observed)	$\gamma_\pm$ (Debye-Hückel)*
0.001598	0.001603	40.832					
		40.836					
		40.830					
		40.835	40.833	0.26084	0.7438	0.7438	0.7475
0.0007991	0.0008015	50.740					
		50.745					
		50.745					
		50.748	50.745	0.29312	0.8012	0.8012	0.8061

* Calculated using $a^\circ = 5.75$ Å

TABLE 14

Activity Coefficients of Praseodymium Chloride Solutions.

Molarity	Molality	E.M.F.	E.M.F. (average)	log $\frac{y_\pm}{y_\pm(\text{Ref.})}$	$y_\pm$ (observed)	$\gamma_\pm$ (observed)	$\gamma_\pm$ (Debye-Hückel)*
0.032181	0.03235	0.000	0.000	0.00000	0.4285	0.4283	0.4279
0.02575	0.02587	2.583 2.584 2.582 2.579	2.582	0.02260	0.4514	0.4512	0.4507
0.01287	0.01293	10.864 10.863 10.863 10.865	10.864	0.09003	0.5272	0.5271	0.5257
0.006436	0.006462	19.546 19.542 19.543 19.546	19.544	0.14986	0.6050	0.6049	0.6033
0.003218	0.003230	28.663 28.663 28.662 28.663	28.663	0.20043	0.6798	0.6798	0.6785
0.002575	0.002583	31.638 31.644 31.655 31.660	31.649	0.21579	0.7042	0.7042	0.7014

TABLE 14 (continued)

Molarity	Molality	E.M.F.	E.M.F. (average)	log $\frac{y_\pm}{y_\pm(\text{Ref.})}$	$y_\pm$ (observed)	$\gamma_\pm$ (observed)	$\gamma_\pm$ (Debye-Hückel)*
0.001287	0.001291	41.395 41.397 41.396 41.399	41.397	0.25183	0.7652	0.7652	0.7669
0.0006436	0.0006456	51.477 51.478 51.499 51.494	51.487	0.28002	0.8165	0.8165	0.8222

* Calculated using $a^\circ = 5.73$ Å

TABLE 15

Activity Coefficients of Neodymium Chloride Solutions.

Molarity	Molality	E.M.F.	E.M.F. (average)	log $\frac{y_\pm}{y_\pm(\text{Ref.})}$	$y_\pm$ (observed)	$\gamma_\pm$ (observed)	$\gamma_\pm$ (Debye-Hückel)*
0.03677	0.03701	0.000	0.000	0.00000	0.4182	0.4180	0.4180
0.03014	0.03024	2.559					
		2.562					
		2.563					
		2.563	2.562	0.02295	0.4408	0.4406	0.4398
0.01507	0.01512	10.762					
		10.762					
		10.759					
		10.761	10.761	0.09118	0.5158	0.5157	0.5122
0.007536	0.007559	19.374					
		19.373					
		19.377					
		19.375	19.375	0.14817	0.5882	0.5881	0.5886
0.003768	0.003779	28.413					
		28.412					
		28.424					
		28.425	28.419	0.19985	0.6625	0.6624	0.6638
0.003014	0.003023	31.363					
		31.369					
		31.349					
		31.345	31.357	0.21623	0.6880	0.6880	0.6870

TABLE 15 (continued)

Molarity	Molality	E.M.F.	E.M.F. (average)	$\log \frac{y_{\pm}}{y_{\pm}(\text{Ref.})}$	$y_{\pm}$ (observed)	$\gamma_{\pm}$ (observed)	$\gamma_{\pm}$ (Debye-Hückel)*
0.001507	0.001512	40.963 40.962 40.964 40.961	40.963	0.25562	0.7533	0.7533	0.7538
0.0007536	0.0007559	50.933 50.936 50.932 50.933	50.934	0.28676	0.8093	0.8093	0.8111

* Calculated using $a^{o} = 5.92$ Å

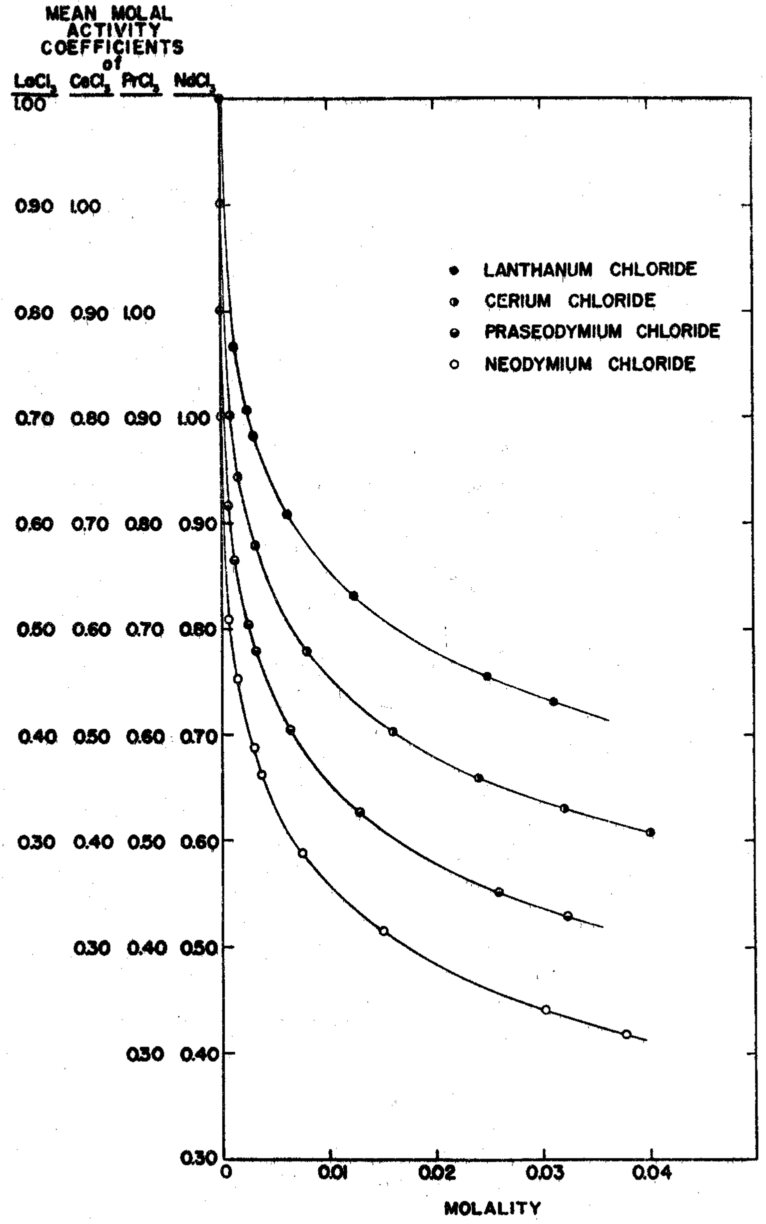


Figure 19. Mean Ionic Activity Coefficients of Rare Earth Chlorides in Aqueous Solutions.

in which

$y_\pm$ is the molar activity coefficient at concentration C;

$y_\pm(\text{Ref.})$ is the activity coefficient of the reference solution;

τ_+, $\tau_+(\text{Ref.})$ are the cation transference numbers at concentrations C and $C(\text{Reference})$, respectively;

E is the overall potential of the cell.

The value of $\int_0^E \delta \, dE$ was obtained by graphical integration using a large scale plot; the other terms can be directly evaluated. Equation (61) gives the ratios of the activity coefficients to that of some reference solution; the individual values were found by extrapolation using the Debye-Hückel equation. The Debye-Hückel equation for the activity coefficient, ignoring the correction from rational to molar since this goes to zero on extrapolation, is:

$$\log y_\pm = \frac{-A\sqrt{C}}{1 + a^o B\sqrt{C}}$$

Subtracting $\log y_\pm(\text{Ref.})$ from both sides of the above expression and rearranging:

$$\left[\log \frac{y_\pm}{y_\pm(\text{Ref.})} + A\sqrt{C}\right] = -\log y_\pm(\text{Ref.}) - a^o B\left[\left(\log \frac{y_\pm}{y_\pm(\text{Ref.})} + \log y_\pm(\text{Ref.})\right)\sqrt{C}\right] \qquad (62)$$

If the bracketed quantities are plotted against one another a straight line should result in case the Debye-Hückel formula is valid. A tentative value must be chosen for log $y_{\pm}$(Ref.) in order to make the plot, but a few successive approximations result in agreement between the assumed value and the value obtained as intercept. In the case of the rare earths studied in this thesis, straight lines were obtained over the whole concentration range; the best lines through the data were calculated by using the method of least squares on all the points. The values of a^o obtained from the final slopes are listed in Table 16, together with the average deviations of the experimental values of the activity coefficients from the activity coefficients calculated from the Debye-Hückel formula using these a^o values.

Mason (108, 109) has determined the osmotic coefficients of aqueous solutions of a number of rare earth chlorides from 0.05 molal up to 2 molal. Up to the present, activities of the salts could not be calculated because of the lack of suitable data for extrapolation to infinite dilution. The present work, together with that of Spedding and Wright (38) provides the necessary extrapolation data. The resulting activity coefficients computed for solutions up to 2.0 molal are given in Figure 20.

TABLE 16

Distances of Closest Approach for Rare Earth Chloride Solutions and the Average Differences between Calculated and Observed Activity Coefficients.

Rare earth	a^o (Angstroms)	Average difference between calculated and observed activity coefficients
Lanthanum	5.75	0.0013
Cerium	5.75	0.0024
Praseodymium	5.73	0.0019
Neodymium	5.92	0.0012

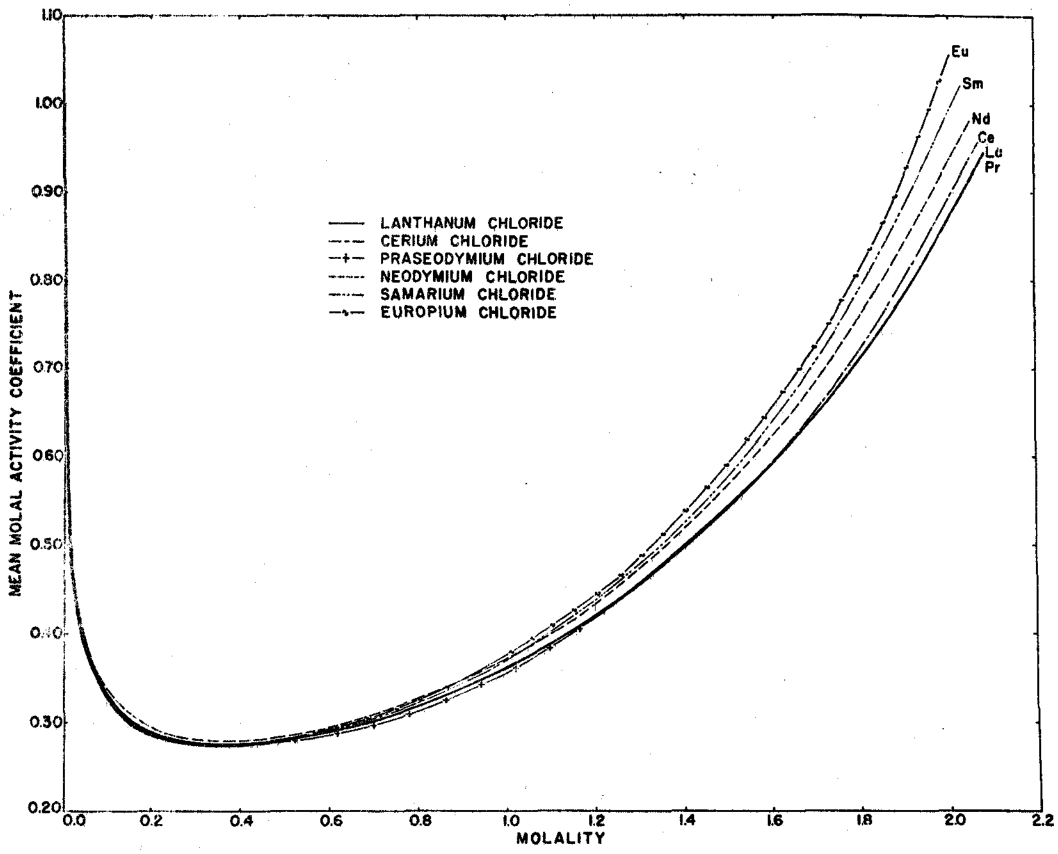


Figure 20. Mean Ionic Activity Coefficients of Rare Earth Chlorides in Aqueous Solutions.

Discussion of Results

The activity coefficients of lanthanum chloride had been previously determined with precision by T. Shedlovsky (110). A comparison of his data with those presented in this thesis is given in Figure 21. The agreement is well within the experimental error.

The activity coefficients for the four rare earth salts, presented in this thesis, agree remarkably well with the Debye-Hückel theory, although evidence that a small deviation is beginning near 0.1 normal is provided by the average differences listed in Table 16. These differences are slightly higher than the experimental errors which should allow an average difference in all cases of about 0.0008. The distances of closest approach, $\underline{a}^{o}$, for lanthanum, cerium, and praseodymium are identical within experimental error, but the values for neodymium chloride are definitely higher. This situation is somewhat anomalous in view of the more or less uniform shrinkage to be expected in the rare earth series; it may be accounted for by the possibility of a second coordination number among the first four ions as mentioned in the discussion of the results of conductance measurements. The values of 5.75 Å are just within the range which suggests that a single molecular layer of water remains around the rare earth ion and is not displaced

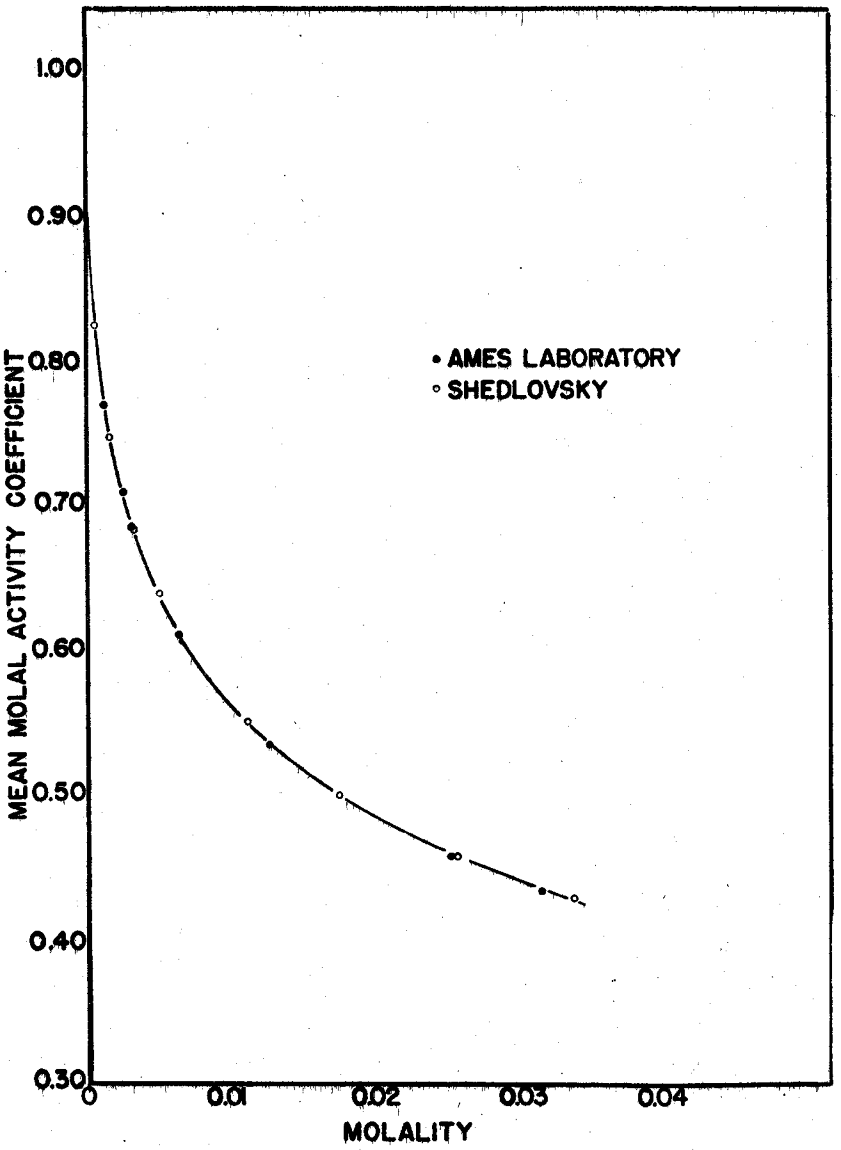


Figure 21. Mean Ionic Activity Coefficients of Lanthanum Chloride in Aqueous Solutions.

by the chloride ion. If a change in coordination number occurs it is possible that the characteristics of this sheath of water might also change. Further study of the coordination of water by the rare earth ions should be made by X-ray crystallographic means in order to determine whether any changes occur in the neighborhood of neodymium.

The data computed from the osmotic coefficients given by Mason (108) and plotted in Figure 20 show the typical rise in stronger solutions that has been attributed to the effective removal of water from its solvent capacity by its coordination with the positive ions. An attempt was made to fit the curves to extended forms of the Debye-Hückel equation, but none of the extensions has been found to correctly fit the data. It is not surprising that a fit of these equations could not be found, since the extensions employed were empirical.

The errors in the determination of activity coefficients include both the errors in the transference numbers and in the potential measurements. The former are known with an accuracy of 0.1 per cent, the latter are determined by the accuracy with which the molarities of the solutions are known. The potentials were measured with an accuracy of about 0.02 per cent; the average deviation among readings of four combinations of silver-silver chloride electrodes was 0.002 millivolts so that this error was negligible; the temperature, which was controlled to within 0.02°C, contributed no appreciable error. The over-all error in the determination of the activity coefficients is about 0.1 per cent.

SUMMARY AND CONCLUSIONS

1. The conductances of aqueous solutions of the chlorides of lanthanum, cerium, praseodymium, and neodymium have been measured for concentrations up to 0.1 normal. The accuracy of all measurements is within 0.1 per cent.

The data for all four rare earths agree with the Onsager limiting law up to about 0.002 normal. A comparison of the data of this thesis with those for samarium, europium, and ytterbium chlorides recently determined at Iowa State College (38), indicates that there is a regular decrease in the conductances of solutions of the rare earth chlorides with increasing atomic number beginning at about neodymium. The chlorides of lanthanum, cerium and praseodymium have about the same conductances, while the conductance of neodymium chloride is slightly higher. The behavior of the first four rare earths is thus anomalous in that the rare earths would be expected to show a regular change in properties over the whole series. A possible explanation of the observed data is that a second coordination number may become possible as the ions become larger with decreasing atomic number, so that an equilibrium may be set up between two kinds of hydrated ions having different coordination numbers. Such an alteration in the coordination numbers should produce substantial changes in the effective radii of the hydrated ions which would greatly influence their conductances. The importance of the degree of hydration of the ions in determining the conductance of the solution is indicated by the fact that, in the latter part of the rare earth series, the conductances decrease with decreasing ionic radius as measured crystallographically. The greater mobility which should result from the smaller ion is more than compensated by the effects of hydration. At the present time, insufficient data are available for any definite conclusions to be made; measurements of conductances should be extended to all members of the rare earth series not only for chlorides but also for other salts of different anion valence types. In addition, more crystallographic data on hydrated salts would be useful, in order to study the coordination numbers of the hydrated ions and to correlate them with the conductive behavior.

2. The transference numbers of lanthanum, cerium, praseodymium, and neodymium, in aqueous solutions of their chlorides, have been measured for concentrations up to 0.1 normal. The accuracy of all measurements is within 0.1 per cent.

The transference numbers do not merge with the theoretical Onsager limiting slope. This is somewhat surprising in that the conductances are in excellent agreement with the Onsager equation and merge with the limiting slope at concentrations as high as 0.002 normal. It appears that some effect must be influencing the motion of the ions which cancels out in the case of conductance, but which causes a difference in the case of transference numbers. The data presented in this thesis, together with those of others (38) for samarium, europium, and ytterbium salts, indicate that the same effects which cause the conductance results for the first four elements to behave in an unexpected manner, also produce an analogous effect in the case of transference numbers. Little change in transference numbers is observed for the first four rare earths; however, beginning with neodymium a regular decrease with increasing atomic number is observed.

An effort should be made to extend the transference number measurements to higher dilutions in order to find an explanation for the fact that the Onsager equation is observed for conductance, but not for transference numbers. In addition, data for all the rare earths should be accumulated, so that a more complete study can be made of the factors entering into the ion mobilities.

3. The activity coefficients of the chlorides of lanthanum, cerium, praseodymium and neodymium, in their

aqueous solutions, have been measured for concentrations up to 0.1 normal. The accuracy of the measurements is within 0.1 per cent. The data have been combined with the osmotic coefficient data of Mason (108, 109) to calculate activity coefficients for solutions up to concentrations of 2 molal.

The activity coefficients for all four salts agree well with the Debye-Hückel theory. The values obtained for $\underline{a}^{o}$ show no regular decrease, but do show an increase up to neodymium. As in the case of conductances, this effect may be due to the simultaneous existence in solution of two coordination numbers for the rare earth ions of low atomic number. The $\underline{a}^{o}$ values for all four rare earths exceed the sum of the ionic radii of the rare earth ions and the chloride ion by approximately the diameter of one water molecule. If the $\underline{a}^{o}$ values have physical significance, this indicates that the first sheath of water molecules adheres tightly to the rare earth ion. The diameter of this sheath would undoubtedly depend largely upon the coordination number of the central ion; hence, if an equilibrium were established between two coordination forms in solution, the magnitude of $\underline{a}^{o}$, which is an average property, would depend upon the position of the equilibrium. Variations in the position of the equilibrium for the first four elements could thus possibly provide an explanation for the observed distances of closest approach.

The precision measurements of thermodynamic and physical properties of aqueous solutions of the chlorides of the four rare earth elements presented in this thesis are of real importance in supplying data which are useful in problems involving equilibria and kinetics of rare earth salt solutions. The data for these salts represent the beginning of an extensive program for the accumulation of precision data on physico-chemical properties of rare earth salts in progress in this laboratory. It is hoped that the completion of this program will make possible the development of a satisfactory theory for concentrated electrolytic solutions. The data presented in this thesis add to the confirmation of the Debye-Hückel and Onsager limiting laws; it is felt that in view of this additional evidence, these laws may be used with confidence for the extrapolation of data for salts of the 3-1 valence type.

ACKNOWLEDGMENTS

The writer wishes to express his appreciation to Drs. F. H. Spedding and E. I. Fulmer for their encouragement and helpful advice during the course of this research and in the preparation of this thesis. The writer also wishes to thank Mr. J. M. Wright for assistance in the measurement of the properties reported in this thesis, and Mr. J. E. Powell and Mr. Thomas A. Butler for the preparation of the pure neodymium and praseodymium oxides.

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