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Conductances, transference numbers and activity coefficients of some rare earth halides

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NOTE TO USERS

CONDUCTANCES, TRANSFERENCE NUMBERS

AND ACTIVITY COEFFICIENTS OF

SOME RARE EARTH HALIDES

by

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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:

In Charge of Major Work

Head of Major Department

Dean of Graduate College

Iowa State College

1952

UMI Number: DP13066

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I. GENERAL INTRODUCTION

An explanation of the behavior of solutions of strong electrolytes has presented an important challenge to modern chemistry. Some progress has been made toward adequate theoretical explanations of such behavior in dilute solutions. Many data for 1-1 electrolytes and smaller amounts for 2-1, 1-2, and 2-2 electrolytes have been obtained by which the various theories may be tested. However, relatively few data have been reported on higher valence-type electrolytes.

In general, electrolytes do not obey the classical Raoult's law. When this law is modified to include the mole fractions of the ion constituents present in solution, rather than the mole fraction of the electrolyte as a whole, better agreement is obtained between experimental data and this modified law; however the law still does not completely explain electrolytic behavior. It has been observed that the colligative properties of solutions of electrolytes are dependent upon the valence-types of the electrolytes. This dependence upon valence-type has been accounted for in modern theory of dilute solutions. However it has been observed that the behavior of poly-valent electrolytes deviates from theory at lower concentrations than does that of mono-valent electrolytes.

Many more precise and accurate data should be obtained on the behavior of poly-valent electrolytes before a complete theoretical explanation can be made to account for this departure from theory.

The main deterrent, until quite recently, to the obtaining of data on poly-valent electrolytes has been the unavailability of salts possessing the required properties. To be satisfactory, not only must a salt be of a high valence-type, but it must not hydrolyze to any appreciable extent, since hydrolysis would complicate the interpretation of any data so obtained. It is for this reason that compounds of $Fe(III)$, $Al(III)$, $Sn(IV)$, and $Zr(IV)$ are unsuited for this type of work. It has been known for some time that, when dissolved under carefully-controlled conditions, the halides of the tri-valent rare earth elements, and of the other members of the III-A family of the periodic table, do not undergo hydrolysis to any noticeable extent. Thus, this family of elements possesses all the desirable characteristics for a study of poly-valent electrolytes.

Until the late 1940's, the only methods useful for the separation and purification of the various rare earth elements involved thousands of tedious recrystallizations or other equally laborious procedures. Few chemists had the facilities or the patience necessary to obtain appreciable quantities of the rare earths in any great degree

of purity. Only when it became possible to separate and
purify large quantities of the various elements of the rare
earth family rapidly, by means of ion exchange resin
columns, could those interested in the behavior of solu-
tions of poly-valent electrolytes obtain the desired data
for most of these elements.

In addition to the high-valence nature of the rare
earths, these elements possess another characteristic
which makes them ideal to test the various theories of
behavior of solutions of strong electrolytes. The rare
earth elements are strikingly similar to each other in
their chemical behavior, exhibiting only a small grada-
tion of properties from element to element. This is
brought about as the 4f electronic shell is progressively
filled in going from lanthanum, with zero 4f electrons,
to lutetium, with fourteen 4f electrons, while the electron
configuration in the outer 5s, 5p, and valence shells
remains unchanged. Since the chemical properties of an
element are principally determined by the valence elec-
trons, the variation in the number of 4f electrons pro-
duces only minor changes in these properties. One such
property which exhibits a readily detectable change is
the atomic radius. As the atomic number, and therefore
the nuclear charge, increases in the series from lanthanum
to lutetium, there is a stronger attractive force exerted

by the atomic nucleus upon the various electrons, causing
a shrinkage of the atomic radius. This effect, known as
the "Lanthanide Contraction", is the principle reason for
the slight differences in properties of the tri-valent
rare earths ions.

Most theories concerning the chemical properties of
electrolytes involve not only the atomic radius, but also
a number of other constants which have to be evaluated
experimentally. The larger the number of constants, the
more closely experimental data can be made to fit any
theory being tested. Providing the theory is valid,
once these constants are fixed for any one rare earth,
they have to hold for any other rare earth of the series,
except as they are modified in a predictable way by the
atomic radius. Thus, when accurate data are available
on the behavior of solutions containing rare earth ions,
the many theories now in existence may be better evaluated.
It should then be possible to determine which of those
assumptions inherent in these theories are not valid for
poly-valent ions.

Prior to the work in this laboratory on these pro-
perties, only one rare earth halide, lanthanum chloride,
had been investigated thoroughly enough to extrapolate
its activity coefficients (1) and its equivalent con-
ductances (2,3) to infinite dilution. Recently, seven

more rare earth chlorides have been similarly investigated
(4,5,6). It is the purpose of this research to extend the
investigation to other rare earth salts, particularly the
bromides, so that more light may be thrown on these pro-
blems of electrolytic behavior.

II. REVIEW OF THEORIES AND METHODS

A. Introduction

The basis for all modern theory of electrolytic be-
havior is the assumption that solutions of electrolytes
contain positively and negatively charged particles,
called ions, in exact electrical balance. This premise
was first elucidated by Arrhenius (7), in 1887, in his
classical theory of electrolytic dissociation. Although
some of his secondary assumptions were not substantiated
by experimental evidence, his theory nevertheless gave a
qualitative picture of the nature of solutions of electro-
lytes. As such, it was used until 1923, when the Debye-
Hückel theory of electrolytic behavior was first pub-
lished (8).

Arrhenius' assumption that ionic mobilities are con-
stant with changing concentration has been shown to be
incorrect by experimental data on transference numbers.

In his theory, Arrhenius also stated that the decrease
in equivalent conductance, Λ, of an electrolyte with an
increase in concentration was due to the decrease in the
number of ions, according to the ratio:

$$\alpha = \frac{\Lambda}{\Lambda_0} ,\qquad (1)$$

in which α is the degree of dissociation, and Λ_0 is

the equivalent conductance of the electrolyte at infinite dilution. Thus, a 0.001 normal solution of potassium chloride would be approximately 98 per cent dissociated, while a 0.1 normal solution would be only 86 per cent dissociated. However it has been found, for example, in the Debye-Hückel theory, that the thermodynamic properties of strong electrolytes in aqueous solution could be more readily explained by assuming complete dissociation. Electrolytes cannot be incompletely dissociated for conductances, and at the same time, be completely dissociated for thermodynamic properties. The resolution of this anomaly has been achieved by applying the inter-ionic attraction theory to the problem of conductance.

B. Conductances

1. Theory

It is well known that a solution of an electrolyte exhibits electrical conductivity. Under proper conditions, an electric current passing through such a solution obeys Ohm's law. Thus, it is possible to measure the specific resistance, ρ , and the specific conductance, $\underline{L}$, of a solution which are related by:

$$\rho = 1/L = R \cdot a/d, \qquad (2)$$

in which R is the resistance in ohms of the solution of cross-sectional area, a, in square centimeters, and d is the distance, in centimeters, between electrodes. It is often desirable to express the conductance of an electrolytic solution in terms of its equivalent conductance, Λ. This quantity is defined as:

$$\Lambda = 1000 \frac{L}{c},\qquad (3)$$

in which c is the concentration of the electrolyte in equivalents per liter.

Kohlrausch (9) discovered that in very dilute solutions the conductances of electrolytes could be expressed empirically by:

$$\Lambda = \Lambda_o - k\sqrt{c},\qquad (4)$$

in which k is an experimentally determined constant. It was generally conceded that this was the correct expression for the variation of equivalent conductance with concentration in dilute solutions, but for some years attempts to derive it theoretically were not successful.

Several excellent reviews have been published on the history and development of modern theories of electrolytic conduction (10,11). The theoretical solution of the problem of conductance is not completely solved as yet, although the limiting law of Onsager (12a,12b) is essentially

in agreement with experimental data at high dilutions, and
is the best extrapolation law for conductivity data at the
present time. Much recent work has been directed toward
extending Onsager's law to higher concentrations (13,14,15)
but as yet, little success has been achieved from a
strictly theoretical standpoint.

Since it was not possible to account for the decrease
in conductivity with increasing concentration by assuming
a decrease in the number of ions, the decrease in con-
ductivity was assumed to be due to the decrease in the
mobility of the ions. This assumption has met with some
success and is the basis for Onsager's law (12a).

J. J. van Laar (16) was the first to explain why ionic
mobilities should change with concentration. He pointed
out that coulombic forces which must exist among the ions
in solution must affect the conductance, osmotic pressure,
and other colligative properties of electrolytic solutions.

In 1904, Noyes (17) presented evidence based on the
optical properties of some electrolytes which indicated
that these must be completely dissociated even at high
concentrations. Three years later, Sutherland (18) made
some qualitative calculations which indicated that the
coulombic forces could produce all of the decrease in con-
ductance with increase in concentration which had been
observed for strong electrolytes.

In 1913, Milner (19,20) developed a mathematical
theory to explain the effects of inter-ionic attraction in
solutions of electrolytes which was essentially correct,
but which was too involved to be of much practical use.
With these same assumptions, Debye and Hückel (8) succeeded
in obtaining an integrated equation which led to a useful
expression for describing the effects of inter-ionic
attractions. They proposed, as a first approximation,
that coulombic interactions of the ions with each other,
and with the solvent, which was treated as a uniform
dielectric medium, could account for all deviations from
ideal behavior of dilute solutions of electrolytes. These
coulombic interactions give rise to an ionic atmosphere
around each ion such that a slight excess of negatively
charged ions exists about each positive ion, and vice
versa. This theory will be discussed more fully later in
this section.

Using this concept of an ionic atmosphere, Debye and
Hückel (21) developed a preliminary theory of conductance.
This theory was later corrected and extended by Onsager
(12a), who derived an equation which is now generally
accepted as the correct limiting law. According to Debye
and Hückel and to Onsager, the concept of an ionic atmos-
phere leads to two effects, the "time of relaxation"
effect and the electrophoretic effect, both of which lower

ionic mobilities with increasing concentration. The electro-
phoretic effect is caused by the ionic atmosphere, which
includes the solvent molecules associated with it, moving
with the central ion, thus exerting a retarding influence
on the mobility of that ion. The "time of relaxation"
effect results from the fact that, under the influence of
a potential gradient, the ionic atmosphere moves in a
direction opposite to that of the central ion. Normally
the ionic atmosphere is symmetrically distributed around
the central ion; when the central ion moves, the atmos-
phere will tend to move with it. Although the adjustment
of the atmosphere to the new condition is rapid, it is
not instantaneous, and so a dipole is formed. As a result
of the formation of the dipole, the effect of the potential
gradient on the central ion is decreased and the mobility
of this ion is decreased.

Although the Onsager differential equation has not
been solved for the general case, certain approximations
can be made and a simplified solution obtained which is
applicable to ions of a dilute solution. For a binary
electrolyte, which is assumed to be completely dis-
sociated, the Onsager limiting law can be expressed as:

$$\Lambda = \Lambda_o - \left[\frac{0.9834 \times 10^6}{(DT)^{3/2}} w \Lambda_o + \frac{28.98 \, z_1 z_2}{(DT)^{1/2} \eta} \right] \sqrt{(z_1 + z_2)c}$$

$$(5)$$

in which D is the dielectric constant of the medium; T is the absolute temperature, z_1 and z_2 are the charges of the two species of ions; η is the absolute viscosity of the solvent;

$$w = z_1 z_2 \left(\frac{2q}{1 + \sqrt{q}} \right);$$

and

$$q = \frac{z_1 z_2 (\lambda_1^o + \lambda_2^o)}{(z_1 + z_2)(z_1 \lambda_2^o + z_2 \lambda_1^o)} .$$

The quantities λ_1^o and λ_2^o are the limiting equivalent conductances of the respective ions. The first term in the brackets of equation (5) accounts for the "time of relaxation" effect, and the second for the electrophoretic effect.

The use of the Onsager equation for extrapolation purposes will be discussed in more detail in the experimental section.

2. **Methods**

Accurate conductance measurements on solutions of electrolytes were first reported in 1868, when Kohlrausch (9) initiated the use of a Wheatstone bridge operating on alternating current instead of the previously-used direct-current bridge, in order to avoid polarization effects during measurements. He also introduced the use of

platinized electrodes in conductance cells to reduce further the effects of polarization (22,23). His formula for the platinizing solution is still in use today. Kohlrausch developed the method of conductance measurements to such a high degree of precision that the only improvements made since his time have been in design rather than in method.

The first major improvement on Kohlrausch's alternating current bridge was made in 1913 by Washburn and Bell (24). They initiated the use of a high frequency generator as a source of alternating current, and a telephone receiver tuned to the applied frequency; in addition, they employed capacitance and inductance-free resistors. Washburn (25) discussed the theory of design, construction, and use of various types of conductance cells, as did Taylor and Acree (26,27,28). Hall and Adams (29) designed an amplifier for use with the null-point detection device, thus improving the sensitivity of detection.

In 1923, Parker (30,31) observed that the cell constants of conductance cells vary with resistance. Shedlovsky (32) and Jones and Bollinger (33) showed that this "Parker Effect" was due to capacitance effects within the cells. Jones and Bollinger also designed cells which minimized this effect. In 1926, Morgan and Lammert (34) reviewed all the conductance data available at that time and carefully studied the effects of the design of the

bridge and the characteristics of the oscillator. They found that the oscillator should be placed a minimum of 30 feet from the bridge before the mutual inductance between the bridge and oscillator is eliminated.

Jones and Josephs' (35) study of the conductance bridge and accessory apparatus in 1928 was so good and so comprehensive that it is still used as the basis for all bridge designs. Shedlovsky (36) also designed a bridge useful for the measurement of accurate conductance data which differed only in the manner of shielding from that recommended by Jones and Josephs. Jones and his co-workers (33,37) also studied the design of conductivity cells; their work is still regarded as the best guide for the construction of such cells. One of the leading manufacturers of conductance apparatus has carefully followed the recommendations of Jones and his co-workers on bridge and cell design in the construction of its most precise commercial conductance apparatus.

It can be seen from equation (2) that the resistance of a solution is proportional to a quantity d/a which has the units of reciprocal length. This quantity is termed the "cell constant" since it depends only upon the dimensions of a cell. The measurement of the correct resistance, and hence conductance, of a solution depends

directly upon the accurate determination of this factor. In principle it is possible to measure this quantity directly; however, for cells in common use it is simpler to prepare standard solutions of known specific conductances, and to determine the cell constants from measurements of the resistances of these solutions in the cells. Kohlrausch (38) established potassium chloride as a standard by measuring the resistances of its solutions in cells of accurately known dimensions. His values of the specific conductances of potassium chloride were used until they were redetermined to a higher degree of accuracy by Parker and Parker (39), by Jones and his co-workers (40,41) and by Shedlovsky (42).

C. Transference Numbers

1. Theory

Closely related to conductance is a ratio called the transference number of an ion. This quantity, $\underline{T_i}$, may be defined as:

$$T_i = \frac{i_i}{I} , \tag{6}$$

in which $\underline{i_i}$ is the amount of current carried by the $\underline{ith}$ ion when a current $\underline{I}$ is passed through a solution containing that ion. For a completely dissociated electrolyte,

$$\Lambda = \sum_i \lambda_i = F(\sum_i U_i), \tag{7}$$

in which F is the Faraday, and U_i is the ionic mobility
of the $\underline{ith}$ ion, that is, the velocity of that ion under
a potential gradient of one volt per centimeter. Thus,
the transference number of an ion is also equal to the
following expressions:

$$T_i = U_i/(\sum_i U_i) = \lambda_i/(\sum_i \lambda_i) = \lambda_i/\Lambda . \tag{8}$$

The sum of the transference numbers of all the ionic
species of a solution must, of course, equal unity. As
can be seen from the above equations, a knowledge of the
transference numbers and of the conductances of solutions
of electrolytes permits the calculation of the ionic
mobilities of the individual ions. Also it permits a
study of the validity of the Onsager limiting law for
individual ions. Data on ionic mobilities are of interest
since variations of these quantities among various ions of
a regular family may be correlated to such properties as
ionic radius and coordination number without assuming any
effects from the other ions present.

Depending upon the standard relative to which the
velocity of the ion is measured, transference numbers are
of three types. The Hittorf transference number is a
measure of the ion velocities relative to the solvent.
The Nernst, or "true" transference number is measured
relative to the molecules of some inert solute present in

solution which is neither affected by the electric current
nor affects the movement of the other ions present. The
third transference number, from moving boundary data, is
obtained relative to fixed positions on the transference
cell. Data from any of these methods may be corrected in
order to obtain the theoretical transference number as
defined in equations (6) and (8).

By use of the Onsager limiting law (equation (5)), a
law for transference numbers may be obtained:

$$T_i = T_i^O + S(T_i) \sqrt{c} \qquad (9)$$

in which

$$S(T_i) = \left[\frac{T_i^O(|z_1| + |z_j|) - |z_1|}{(|z_1| + |z_j|) \Lambda_o} \right] \left[\frac{28.98(|z_1| + |z_j|)(\nu|z_1 z_j|)^{\frac{1}{2}}}{\eta (DT)^{\frac{1}{2}}} \right] ;$$

T_i^O is the limiting transference number of the <u>ith</u> ion of
charge z_i; and $\underline{\nu}$ is the number of ions formed from the
dissociation of one molecule of the binary electrolyte.
This equation appears to be valid for some 1-1 electrolytes
in low concentrations. However, the predicted slope is
not obtained for higher-valence electrolytes, although
there appears to be a linear relationship between the
transference number and the square root of the concentra-
tion.

2. Methods

Daniell (43,44), in 1839, was the first to demonstrate that the positive and negative ions of an electrolyte do not carry equal amounts of current. In the next decade, Hittorf (45,46,47,48,49,50,51) began his studies on ion migration and confirmed the earlier reports. His work extended over a 50-year span, and although his data are not sufficiently accurate for use today, they provided the basis for subsequent work. The Hittorf apparatus consisted essentially of a three-compartment electrolysis cell with a coulometer connected in series. The three compartments, termed the anode, the middle, and the cathode compartments, were filled initially with the same solution. After the passage of a measured number of coulombs of electricity, the solution in each compartment was analyzed. From a knowledge of the initial concentration of electrolyte, the transference number of the ith ion can be calculated as follows (52):

$$T_i = \frac{N_e + N_0 - N_f}{N_e} \tag{10}$$

in which N_0 equals the initial number of equivalents of the ith ion per gram of solvent; N_f equals the final number of equivalents of that ion per gram of solvent; and N_e equals the number of equivalents of that ion added to

the solvent by the electrode reaction, and is equal to the number of Faradays of current passed through the cell.

While the Hittorf method is basically quite accurate, it is limited by the accuracy of the methods of analysis. Since it is also very time-consuming, very little work is done with this method today, although MacInnes and Dole (53) and Jones and Bradshaw (54) have greatly perfected the techniques involved.

The electromotive force method for the determination of transference numbers involves the measurement of the potentials of two types of concentration cells, those with, and those without transference. Although this method is theoretically sound, it is not considered to be as accurate or as precise as the other available procedures for obtaining transference numbers. The evaluation of transference numbers by this method involves either the use of graphical methods or of empirical relations to express the potentials of the cells as functions of the concentration. Furthermore, it is often difficult to find suitable electrodes or bridges which are reversible to the cation for the cell without a liquid junction. Although this method has been used by many investigators (55,56,57), mainly because of its thermodynamic soundness, it is not regarded as being capable of yielding accurate data of the desired precision.

The basic theory of the moving boundary method for the determination of transference numbers is outlined below. The method consists of forming a boundary between two solutions, (x-x) as in the diagram at the right, and observing the motion of that boundary under the influence of the current induced by an applied potential difference. During the passage of the current, all of the cations will migrate toward the negative electrode, and all of the anions toward the positive electrode, giving rise to two boundaries, A-A, between the two anions, and C-C, between the two cations. For a solution containing c equivalents of a binary salt per liter, the passage of one Faraday of current will cause the two boundaries to sweep out a total volume of 1000/c milliliters. Of this volume, $T_+(1000/c)$ milliliters will be due to the motion of the cations, and $T_-(1000/c)$ milliliters will be due to the motion of the anions. Therefore, the following equation may be written:
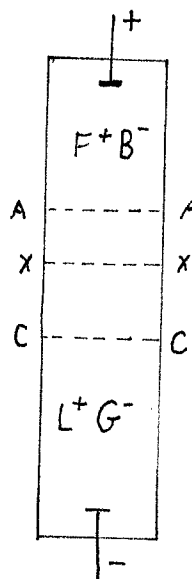
$$F_{coulombs} = k\ T_1(1000/c), \tag{11}$$

in which T_1 is the transference number of either of the ions, and k is a proportionality constant. If a different number of coulombs, F', were passed through the solution, a different volume, v, would be swept out by the ith species, and thus:

$$F' = kv. \tag{12}$$

Combining equation (11) and equation (12), and solving for T_1 results in the equation:

$$T_1 = \frac{Fcv}{1000F'} . \tag{13}$$

For a constant current of I amperes passed for t seconds,

$$F' = It, \tag{14}$$

and equation (15) follows directly:

$$T_1 = \frac{Fcv}{1000It} . \tag{15}$$

Since many excellent reviews have been published on the theory and history of the moving boundary method (10,11,58,59,60) only the more important contributions will be discussed. Lodge (61) in 1886, was the first to investigate the possibility of observing directly the

motion of an ion constituent in an electric field.
Whetham (62, 63, 64, 65, 66, 67) and Nernst (68) studied
the movement of a boundary between two solutions, one of
which was colored. In 1899, Masson (69,70) indicated the
proper conditions for quantitative work in this field.
Following the suggestion made by Lenz (71) and Bein (72),
that a boundary between two colorless solutions may be
visible due to the differences in indices of refraction
of the two solutions, Denison and Steele (73,74,75,76)
obtained transference numbers of the more common electro-
lytes. This method for observing moving boundaries is
in common use today.

There are two general procedures for forming a
boundary between solutions, the sheared boundary and the
autogenic boundary methods. The sheared boundary is
formed when two solutions in a suitable cell are separated
initially by a movable barrier. When the barrier is
removed, the two solutions come in contact with each
other, with one solution on top of the other. Denison
and Steele (73) used a movable parchment-covered plunger
to form the boundary in their early work. Methods for
improving the boundary were devised by MacInnes and Smith
(77); MacInnes and Brighton (78); and Spedding, Porter,
and Wright (5). The last named authors simplified MacInnes

and Brighton's "sheared disk" apparatus by developing the boundary with a hollow-bore stopcock.

The autogenic method, first applied by Franklin and Cady (79) in 1904, involves the use of an anode composed of a metal which forms a soluble salt with the anion of the leading solution, that is, the solution under investigation. As the electrolysis proceeds, the soluble salt is produced and forms a boundary with the leading solution. This method is more restricted in its application than the method of sheared boundaries, but is nevertheless quite simple to use.

There are several properties which are required of the following or indicator solution, that is, the solution which forms the boundary with the leading solution. A few properties are self-evident. First: the two solutions must not react with each other. Second: for cation transference numbers, the transference number of the cation of the following solution must be less than that of the leading solution, and correspondingly so for anion transference numbers. Third: although either rising or falling boundary systems may be used, since the effect of gravity over the few centimeters' length of measuring tube is negligible, the following solution must be lighter than the leading solution for falling boundaries, and vice versa for rising boundaries. Fourth: there must

be a difference in color, in indices of refraction, or in
some other property, between the two solutions so that
the boundary may be observed and followed. Other requisite
properties of the following solution are discussed below.

For the passage of one Faraday of current, it is
evident from equation (13) or (15) that:

$$T_+ = cV \tag{16}$$

in which V is now the volume in liters moved due to the
motion of the cation. Since no voids appear in the system,
it is obvious that the same volume must be moved by the
cation of the following solution, so that:

$$T_{+f} = c_f V, \tag{17}$$

in which T_{+f} is the cation transference number of the
following solution of concentration c_f equivalents per
liter. By eliminating V between equations (16) and (17),
the following ratio is obtained:

$$T_+/c = T_{+f}/c_f . \tag{18}$$

This ratio was first derived by Kohlrausch (80,81) in
1897, who called it the "beharrliche" or regulating func-
tion, although it is now more commonly called the Kohlrausch
ratio. According to Kohlrausch, regardless of the initial
concentration of the following solution, under the influence

of the electric current passing through the solution, the
concentration of the following solution at the boundary
will automatically adjust itself in conformity with the
above ratio. Since the leading solution initially
occupies the space into which the boundary moves, it has
the power to regulate the concentration of the following
solution which replaces it. Thus the moving boundary
method yields direct information, for only the leading
solution.

In the 1920's, MacInnes and Smith (77,82) made a
study of this theory. They varied the concentration of
the following solution, with the concentration of the
leading solution kept constant. According to Kohlrausch,
all of the transference numbers so obtained should have
been the same. However MacInnes and Smith obtained a
curve such as that shown to the right. The flat portion
of the curve, y-y, gave the
correct value of the
transference number,
and the mid-point of
this plateau, x,
yielded the correct
concentration of the
following solution
according to the Kohlrausch ratio. Thus it was found that
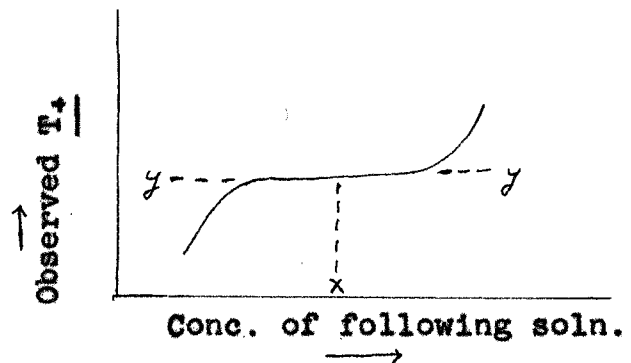
the adjustment range is limited, although the limits depend upon factors which are not well understood. The above authors found that the range is greater for more dilute solutions, and greater for rising boundaries than for falling boundaries. Also the range of adjustment is wider for small-bore tubes than for those with large bores. One possible reason for the failure of the following solution to adjust itself to the concentration required of the Kohlrausch ratio may be as follows. With a rising boundary, if the initial concentration of the following solution were lower than the adjusted concentration, then the adjusted concentration would be denser than the initial, and the two solutions would mix. This same reasoning would apply in the case of a falling boundary if the initial concentration of the following solution were greater than that required by the regulating ratio.

Although it would appear that the two transference numbers must be known before the experimental determination of one of them may be made, the values need only be known to within five to ten per cent and can usually be estimated from other known properties, such as conductances.

The Kohlrausch ratio gives rise to another effect which is quite beneficial. Since a slower ion is required of the following solution than of the leading solution, a

lower concentration is also required of the former. The combination of these two factors usually leads to a solution of greater specific resistance than that of the leading solution, causing a greater potential gradient in the following solution. If some of the faster ions of the leading solution were to diffuse or to be carried by convection across the boundary, they would enter a region of higher potential gradient and would be forced forward into the leading solution. Conversely, if the following solution ions were to diffuse into the leading solution region, they would move more slowly than the leading solution, and the boundary would overtake them. Thus the boundary is self-sharpening. MacInnes and co-workers (58,83,84,85) have demonstrated that this corrective mechanism does exist. After forming a boundary, they interrupted the current for as long as 200 minutes, after which time the boundary was quite diffuse. Upon restarting the current, the boundary resharpened and the correct transference number was obtained.

Since the indicator solution has a higher specific resistance than does the leading solution, more heat is generated in the former solution than in the latter. This heat produces convection currents which tend to disturb the boundary. The self-sharpening effect of the boundary overcomes this convection disturbance

providing the disturbance is not too great. Since more heat is generated in the indicator solution, sharper boundaries are obtained if a falling boundary system is used. With such a system, the heat from the solution with higher resistance would rise away from the boundary, rather than up into the boundary if the reverse system were employed. Furthermore, the use of a small-bore tubing, rather than large-bore, permits a more rapid conduction of the generated heat from the cell to the thermostat.

Although indicator solutions which have an ion in common with the leading solution have been ordinarily employed, this is not a necessary requirement. Although a boundary may be initially formed between totally dissimilar ions, as soon as the boundary moves, a common ion is on both sides of the boundary. For example, if lithium bromide were employed as a following solution in conjunction with a leading solution of gadolinium chloride, the boundary would initially be between these two solutions. However, as soon as current is passed through the cell, the bromide ions will move away from the cation boundary and the chloride ions will migrate across that boundary. Thus, while lithium bromide initially forms the boundary, it will be lithium chloride which will be following the gadolinium chloride. Although

the use of a non-common ion following solution has been
reported (86), this technique is not often used since it
complicates the calculation of the correct concentration
of the following solution because the Kohlrausch ratio
applies to the solutions which actually form the boundary
during the determination. Furthermore, the volume cor-
rection, discussed below, would have to be empirically
approximated instead of being exactly calculated.

Early in the development of this method, it was
recognized that volume changes due to the electrode
reactions might displace the boundary. Miller (87) had
made the observation that "subject to a correction for
the expansion and contraction caused by electrolysis",
the transference numbers obtained by the moving boundary
method and by the Hittorf method should be identical.
Lewis (88) was the first to compute the correction which
is necessitated by the volume changes. Since the Hittorf
method yields transference numbers referred to the water
of the solution, and the moving boundary method yields
these numbers in reference to fixed graduations on the
measuring tube, the motion of the water with respect to
the graduations must be computed. This computation is
quite simple if one electrode chamber is closed during a
determination and the other chamber is left open to the
atmosphere. With this arrangement, only those volume

changes which occur between the closed chamber and the
boundary will affect the position of the boundary. The
volume change, for a metal anode, $\underline{M}$, a leading solution
$\underline{LX}$, providing $\underline{X}$ is the only anion between the boundary
and the anode, is:

$$\Delta V = \frac{1}{|z_M \nu_M|} \cdot \bar{V}_{MX} - \frac{1}{|z_M|} V'_M - \frac{1}{|z_L \nu_L|} T_+ \bar{V}_{LX} \qquad (19)$$

in which $\underline{\bar{V}}$ is the partial molal volume of the indicated
electrolyte, and $\underline{V'}$ is the molar volume. The following
expression for the corrected transference number results
by use of equation (16):

$$T_+ = Vc = \frac{(V''- \Delta V)c}{1000} = T_+' - c \, \Delta V/1000, \qquad (20)$$

in which $\underline{V''}$ is the measured volume in milliliters, $\underline{\Delta V}$ is
the change in volume, and $\underline{T_+'}$ is the uncorrected or
observed transference number.

In 1932, Longsworth (89) observed that within experi-
mental error the sum of the transference numbers of both
ions of a binary electrolyte were not equal to unity. This
was especially so in dilute solutions. He finally con-
cluded that this discrepancy was due to the presence of
charged impurities in the solvent which carried a small

fraction of the total current. He derived the following quantity to correct for these impurities:

$$\Delta T_+ = T_+(L_{solvent})/(L_{solution}),\qquad(21)$$

in which T_+ is the correct transference number, and L is the specific conductance of the indicated quantity. Thus the final equation for the determination of true transference numbers by the moving boundary method becomes:

$$T_+ = \frac{Fcv}{1000It} - \frac{c \cdot \Delta V}{1000} + T_+ \frac{L_{solvent}}{L_{solution}} .\qquad(22)$$

It should be noted that the first correction term is important mainly in concentrated solutions and the second in dilute solutions.

D. Activity Coefficients

1. Theory

An ideal solution is one in which all of the components obey Raoult's Law; that is:

$$p_i = p_i^O N_i ,\qquad(23)$$

in which p_i is the partial pressure of the ith component in a solution in which N_i is the mole fraction of that component and p_i^O is the vapor pressure of that pure component. The chemical potential of such an ideal solution is given by:

$$\mu_1 = \mu_1^o + RT \ln N_1 , \qquad (24)$$

in which μ_1 is the chemical potential of the ith component in a solution containing a mole fraction N_1 of this component, and μ_1^o is the chemical potential of the pure component. Ideal solutions are found only in cases in which the solvent and solute are similar in nature, for example, benzene in toluene. Many solutions, however, are not composed of such similar components, and hence are not ideal.

To describe this deviation from ideality, Lewis (90), in 1907, developed the concept of activity, one definition of which is as follows:

$$d\mu_1 = RT \, d (\ln a_1) , \qquad (25)$$

and

$$\lim_{N_1 \to 0} a_1/N_1 = 1 , \qquad (26)$$

in which a_1 is the activity of the ith component of mole fraction N_1. Equation (25) defines the change in activity in terms of the change in chemical potential, and equation (26) establishes the reference state of the ith component. Alternate reference states may be chosen to suit the particular conditions of any system; the reference state expressed above is particularly well-suited for discussing

the solute in a solution. In order to integrate equation (25) a reference solution may be chosen with composition N_i^*, for which a_i^* essentially equals N_i^*. Equation (25) may be integrated between this very dilute reference state and any arbitrary state, so that:

$$\mu_i - \mu_i^* = RT (\ln a_i) - RT (\ln a_i^*) . \tag{27}$$

Since the standard state of the <u>ith</u> component is defined as that state in which its activity is unity, the chemical potential of the <u>ith</u> ion in its standard state, μ_i^o, is:

$$\mu_i^o = \mu_i^* - RT (\ln N_i^*) . \tag{28}$$

Thus, equation (27) may be rewritten as:

$$\mu_i = \mu_i^o + RT (\ln a_i) , \tag{29}$$

in which μ_i^o is a function of only the temperature. Equation (29) is applicable to all solutions, ideal or non-ideal. By defining a rational activity coefficient, f_i, as:

$$a_i = f_i N_i , \tag{30}$$

the activity coefficient becomes a measure of the deviation of the <u>ith</u> component from ideality.

For work with strong electrolytes, it is common practice to express the composition of a solution in terms

of the molarity or the molality of the solute, rather than in terms of the mole fraction. This has led to the definition of the molar activity coefficient, y_1, and the molal activity coefficient, γ_1, as follows:

$$a_1 = \gamma_1 m_1 , \tag{30a}$$

$$f_1 = \gamma_1 (1 + mM_1/1000) , \tag{31}$$

$$f_1 = y_1 \left[(\rho/\rho_0) + C(M_1-M_2)/1000\,\rho_0 \right] , \tag{32}$$

$$\gamma_1 = y_1 \left[\frac{\rho - CM_2 \times 10^{-3}}{\rho_0} \right] , \tag{33}$$

$$m = C/(\rho - CM_2 \times 10^{-3}) , \tag{34}$$

in which m and C are, respectively, the molality and the molarity of the solution; M_1 and M_2 are the molecular weights of the solvent and the solute, respectively; and ρ and ρ_0 are the densities of the solution and of the pure solvent, respectively.

Since it is impossible to separate the activity of one ion constituent from those of the other ion constituents present in a solution of an electrolyte, these individual quantities cannot be determined. However, it is possible to determine the mean activity of the electrolyte as a whole. The mean activity of an electrolyte, $a_\pm$, is defined as:

$$a_{\pm}^{\nu} = a = \prod_i a_i^{\nu_i} , \tag{35}$$

in which ν_i is the number of $\underline{i\text{th}}$ ions from one molecule of the electrolyte which dissociates into a total number of ions, ν, and $\underline{a}$ is the activity of the electrolyte. For a binary electrolyte, of molarity $\underline{C}$, the following expressions may be employed to define the activity coefficients:

$$a_{\pm}^{\nu} = (y_{\pm} C_{\pm})^{\nu} = y_{+}^{\nu_{+}} y_{-}^{\nu_{-}} C_{+}^{\nu_{+}} C_{-}^{\nu_{-}} = a_{+}^{\nu_{+}} a_{-}^{\nu_{-}} ; \tag{36}$$

$$y_{\pm}^{\nu} = y_{+}^{\nu_{+}} y_{-}^{\nu_{-}} ; \tag{37}$$

$$C_{\pm}^{\nu} = C_{+}^{\nu_{+}} C_{-}^{\nu_{-}} = C(\nu_{+}^{\nu_{+}} \nu_{-}^{\nu_{-}}); \tag{38}$$

in which $y_{\pm}$ is the mean molar activity coefficient; $C_{\pm}$ is the mean ionic molarity; and C_{+} and C_{-} are the molarities of the cation and of the anion, respectively. Similar expressions may be obtained for the mean molal quantities. Lewis and Randall (91) observed empirically that, as a first approximation, the activity coefficient of a particular electrolyte is a function of only the ionic strength of the solution. The ionic strength, $\underline{w}$, of a solution is defined as:

$$w = \tfrac{1}{2} \sum_i C_i z_i^2 , \tag{39}$$

in which $\underline{C_i}$ is the molarity of the $\underline{i\text{th}}$ ion of valence $\underline{z_i}$.

They were unable to account for this dependence from theoretical considerations.

Numerous attempts have been made to account theoretically for the deviation of activity coefficients from unity. In 1912 and 1913, Milner (19,20) arrived at a partial solution to the problem by making the assumption that the deviations were due to interionic attractions and repulsions. He encountered mathematical difficulties, however, and was unable to obtain a satisfactory solution. Ten years later, Debye and Hückel (8) used the same assumptions with much greater success.

Debye and Hückel assumed that the coulombic interactions give rise to an ionic atmosphere around each ion, such that there is a slight excess of oppositely-charged ions around each central ion. They also assumed that the time average charge distribution of this atmosphere is adequately expressed by the Boltzman distribution. By expanding the Boltzman exponential into a power series and disregarding all terms higher than the first order they were able to combine the charge distribution with Poisson's equation for a spherically-symmetric distribution of charge, and to obtain an expression for the electrostatic potential of an ionic atmosphere on the central ion. The interaction of the charge of this ion with the potential was identified with a contribution to the Gibbs' free

energy per ion (92,93). The expression derived by Debye and Hückel for the mean activity coefficient of a binary electrolyte having ions of charge z_+ and z_- is:

$$- \ln \gamma_{\pm} = \frac{|z_+ z_-| \; A \sqrt{w}}{1 + \overset{o}{a} B \sqrt{w}} , \tag{40}$$

in which $\overset{o}{a}$ is the mean distance of closest approach of the ions to each other. A and B are constants of the solvent and of the temperature; they are defined as:

$$A = \frac{\epsilon^3}{(DkT)^{3/2}} \cdot \sqrt{\frac{2 \pi N}{1000}} , \tag{41}$$

and

$$B = \sqrt{\frac{8 \pi N \epsilon^2}{1000 DkT}} , \tag{42}$$

in which ϵ is the electronic charge; D is the dielectric constant of the solvent; k is the Boltzman constant; T is the absolute temperature; and N is Avogadro's number.

The fundamental assumptions of the Debye-Hückel theory can be summarized as follows. One: the electrolyte is completely dissociated. Two: if the electrical charges could be removed from the ions, the solutions should exhibit ideal behavior. Three: the properties of the solvent are continuous, with no variation of the dielectric constant about the ions. Four: the Boltzman

distribution law correctly expresses the distribution of the ions in the ionic atmosphere. Five: the Poisson equation is applicable to systems of ionic charges in a solvent. Six: the net electrostatic potential of the ionic atmosphere of any ion is small compared to the quantity kT, so that the higher terms of the expansion of the Boltzman distribution law may be ignored. These assumptions become more nearly correct as the solution becomes more dilute. Thus the Debye-Hückel theory is applicable only to dilute solutions.

Attempts to extend this theory to higher concentrations have met with only partial success. Müller (92,94), Gronwall, LaMer and Sandved (95), and Bjerrum (96) have attempted to extend the applicability of the theory by including some of the higher terms of the Boltzman expansion. However the resulting equations are too involved to be of much practical use.

2. Methods

The various methods available for the experimental determination of activity coefficients are based upon a wide variety of measurements including freezing point depression; boiling point elevation; osmotic pressure; and electromotive force of cells both with and without

transference. Adequate references are available for all of these methods (10,11,97,98).

Since the determination of activity coefficients from concentration cells with transference was employed for the work presented in this thesis, this method will be discussed in detail. The theory involved in such a determination is simple and straightforward. For this discussion it is convenient to consider a general cell of the following type:

$$M, MX, B_{\nu_+}^{z_+} X_{\nu_-}^{z_-} (m_1) \quad \vert \quad B_{\nu_+}^{z_+} X_{\nu_-}^{z_-} (m_2), MX, M, \quad (43)$$
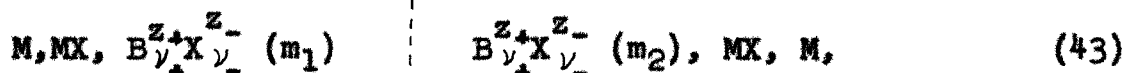
in which $\underline{M, MX}$ is an electrode reversible to the $\underline{X^{z_-}}$ ion, of charge $\underline{z_-}$; $\underline{B^{z_+}}$ is the cation of charge z_+ of the electrolyte $\underline{B_{\nu_+}^{z_+} X_{\nu_-}^{z_-}}$ whose mean activity is to be determined; and m_1 and m_2 are the molalities of the electrolyte in the two compartments. By convention $\underline{m_1}$ is assumed to be greater than $\underline{m_2}$. For the passage of one Faraday of current, the following changes will occur in the left-hand compartment of the cell:

1) a loss of $\underline{T_+}$ equivalents of $\underline{B^{z_+}}$, due to the migration of that ion under the influence of the current;

2) a gain of $\underline{T_-}$ equivalents of $\underline{X^{z_-}}$ due to the migration of that ion under the influence of the current; and

3) a loss of one equivalent of $\underline{X^{z_-}}$ due to the electrode reaction.

For the same reasons exactly the opposite changes will occur in the right-hand compartment. The net change in the cell is obtained by summing the above changes, and is equal to a transfer from the left-hand compartment to the right-hand compartment of T_+ equivalents of the electrolyte $B_{\nu_+}^{Z_+} X_{\nu_-}^{Z_-}$.

The free energy change, $d\mathcal{F}$, for a reversible reaction in a cell of the above type, in which m_1 is greater than m_2 by an infinitesimal amount, is:

$$d\mathcal{F} = nRT \frac{da}{a} = \frac{T_+}{z_+ \nu_+} RT\, d\,(\ln a)\,, \qquad (44)$$

in which n is the number of equivalents of electrolyte undergoing the change, and da is the change in activity experienced by the electrolyte transferred. Since:

$$d\mathcal{F} = - nF\, dE, \qquad (45)$$

it follows that:

$$dE = -\left(\frac{RT}{F}\right)\left(\frac{T_+}{z_+ \nu_+}\right) d\,(\ln a)\,. \qquad (46)$$

For an actual cell with finite concentration differences, equation (46) can be integrated over the concentration gradient only if the variation of T_+ with activity (or concentration) is known. A method of calculation

used for this purpose will be discussed in Section VI.
The experimental procedure just described has been used
widely for the determination of activity coefficients
of electrolytes for which there is no suitable electrode
available which is reversible to the cation.

Before electromotive force measurements in concen-
tration cells with transference could be used for the
determination of activity coefficients, it had to be
ascertained whether the potential developed in the con-
centration cells depends only upon the concentrations of
the solutions in contact with the electrodes and is in-
dependent of the concentration gradients of the junction
between the two solutions. Since this method was first
used (99), in 1900, ample evidence has been presented
to show that these conditions are fulfilled.

Cummings and Gilchrist (100) were the first to
demonstrate that reproducible potentials could be obtained
providing the liquid junction has a cross-sectional
diameter of at least four millimeters. Their work was
later confirmed by MacInnes and Parker (101), and by Lewis,
Brighton and Sebastian (102). MacInnes and his co-workers
(56,103) fully demonstrated that the potential developed
between the two solutions is a function only of the solu-
tions in contact with the electrodes. Brown and MacInnes
(103) were the first to determine activities by the use of

concentration cells with transference. Subsequently, many other investigators (6,104,105) have extensively used concentration cells with transference to determine activity coefficients.

E. Present Status of the Theories

The Onsager equation is regarded as the best extrapolation law now available for conductance data. This law, which is valid only in dilute solutions, was derived using the assumption that inter-ionic attractions and repulsions are responsible for the deviations from ideal behavior. As yet no extension of the Onsager equation to higher concentrations has been satisfactory.

The Debye-Hückel law, which is based upon the same fundamental assumptions as the Onsager law, is regarded as the best theory yet developed to explain activities; however, it agrees with experimental data only at low concentrations. Attempts to extend the law to higher concentrations have given limited improvement but have not been generally successful.

A limiting law for transference numbers can be obtained from the Onsager law. Although this limiting law predicts the correct transference numbers for a few 1-1 electrolytes, it fails completely for higher valence-type electrolytes. In the concentration ranges generally

studied, from about 0.01 normal to approximately 0.1 normal, the transference numbers for poly-valent ions are found to be linear functions of the square root of the concentration, as predicted by the limiting law, but the experimental slopes vary widely from those predicted by theory.

Regardless of this anomaly between conductances and transference numbers, activity coefficients obtained from cells with transference, which utilize these "non-theoretical" transference numbers, are in accord with those predicted by the Debye-Hückel law, which in turn, is based upon the same premises as the Onsager law.

It is hoped that this anomaly can be resolved when more data become available for poly-valent electrolytes.

III. MATERIALS

A. Preparation of Salts

The various rare earth salts employed in this investigation were separated and purified by the rare earth separation group of the Ames Laboratory of the Atomic Energy Commission, under the direction of Dr. F. H. Spedding (106,107,108,109,110,111,112,113,114). The purities of the various oxides used are given in Table I. In all cases the oxides were purified further by a minimum of two precipitations from an acid solution with doubly-recrystallized oxalic acid. Before precipitation either Cl_2 or Br_2 was added to the solution which was then boiled. The final oxalate precipitate was ignited to the oxide in platinum dishes.

The rare earth bromide solutions were prepared as follows. The freshly ignited oxide was dissolved at room temperature in a slightly insufficient quantity of redistilled hydrobromic acid. When the reaction was complete the undissolved oxide was filtered from the solution. The $PrBr_3$ solution had to be boiled after filtration to remove the bromine formed by the reaction:

$$Pr_6O_{11} + 22 HBr \longrightarrow 6PrBr_3 + 11 H_2O + 2Br_2 . \quad (47)$$

All solutions were diluted to a predetermined volume with

Table I

Purities of the Rare Earth Oxides

Oxide	Purity[*]
La_2O_3	Neither thorium nor any other rare earth detected. Slight trace of calcium detected prior to two acid oxalate precipitations.
Pr_6O_{11}	Neither thorium nor any other rare earth detected. Slight trace of calcium detected prior to two acid oxalate precipitations.
Nd_2O_3	Neither thorium nor any other rare earth detected. No common element detected.
Gd_2O_3	Less than 0.1% Sm_2O_3 detected. $0.025 \pm 0.005\%$ Tb_4O_7 detected by a new fluorescimetric technique.
Er_2O_3	About 0.05% Yb_2O_3, Tm_2O_3, and Ho_2O_3; about 0.2% Y_2O_3 detected. No Dy_2O_3 detected. Trace of calcium detected prior to two acid oxalate precipitations.

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

conductivity water and were analyzed for both the bromide and for the rare earth content. In all cases the number of the bromide and the rare earth equivalents did not differ from each other by more than 0.05%. The pH values of the rare earth bromide solutions varied from 6.40 for erbium bromide to 6.65 for lanthanum bromide, which was in agreement with the values obtained by previous investigators (2,4,115). Rare earth analyses were made by precipitating the rare earth from a hot solution as the oxalate and igniting the oxalate to the oxide at 900°C. Halide analyses were made by precipitating the halide with silver nitrate, in darkened beakers, and drying at 110°C.

Gadolinium chloride solutions were prepared from the anhydrous salt. The method used to obtain the anhydrous chloride was that described by Spedding, Porter and Wright (4). In brief, the rare earth oxide was dissolved in an excess of redistilled hydrochloric acid. After chlorine had been bubbled through the solution to remove any bromide contamination, the solution was boiled to remove excess chlorine and evaporated to a thick syrup. The syrup was transferred to a pyrex tube and heated, under vacuum, in a water bath until the crystals appeared dry and flaky. The crystals were then transferred to a long drying tube and slowly heated under a flowing

atmosphere of pure dry hydrogen chloride to a final temperature of 400°C. To prevent the partially dehydrated crystals from melting, the temperature was raised by stages, first to 60°, then to 90°, 120°, 150°, and finally to 400°C. The salt was kept at each temperature until no moisture could be seen condensing in the cold portion of the tube. After the final temperature was reached, dry purified argon gas was passed over the salt until the exit gas gave a neutral reaction to pH paper. The salt was then cooled with the gas still passing over it. When at room temperature, the anhydrous salt was transferred, in a dry atmosphere, to a previously dried and tared weighing bottle. After being weighed, the salt was dissolved, in a closed system, in a large volume of conductivity water. The solution was finally diluted to a predetermined volume and analyzed. Both the chloride and the gadolinium analyses agreed within experimental error with the weighed-in concentration.

Several attempts were made to prepare solutions of the anhydrous bromides by this method. Although clear solutions could be obtained, analyses of these solutions showed a deficiency of bromide content, indicating the formation of a soluble basic or oxy-bromide. These solutions were found to have pH values from 7.10 to 7,30, which also indicated the presence of some basic salt.

The potassium bromide, used in preliminary trans-
ference number experiments, and for soaking the Ag, AgBr
electrodes, was purified by a double recrystallization
from conductivity water; purified bromine was added
before the first recrystallization and the solution
boiled to remove any iodine contamination. The salt was
finally dried at $150^{\circ}C$.

Potassium chloride was purified according to the
procedure of Pinching and Bates (116). Lithium bromide
was prepared from purified lithium carbonate by the
addition of redistilled hydrobromic acid to a solution
of the carbonate until the pH reached a value of 6.6.
The solution was then boiled to remove all carbon dioxide.
When cool, the solution was analyzed; the lithium was
weighed as lithium sulfate, and the bromide as silver
bromide. The results of the analyses indicated that
both constituents were present in the proper stoichio-
metric quantities. Lithium chloride was prepared in an
analogous manner.

Purified silver oxide, used in the preparation of
silver, silver halide electrodes, was prepared by adding
a dilute solution of carbonate-free sodium hydroxide to
a dilute solution of reagent-grade silver nitrate (117).
The resulting precipitate was washed by decantation a
minimum of 40 times with boiling conductivity water.

The silver bromate used to prepare some of the silver, silver bromide electrodes by the thermal method (118) was made by the reaction of silver nitrate with potassium bromate. The salt was recrystallized twice from conductivity water and dried at $110^{\circ}C$.

All starting materials were the best commercially-available reagent-grade chemicals. The water used to prepare the salts and the solutions had a specific conductivity which was not greater than 0.98×10^{-6} mhos per centimeter.

B.   Calibration of Glassware

All flasks used to prepare the final solutions were recalibrated "Pyrex", Kimble "Exax" or Kimble "Normax" brand volumetric flasks. All pipettes used to make dilutions were of similar quality. In no case did the recalibrations, made at $25.0 \pm 0.1^{\circ}C$, indicate that the actual volume of the glassware varied from the volume stated by the manufacturer by more than 0.01 per cent.

C.   Preparation of Rare Earth
Halide Solutions

Aliquots were taken from the concentrated stock solution to prepare all solutions above 0.01 normal. Aliquots of these solutions were then taken for one-to-ten

dilutions to obtain solutions down to 0.001 N. This process was repeated on the second set of dilutions to obtain the very dilute solutions. All dilutions were made with the solutions at $25.0 \pm 0.1^{\circ}C$.

D. General Apparatus

For all weighings, an Ainsworth magnetically-damped, notched beam, chainomatic balance was used. The platinum plated weights were of the high precision, Class S type, and were certified by the manufacturer.

A Beckman Model G pH meter was used for pH measurements. The calibration of the instrument was checked before each measurement with buffer solutions supplied by the manufacturer.

IV. CONDUCTANCES

A. Apparatus

The apparatus used for the determination of the conductances of the rare earth salts included a Jones Conductivity bridge, an audiofrequency oscillator, a tuned audiofrequency amplifier, a cathode-ray oscillograph, three conductivity cells, and a constant-temperature oil bath.

All of this equipment, with the exception of the oscillograph and the constant-temperature bath, was purchased from the Leeds and Northrup Company. The conductivity bridge (catalog number 4666), manufactured in accordance with the specifications of Jones and his coworkers (33,35,37), has been completely described by Dike (119). The oscillator and amplifier (Leeds and Northrup catalog numbers 9842 and 9847) also conformed to the recommendations of Jones.

A Dumont Type 208B five-inch cathode-ray oscillograph was used as the null-point indicator. The use of this instrument, instead of the standard ear-phones, greatly facilitated the detection of the null-point, which was a minimum in the amplitude of the wave form projected on the oscillograph screen.

The constant-temperature bath, purchased from the Arthur H. Thomas Company (catalog number 9926-D), maintained the temperature constant to within $0.02^\circ C$. The temperature was determined by a thermometer calibrated in 0.01° divisions, which had been certified by the National Bureau of Standards. All measurements were taken with the bath at $25.00 \pm 0.02^\circ C$. A high grade of transformer oil was used as the bath liquid, instead of water, to reduce the capacitance effects between the leads to the cell.

Three conductivity cells (Leeds and Northrup catalog numbers 4911, 4914 and 4915) were used for the low, medium and high conductivity solutions, respectively. The electrodes for each cell were platinized by the method of Jones and Bollinger (33). Since Parker effects were observed in the medium and low conductivity cells, graphs of cell constants against observed conductances were prepared and used to determine the correct cell constant for the particular conductance measured. Standard solutions of potassium chloride were prepared to calibrate the cells, and the equivalent conductances determined by Shedlovsky (42) were used as references.

B. Procedure

The high conductivity cell was used for solutions having a specific conductance of 0.003 mhos per centimeter or greater; the medium conductivity cell was used for solutions between 0.0003 and 0.003 mhos per centimeter; and the low conductivity cell was used for solutions below 0.0003 mhos per centimeter in specific conductance. Before being filled, each cell was rinsed at least three times with the solution to be measured. After a cell was immersed in the constant temperature bath and allowed to reach thermal equilibrium with the bath, the null-point was determined by varying the resistances of the Jones bridge until the oscillograph indicated no flow of current. The capacitance effects were also nulled with the bridge. Using fresh solution, each measurement was repeated; these duplicate determinations agreed with each other to well within 0.1 per cent. A correction for the conductance of the solvent was applied by subtracting the specific conductance of the water from the specific conductance of the solution.

C. Data and Calculations

Data obtained from the Jones bridge were read in ohms. Therefore the following equations were used to

calculate the specific conductances and the equivalent
conductances of the solutions:

$$L_s = (k/R) - L_{H_2O} , \tag{48}$$

and

$$\Lambda = 1000L_s/c = (1000/c) \sqrt{(k/R) - L_{H_2O}} , \tag{49}$$

in which L_s is the specific conductance of the solution
due only to the solute; k is the cell constant; R is
the measured resistance of the solution in ohms; and
L_{H_2O} is the specific resistance of the water used to
prepare the solution.

The equivalent conductances of lanthanum, praseo-
dymium, neodymium, gadolinium and erbium bromides, and
of gadolinium chloride are listed in Tables II through
VII respectively. The data listed are the averages of
at least two duplicate determinations. Graphs of these
data are shown in Figures 1 and 2. The ordinates of
these figures are staggered in order to separate the
various curves. The curves for the lanthanum, praseo-
dymium and neodymium bromides are identical within
experimental error.

Values of the equivalent conductances at infinite
dilution were obtained by extrapolation using the Onsager

Table II

Equivalent Conductances of Lanthanum Bromide at 25°C

Normality	Equivalent Conductance
0.0002974	142.7
0.0005947	140.9
0.002974	133.5
0.005947	128.8
0.007434	127.1
0.01041	124.4
0.01487	121.2
0.02974	115.1
0.05947	108.5
0.07434	106.5
0.1041	103.5

Table III

Equivalent Conductances of Praseodymium Bromide at 25°C

Normality		Equivalent Conductance
0.0002572	$\sqrt{} = 0.01604$	143.2
0.0005144	$\sqrt{} = 0.02268$	141.0
0.0007716		139.9
0.001029		138.6
0.002572		134.0
0.005144		129.4
0.007716		126.5
0.01029		124.4
0.02572		116.0
0.05144		109.6
0.07716		105.9
0.1029		103.3

Table IV

Equivalent Conductances of Neodymium Bromide at 25°C

Normality		Equivalent Conductance
0.0002639	$\sqrt{} = 0.01624$	143.0
0.0004750		141.5
0.0005278		141.2
0.0007917		139.9
0.0009499		138.8
0.001056		138.5
0.002375		134.5
0.002639		133.8
0.005278		129.3
0.007124		127.2
0.007917		126.4
0.01056		124.0
0.02639		116.0
0.05278		109.5
0.07917		105.8
0.1056		103.2

Table V

Equivalent Conductances of Gadolinium Bromide at 25°C

Normality	Equivalent Conductance
0.0002544	141.1
0.0005089	139.3
0.0007633	137.8
0.001272	135.5
0.002544	131.6
0.005089	127.2
0.007633	124.3
0.01018	122.0
0.01272	120.2
0.02544	114.2
0.05089	107.9
0.07633	104.4
0.1018	101.8

Table VI

Equivalent Conductances of Erbium
Bromide at 25°C

Normality	Equivalent Conductance
0.0003077	139.1
0.0006154	137.2
0.0009231	135.9
0.001538	133.6
0.003077	129.8
0.006154	125.2
0.009231	121.9
0.01538	118.0
0.03077	111.8
0.06154	105.6
0.09231	102.0

Table VII

Equivalent Conductances of Gadolinium Chloride at 25°C

Normality	Equivalent Conductance
0.0003503	138.4
0.0005839	136.7
0.0008174	135.8
0.001168	134.8
0.003503	127.8
0.005839	124.3
0.008174	121.9
0.01168	118.8
0.02335	112.6
0.03503	108.4
0.05839	103.4
0.08174	100.3
0.1051	97.88
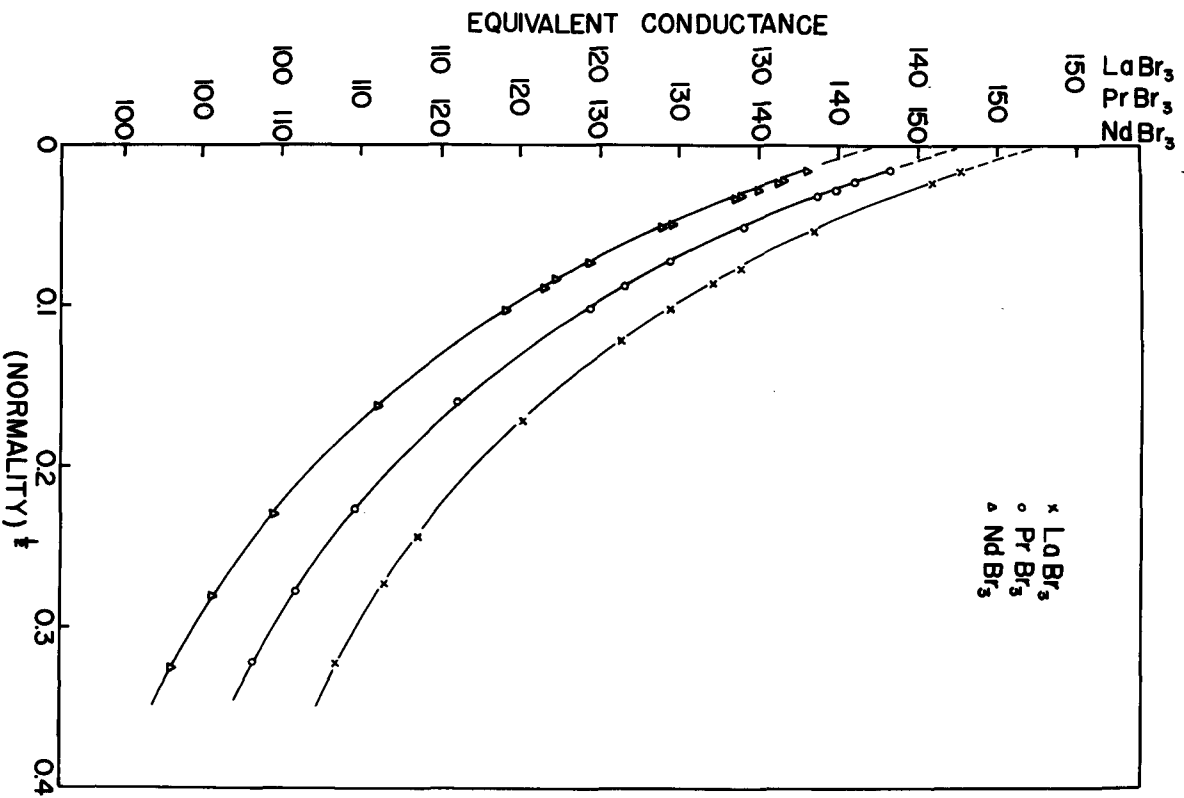
Figure 1 - Equivalent conductances of lanthanum, praseodymium and neodymium bromides at 25°C.
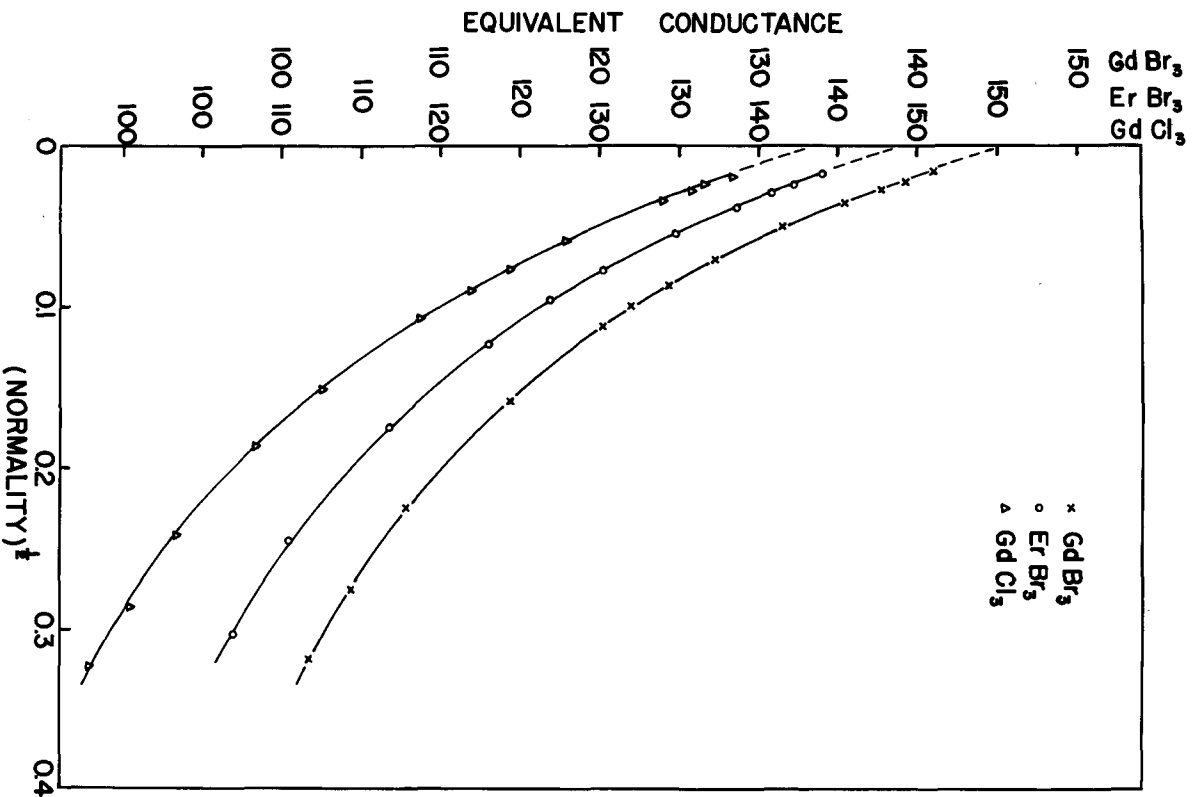
Figure 2 — Equivalent conductances of gadolinium and erbium bromides and of gadolinium chloride at 25°C.

limiting law. For aqueous solutions of 3-1 electrolytes at $25^{\circ}C$, this law has the form:

$$\Lambda = \Lambda_o - (3.3158 \text{ Y } \Lambda_o + 170.25) \text{ } c^{\frac{1}{2}} \text{ ,} \tag{50}$$

in which

$$Y = \frac{0.7500 \text{ } \Lambda_o/(\Lambda_o + 2 \text{ } \lambda^o_-)}{1 + \sqrt{0.7500 \text{ } \Lambda_o/(\Lambda_o + 2\lambda^o_-)}} \text{ .} \tag{51}$$

In all calculations, the values of the numerical constants used are those listed in the appendix. The limiting ionic conductance, $\underline{\lambda^o_-}$, of the chloride ion was taken to be 76.34 mhos/cm./equiv., and that of the bromide ion to be 78.15 mhos/cm./equiv. The first value was the average obtained for the chloride ion in hydrochloric acid (42,120), lithium chloride (42,121), sodium chloride (122,123), and potassium chloride (122,123). The value for bromide ion was obtained by averaging the values of the equivalent conductance at infinite dilution of potassium bromide as determined by various investigators (2,11,124), and by subtracting from that average the value of the ionic conductance at infinite dilution of the potassium ion (10,125,126,127,128).

The extrapolation was made by calculating a $\underline{\Lambda'_o}$ value for each experimentally-determined $\underline{\Lambda}$ value using a method of successive approximations. The prime is used

to differentiate these calculated values from the true Λ_o value. Since the Onsager equation becomes valid as the concentration is reduced, these Λ_o' values should approach the true value of Λ_o as the concentration approaches zero. Since the true Λ_o is a constant for the salt, the values of Λ_o' should be constant in the range of concentrations in which the Onsager law is applicable and a curve of these values should have zero slope at the axis of zero concentration, intercepting the ordinate at the true Λ_o value. These extrapolation curves are shown in Figures 3 and 4. The ordinates of these figures are staggered in order to separate the various curves. The resulting values of Λ_o are listed in Table VIII along with the cation conductances at infinite dilution, obtained by the following equation:

$$\Lambda_o = \lambda_+^o + \lambda_-^o . \tag{52}$$

D. Discussion and Conclusions

Recently, the conductances of several rare earth chlorides in aqueous solutions at 25.0°C have been determined with precision (2,3,4). Because of the additivity of ionic conductances at infinite dilution, there should be a constant difference of 1.8 mhos per centimeter per
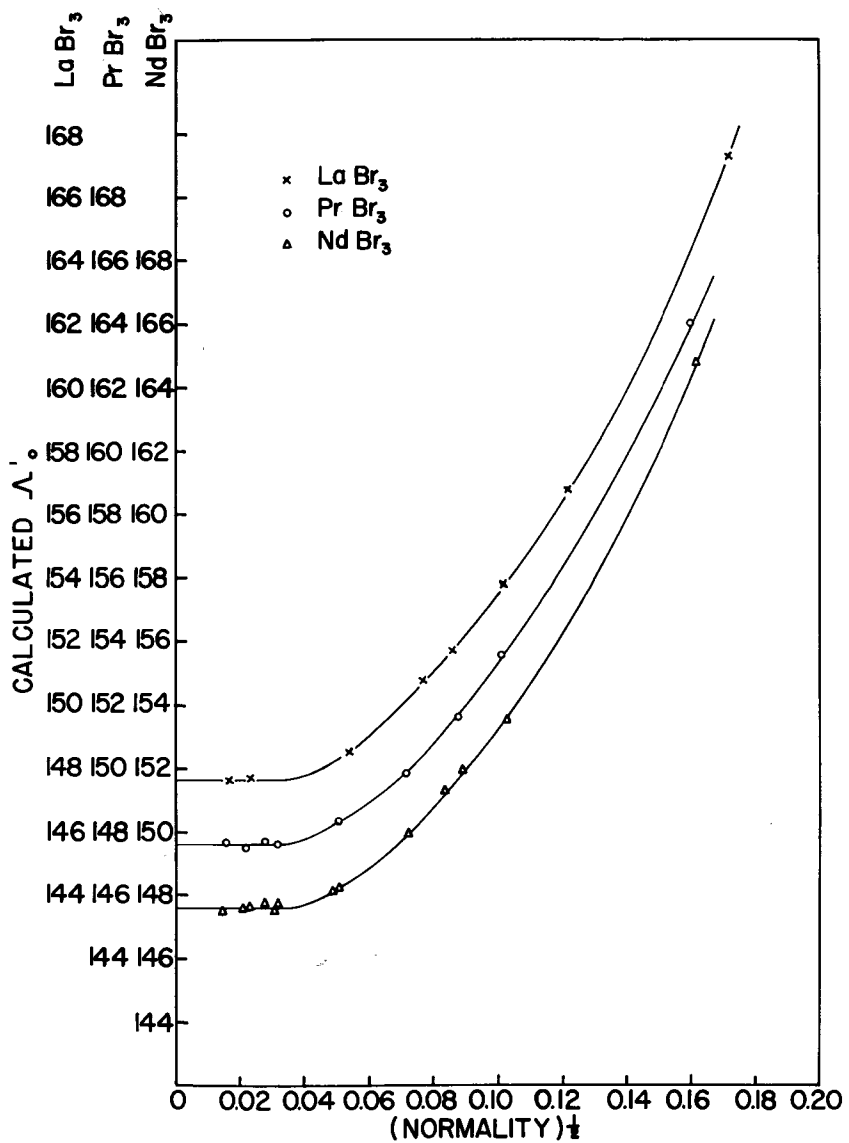
Figure 3 - Extrapolation of equivalent conductances
to infinite dilution of lanthanum, praseo-
dymium and neodymium bromides.
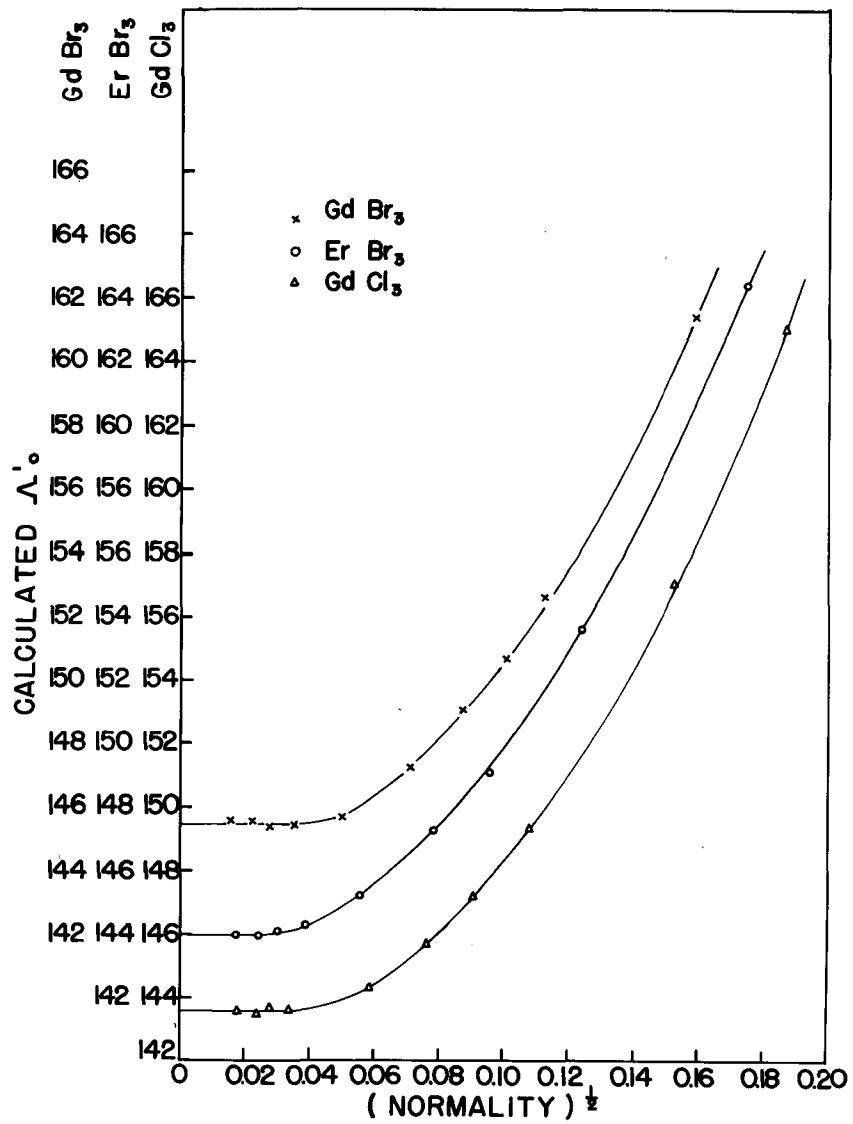
Figure 4 - Extrapolation of equivalent conductances to infinite dilution of gadolinium and erbium bromides and of gadolinium chloride.

Table VIII

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

Salt	Λ_o	λ_o^+
$LaBr_3$	147.6	69.5
$PrBr_3$	147.6	69.5
$NdBr_3$	147.6	69.5
$GdBr_3$	145.6	67.4
$ErBr_3$	144.0	65.9
$GdCl_3$	143.7	67.3

equivalent between the equivalent conductances at infinite dilution of the chloride and of the bromide of the same rare earth. Within experimental error, this constant difference was obtained with all but one cation. This difference is illustrated in Figure 5, in which the values of Λ_o for the rare earth halides have been plotted against their respective atomic numbers. The only exception to this constant difference is neodymium. However, two separate sets of neodymium bromide solutions were measured, and their extrapolated values agreed exactly with each other. Thus it is felt that the value of the equivalent conductance at infinite dilution of neodymium bromide, which is reported in this thesis, is correct.

In 1937, Jantsch, Grabitsch and Lischka (129) studied the conductances of several rare earth halides, including gadolinium chloride and gadolinium bromide. They used pure rare earth samples and followed the procedure of Kohlrausch (9) for measuring conductances. Above 0.01 normal, their data for both of the gadolinium halides are slightly higher than the data reported in this section; below 0.01 normal, their data are slightly lower. In addition, their data on these gadolinium halides do not appear to be self-consistent. Although their conductances of gadolinium bromide are higher than those of gadolinium
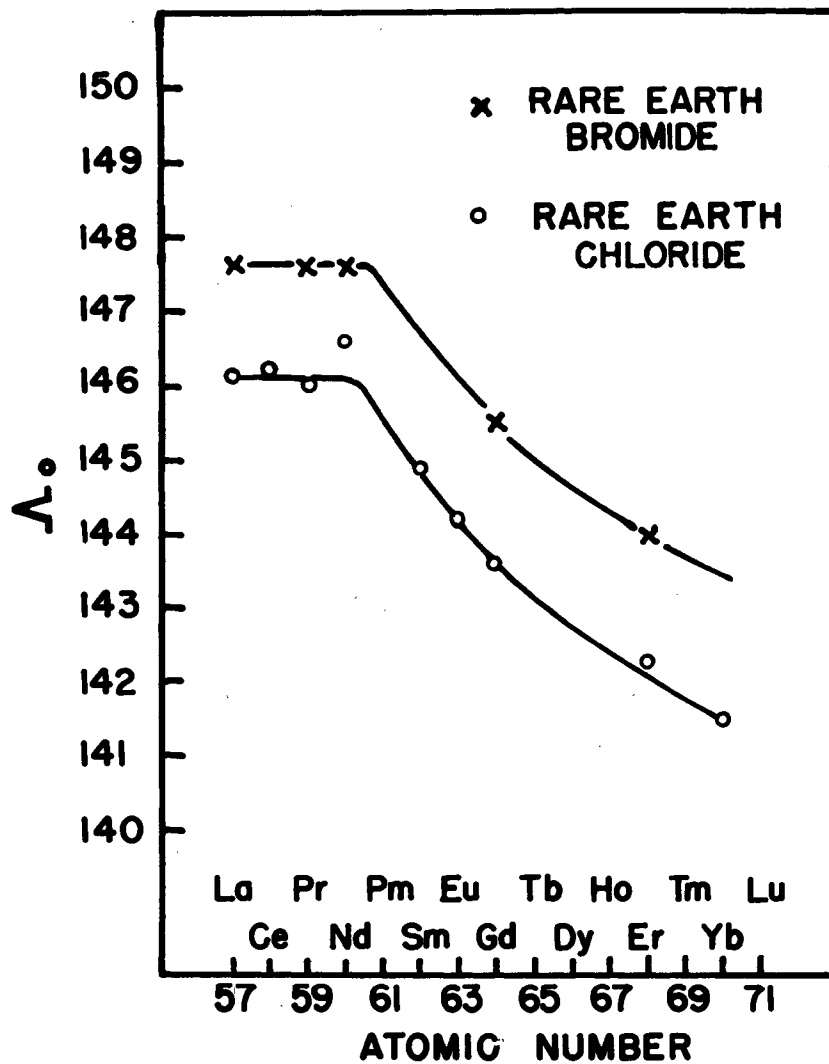
Figure 5 - Equivalent conductances at infinite dilution of some rare earth halides at 25°C.

chloride in concentrated solutions as would be expected,
their bromide data are lower than those of the chloride
in dilute solutions. In view of the close correlation of
the conductance data reported here with that of Jones and
Bickford (2), of Longsworth and MacInnes (3), and of
Spedding, Porter and Wright (4), it is believed that
these more recent data are the more accurate.

The data reported in this thesis indicate that the
Onsager limiting law is obeyed for all salts studied up
to a concentration of approximately 0.001 normal. This is
illustrated by the flat portion of the extrapolation curves
in Figures 3 and 4.

Although there is a regular decrease in atomic radius
from lanthanum through lutetium, which would imply an
increase in conductance with increasing atomic number,
such is not the case. Instead, the conductances remain
constant between lanthanum and neodymium, and then decrease
with the heavier elements. This decrease with the heavier
rare earths indicates that the hydration of the ions
plays a predominent role in determining their mobilities
and conductivities. This is known to be true in the case
of the alkali metal ions.

The similarity of the equivalent conductances of the
first few members of the rare earth family may be inter-
preted, in view of the apparent importance of hydration,

as follows. As the ion becomes larger with decreasing atomic number, a second coordination number may become possible, so that an equilibrium is established between the two types of hydrated ions. A crystallographic study of lanthanum sulfate enneahydrate (130) indicated that lanthanum has two coordination numbers for oxygen, namely nine and twelve; a preliminary study, still in progress, of neodymium sulfate octahydrate (131) indicates that neodymium has only one such coordination number, presumably nine. As a change in the coordination number would undoubtedly change the effective radius of the hydrated ion, it is possible that this effect on lanthanum reduces the conductances of lanthanum solutions to that of neodymium. It is also possible that this same effect lowers the conductances of praseodymium solutions.

The limits of error of the conductance data presented in this thesis were set by the accuracy of analyses of the solutions. The temperature control was adequate for an accuracy in conductance measurements of within 0.1 per cent. The errors in measuring the resistances of the cells and in calibrating the cells were estimated to be below 0.05 per cent, while the error of analyses of the solutions was believed to be less than 0.1 per cent.

V. TRANSFERENCE NUMBERS

A. Apparatus

For the determination of transference numbers by the moving boundary method, the sheared boundary technique was used. The apparatus required for this method consisted of: 1) an electrolytic cell, 2) a timing device, 3) a device for observing and following the boundary formed between the leading and the following solution, 4) a constant temperature bath, and 5) a constant-current apparatus. With the exception of the current controller, all of the apparatus used was identical with that employed and described by Spedding, Porter and Wright (5).

Pictures of the electrolytic cell are shown in Figures 6 and 7. The cell consisted of a 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 connected to the lower end of the measuring tube. The measuring tube was a two-milliliter pipette graduated in 0.1 ml. intervals, which had been calibrated with mercury by the method of Longsworth (89). The anode compartment was equipped with a standard-taper joint to fit the one of the cadmium metal electrode, with an electrode cup, and with an overflow tube which could be closed by a stopcock. The cup was
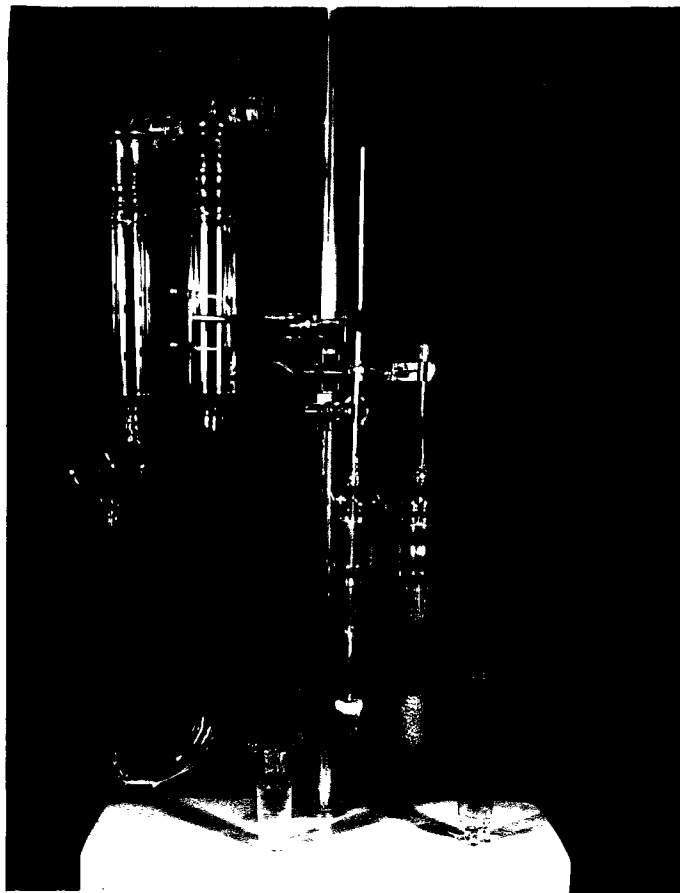
Figure 6 - Unassembled moving boundary
electrolytic cell.
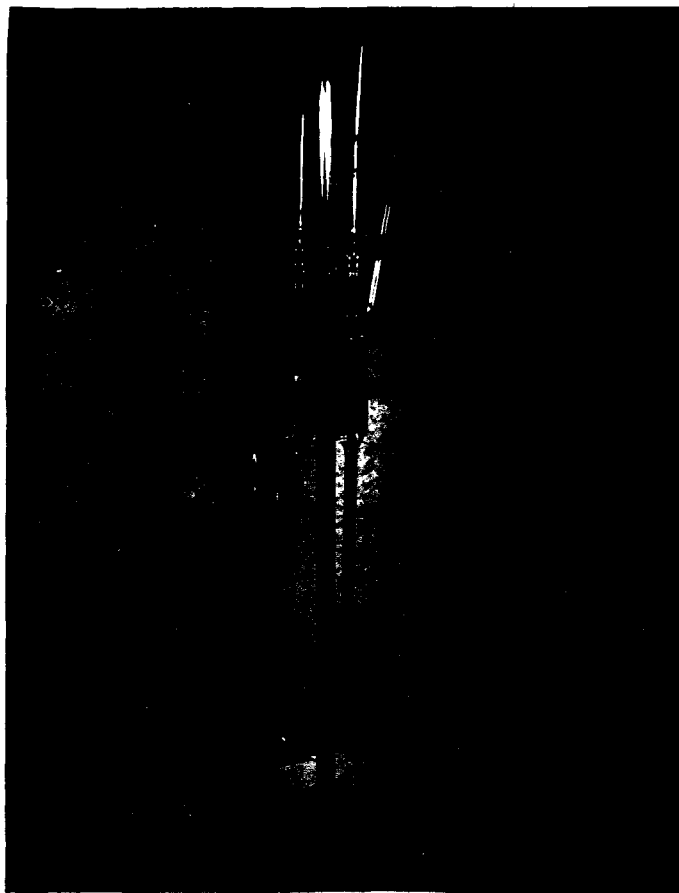
Figure 7 - Assembled moving boundary
electrolytic cell.

used to contain the products formed by the electrolysis,
thus preventing them from reaching the measuring tube.
The cathode compartment was similarly equipped with the
exception that a silver-silver halide electrode was sub-
stituted for the cadmium electrode. This cell, in which
the anode compartment was closed to the atmosphere during
a determination, was designed for measuring falling
boundaries.

The silver, silver halide electrodes were purchased
from the Klett Manufacturing Company. They consisted of
a smooth silver metal sheet wound around a central hollow
silver tube, with corrugated silver sheet separating the
various layers of smooth silver. The central silver tube
was about 15 inches long, and was sealed through a stand-
ard-taper glass joint. Silver chloride or silver bromide
was deposited electrolytically from a one normal solution
of the corresponding halogen acid. The silver, silver
bromide electrode was used with bromide solutions, and
the silver, silver chloride electrode with chloride solu-
tions. It was found necessary to bromidize the silver,
silver bromide electrode before each determination, pro-
bably because of the photo-sensitivity of the silver
bromide.

Two stopwatches, mounted on the side of a box with
a pivoted lid, were used to time the boundary between

calibrations on the measuring tube. The lid of the box extended over the crowns of the watches and rested on them, so that the watches could be started or stopped by pressing down on the lid. These watches were checked on a "Watchmaster" manufactured by American Time Products, Incorporated and were found to be accurate to within five seconds over a 24-hour period.

The position of the boundary was observed by making use of the differences in indices of refraction between the two solutions forming the boundary. Light striking this interface between the solutions is deviated in accordance with Snell's law. At a critical angle of incidence, the deviated beam leaves the measuring tube parallel to the boundary surface; refraction does not occur above this angle and the beam is reflected. Thus if a narrow light source is placed so that all the light falling on the boundary comes from below the boundary surface, there is a narrow angle on the opposite side of the tube into which light is neither reflected nor refracted.

The apparatus used for observing the boundary is illustrated in Figure 8. The light source was a 50-watt light bulb mounted in a box which was suspended by a flexible wire from the shaft of a motor. The light passed through a two-centimeter-wide slit covered by a
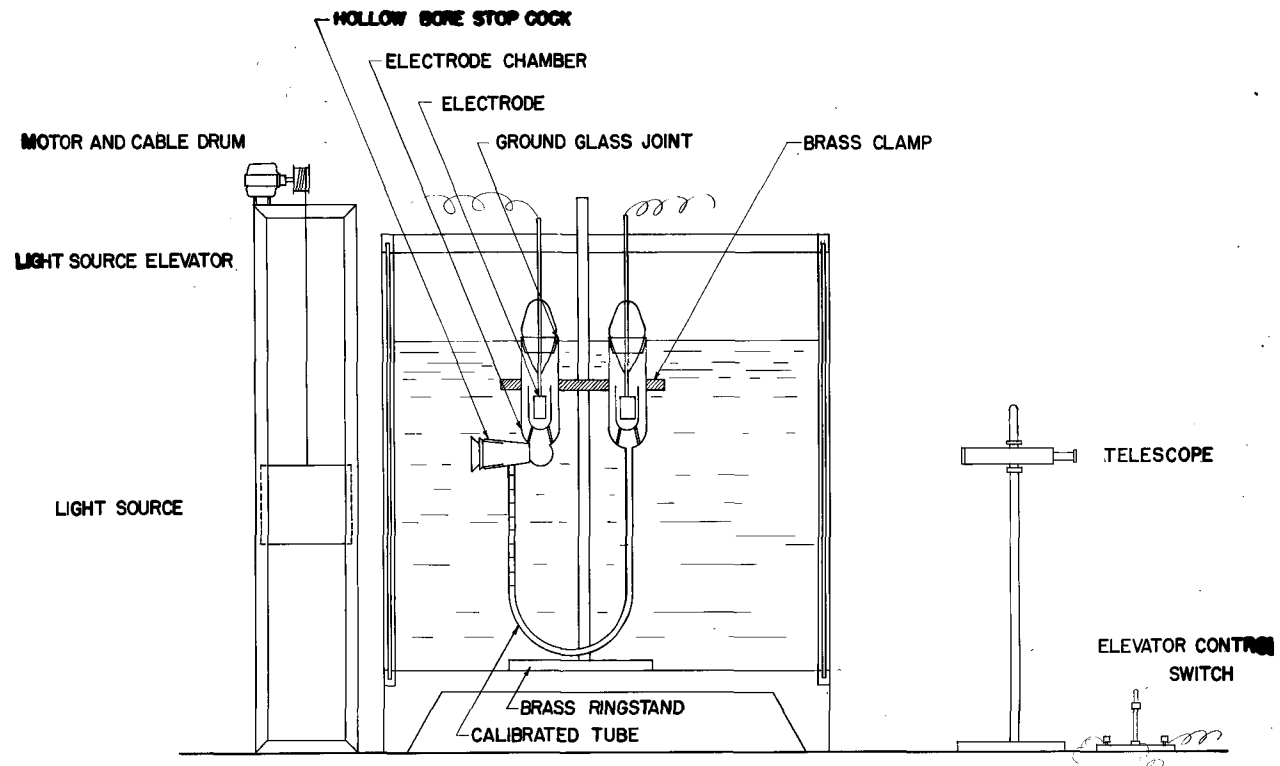
Figure 8 - Apparatus assembly for determination of transference numbers.

pane of frosted glass on one side of the box. The height
of the box could be adjusted by means of the reversible
motor, the controls of which were situated within easy
reach of the operator. The telescope was focused on the
center of the measuring tube. The vertical position
of the telescope, as well as that of the light source,
could be varied to follow the boundary.

The water bath was a large aquarium-type glass-
sided bath, which maintained the temperature at
25.00 ± 0.05°C.

The current through the cell was measured by deter-
mining the potential drop across a standard resistor
placed in series with the cell. A Rubicon Type B High
Precision potentiometer, in series with an automatic
Brown recording potentiometer, was placed across this
resistor. All but five to ten millivolts of the potential
drop were balanced by the Rubicon potentiometer; the
remaining voltage was continuously recorded on the chart
of the Brown potentiometer.

The constant-current apparatus was designed by A. A.
Read and his colleagues at the Electronics Shop of the
Ames Laboratory of the Atomic Energy Commission. A cir-
cuit diagram of the controller is shown in Figure 9. Dur-
ing a determination, the total resistance in the cell in-
creased as the indicator solution replaced the leading
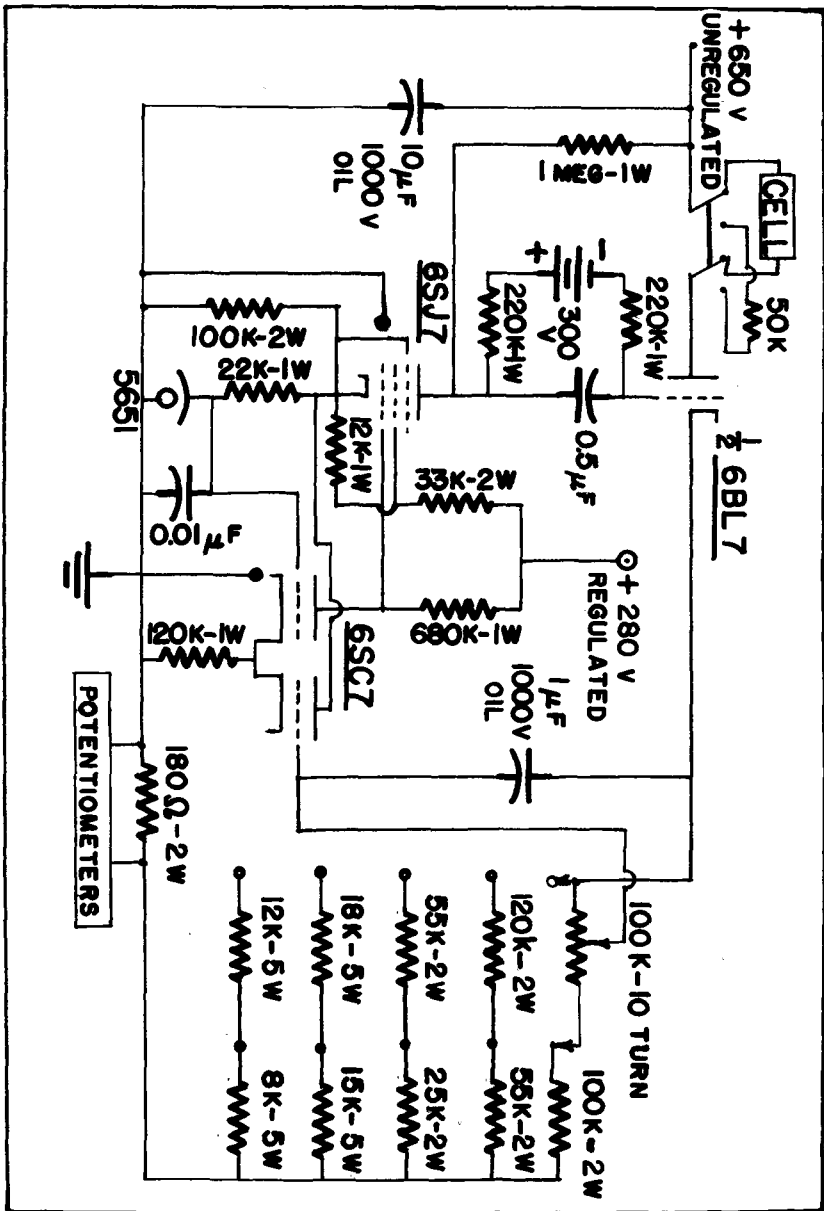
Figure 9 - Circuit diagram of the current controller.

solution; this tended to decrease the current, which produced a negative signal at the input to the direct-current amplifier. The amplifier then provided a positive output signal which was coupled through a dropping battery to the grid of the 6BL7 series tube. By cathode follower action this reduced the magnitude of the negative signal at the input of the direct-current amplifier, tending to nullify the change in current. Without infinite gain, however, the original negative signal could not be completely cancelled, although the amplifier gain in the present system was sufficient to reduce the current variation for the type of cells used to approximately 0.04 per cent for extreme conditions of use. The continuous record of the current provided by the Brown potentiometer reduced the error of a knowledge of the total current to less than 0.02 per cent.

B. Procedure

Before determining a transference number, the transference cell was cleaned with a detergent, or with acid cleaning solution, and thoroughly rinsed with distilled water. The hollow-bore plug and stopcock were carefully dried and gently heated. While still warm, the plug was coated with a silicone stopcock lubricant and inserted. With the plug turned to the open position, the cathode

compartment and measuring tube were rinsed at least three times with the leading solution. The compartment was filled to the level of the stopcock, the stopcock closed, and the rest of the compartment filled. The electrode cup and the silver, silver halide electrode were rinsed several times with the leading solution and placed in the compartment. After the electrode was in place (with a small amount of silicone grease placed around the upper half of the standard taper to help seal the system), the stopcock on the overflow tube was closed. The anode compartment was then rinsed several times with water, and at least three times with the correct concentration of the lithium halide following solution. Care was taken not to trap any air in the stopcock while the compartment was being filled. The electrode cup and cadmium anode were thoroughly rinsed and placed in position. The overflow tube was closed and the outside of the cell was washed several times with distilled water to remove any electrolyte which might cause a short to develop between the electrodes and the water bath.

The filled cell was placed in the water bath maintained at $25.00 \pm 0.05^{\circ}C$; the cell was so placed that the measuring tube was in line with the light source and the telescope. The cell was checked for electrical leaks with a vacuum tube test meter. After first balancing the

Rubicon potentiometer against a standard cell, the leads
from the constant current apparatus were connected to the
proper electrodes, the stopcock was opened to form the
boundary, and the current was turned on. The current
was adjusted to such a value that the time required for
the boundary to pass from one mark to the next was between
200 and 300 seconds. No extra time was allotted for the
cell to reach thermal equilibrium with the bath, since a
minimum of 40 minutes was required from the time the cell
was placed in the bath until the time the boundary passed
the first mark on the measuring tube.

The transference number of the rare earth solution
to be determined was first estimated from transference
numbers previously determined. Then, by use of the
Kohlrausch ratio (equation (18)), an indicator solution
of the proper concentration was prepared. If the observed
transference number differed from the estimated value by
more than three per cent, a new indicator solution was
prepared, based upon the observed transference number,
and the transference number was redetermined. This pro-
cess was repeated until the proper correlation between
the estimated and the observed transference numbers was
obtained.

The transference numbers of lithium chloride have
been determined previously by Longsworth (89), and his

data were used for the computation of the indicator solution concentration of that salt. However, no direct determination of the transference numbers of lithium bromide has been reported. Therefore these transference numbers were calculated from the data of Longsworth on the transference numbers of potassium bromide (132) and lithium chloride (89), and from the conductance data of these same salts by several investigators (11,42,121,125). These data, extrapolated to the listed concentrations, and the calculated cation transference numbers of lithium bromide are given in Table IX. In view of the close correlation of the properties of alkali halides to theory, it is believed that these calculated transference numbers are in error by not more than five per cent, which is within the regulating range of the Kohlrausch ratio. As a check upon these values, the cation transference numbers of potassium bromide were determined at different concentrations. The values obtained agreed within experimental error with those previously obtained by Longsworth (132), who used the autogenic boundary method.

To correct for the volume changes during the determination, the values of the partial molal volumes of the rare earth salts are required. These data were computed from density measurements made with a calibrated 50 ml. pycnometer.

Table IX

Data Used for the Calculation of the Transference Numbers of Lithium Bromide

Salt	Property	Concentration (equivalents per liter)			
		0.01	0.02	0.05	0.10
KBr	$\underline{T_+}$	0.4833	0.4832	0.4831	0.4833
	$\underline{T_-}$	0.5167	0.5168	0.5169	0.5167
	$\underline{\Lambda}$	143.43	140.48	135.68	131.39
	$\underline{\lambda_-}$	74.11	72.60	70.12	67.89
LiCl	$\underline{T_+}$	0.3289	0.3261	0.3211	0.3168
	$\underline{\Lambda}$	107.32	104.65	100.11	95.86
	$\underline{\lambda_+}$	35.30	34.13	32.15	30.37
LiBr	$\underline{\Lambda}$	109.41	106.73	102.27	98.26
	$\underline{T_+}$	0.3226	0.3198	0.3144	0.3091

C. Data and Calculations

The cation transference numbers of lanthanum, praseo-
dymium, neodymium, gadolinium, and erbium bromides, and
of gadolinium chloride were determined in the approximate
concentration range of 0.01 to 0.10 normal. The indis-
tinctness of the boundary in dilute solutions prevented
the obtaining of data on concentrations much below 0.01
normal. The data obtained are presented in Tables X
through XV, and in Figures 10 and 11. The ordinates in
these figures are staggered in order to separate the
various curves.

The volume corrections were made according to the
method of Lewis (88). The molar volume of cadmium was
taken to be 13.0 ml. (133), and the partial molal volumes
of cadmium bromide (132) and of cadmium chloride (132)
were taken as:

$$\overline{V}_{CdBr_2} = 33.3 + 18.9 \ m^{\frac{1}{2}} , \tag{53}$$

and

$$\overline{V}_{CdCl_2} = 23.24 + 8.82 \ m^{\frac{1}{2}} . \tag{54}$$

The densities of all of the rare earth halide solu-
tions investigated were found to be linear functions of
the concentration, within the range studied, and were
fitted to equations of the type:

Table X

Cation Transference Numbers for Lanthanum Bromide at 25°C

Normality	T_+ Observed	T_+ Average	Volume Correction	Solvent Correction	T_+ Corrected
0.1041	0.4331	0.4327	-0.0007	0.0000	.4320
	0.4326				
	0.4323				
0.07434	0.4375	0.4374	-0.0005	0.0001	.4370
	0.4372				
0.05947	0.4407	0.4408	-0.0004	0.0001	.4405
	0.4408				
0.02974	0.4481	0.4481	-0.0002	0.0001	.4480
0.01487	0.4535	0.4536	-0.0001	0.0002	.4537
	0.4536				
0.01041	0.4561	0.4561	-0.0001	0.0003	.4563

Table XI

Cation Transference Numbers of Praseodymium Bromide at 25°C

Normality	T_+ Observed	T_+ Average	Volume Correction	Solvent Correction	T_+ Corrected
0.1057	0.4319	0.4319	-0.0009	0.0000	0.4310
0.09059	0.4336	0.4337	-0.0008	0.0000	0.4329
	0.4338				
0.06039	0.4407	0.4407	-0.0005	0.0001	0.4403
0.03020	0.4488	0.4489	-0.0002	0.0001	0.4488
	0.4490				
0.01510	0.4550	0.4550	-0.0001	0.0003	0.4552
0.009059	0.4589	0.4586	-0.0001	0.0003	0.4588
	0.4584				

Table XII

Cation Transference Numbers of Neodymium Bromide at 25°C

Normality	T_+ Observed	T_+ Average	Volume Correction	Solvent Correction	T_+ Corrected
0.09499	0.4344 0.4352	0.4348	-0.0009	0.0000	0.4339
0.07124	0.4393	0.4393	-0.0006	0.0001	0.4388
0.04750	0.4450 0.4449	0.4450	-0.0004	0.0001	0.4447
0.02395	0.4512	0.4512	-0.0002	0.0001	0.4511
0.009499	0.4606 0.4602	0.4604	-0.0001	0.0003	0.4606

Table XIII

Cation Transference Numbers of Gadolinium Bromide at 25°C

Normality	T_+ Observed	T_+ Average	Volume Correction	Solvent Correction	T_+ Corrected
0.1018	0.4273 0.4383	0.4278	-0.0009	0.0000	0.4269
0.07633	0.4336 0.4330	0.4333	-0.0006	0.0000	0.4327
0.05089	0.4391	0.4391	-0.0004	0.0000	0.4387
0.02544	0.4488 0.4480 0.4486	0.4485	-0.0002	0.0001	0.4484
0.01272	0.4542	0.4542	-0.0001	0.0002	0.4543
0.01018	0.4547 0.4555	0.4551	-0.0001	0.0002	0.4552

Table XIV

Cation Transference Numbers of Erbium
Bromide at 25°C

Normality	T_+ Observed	T_+ Average	Volume Correction	Solvent Correction	T_+ Corrected
0.1104	0.4114	0.4113	-0.0010	0.0000	0.4103
	0.4112				
0.08278	0.4163	0.4163	-0.0007	0.0000	0.4156
0.05519	0.4238	0.4238	-0.0005	0.0001	0.4234
	0.4238				
0.02759	0.4328	0.4328	-0.0002	0.0001	0.4327
0.01380	0.4398	0.4398	-0.0001	0.0003	0.4400
0.01104	0.4405	0.4405	-0.0001	0.0003	0.4407

Table XV

Cation Transference Numbers of Gadolinium Chloride at 25°C

Normality	T_+ Observed	T_+ Average	Volume Correction	Solvent Correction	T_+ Corrected
0.1051	0.4321	0.4319	-0.0004	0.0000	0.4315
	0.4317				
0.08174	0.4369	0.4369	-0.0003	0.0000	0.4366
0.05839	0.4412	0.4416	-0.0002	0.0001	0.4415
	0.4420				
0.03503	0.4488	0.4488	-0.0001	0.0001	0.4488
0.02335	0.4532	0.4532	-0.0001	0.0001	0.4532
0.01168	0.4599	0.4599	0.0000	0.0003	0.4602
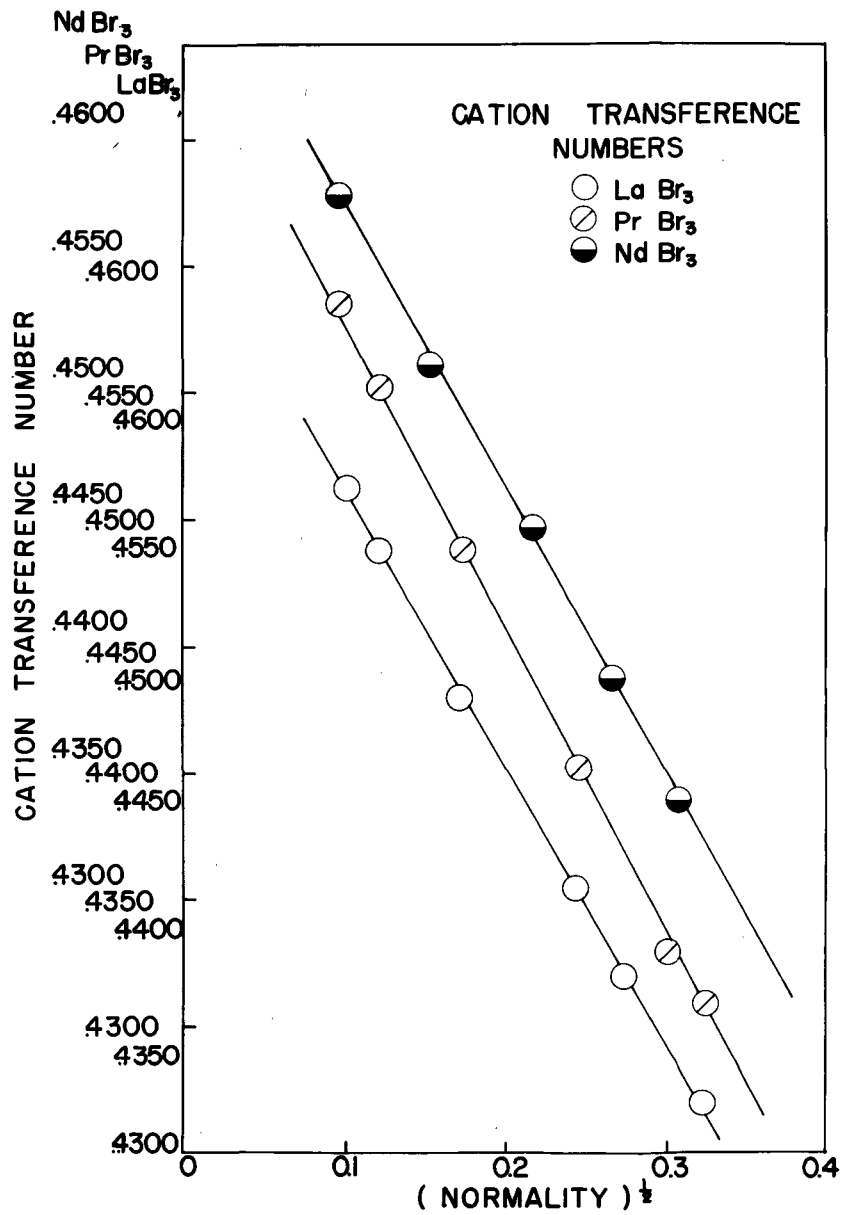
Figure 10 - Cation transference numbers of lanthanum, praseodymium and neodymium bromides at 25°C.
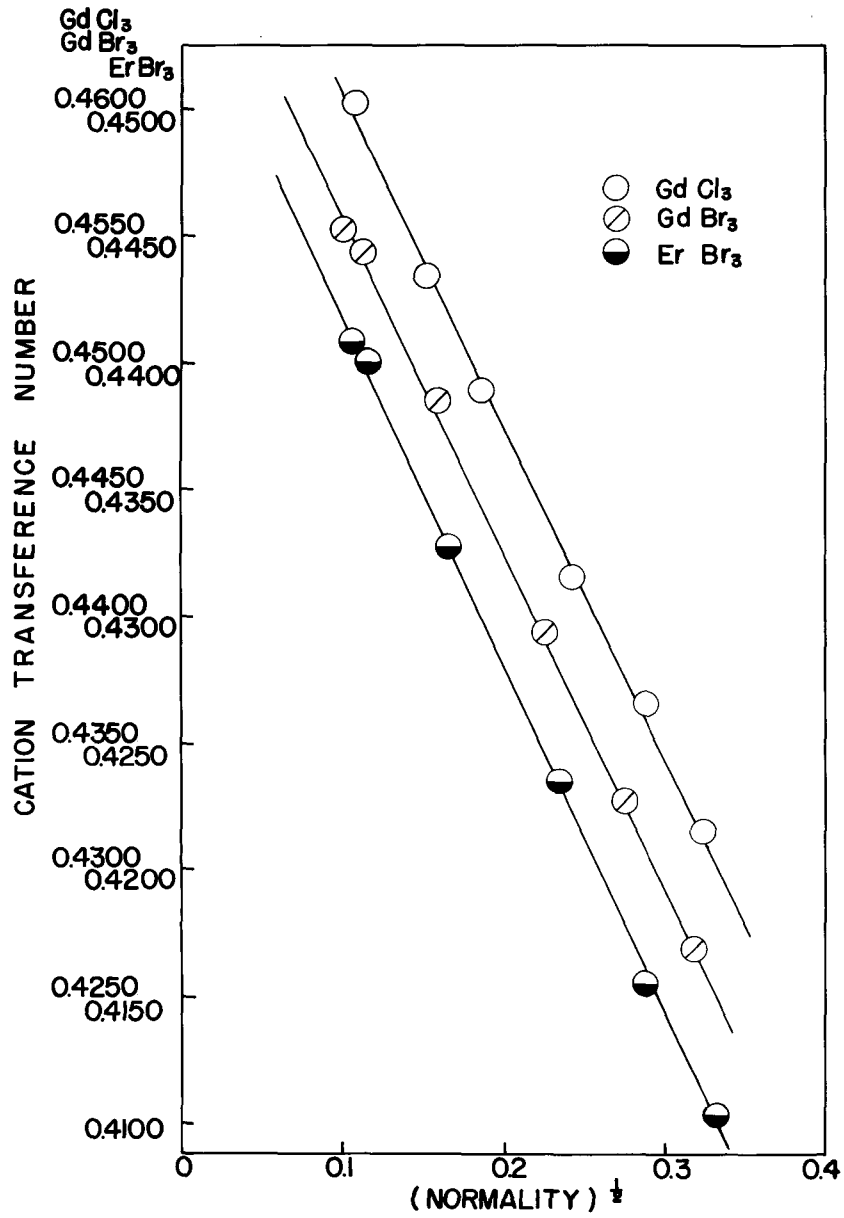
Figure 11 - Cation transference numbers of gado-
linium and erbium bromides and of
gadolinium chloride at $25^{\circ}C$.

$$\rho = 0.99707 + AC \, , \tag{55}$$

where A is an experimentally determined constant. These equations are shown in Table XVI, along with the partial molal volumes of the salts, calculated from the expression:

$$V = \frac{M - 1000(d\rho/dm)}{\rho - m(d\rho/\, dm)} \, , \tag{56}$$

in which $\underline{M}$ is the molecular weight of the salt. For the volume correction, the molarity was substituted for the molality, since the small difference between these two quantities did not affect the correction.

The solvent correction was calculated using the values of the conductances of the various solutions which are reported in Tables II through VII.

A typical set of data is shown in Table XVII. In order to minimize the errors in timing, a minimum of eight individual readings were summed, as is illustrated before an individual transference number was calculated. The values reported in Tables X through XV are the result of averaging at least 20 such calculations.

Since it appeared that there was a linear relationship between the transference numbers and the square root of the concentration, the data were subjected to a least squares analysis (134). The straight lines in Figures 10 and 11 are these least squares lines. The

Table XVI

Densities and Partial Molal Volumes of Some Rare Earth Halides at 25°C

Salt	Density Equation[*]	Partial Molal Volume
$LaBr_3$	$\rho = 0.99707 + 0.3471\ C$	31.60
$PrBr_3$	$\rho = 0.99707 + 0.3525\ C$	28.25
$NdBr_3$	$\rho = 0.99707 + 0.3572\ C$	26.95
$GdBr_3$	$\rho = 0.99707 + 0.3723\ C$	24.42
$ErBr_3$	$\rho = 0.99707 + 0.3845\ C$	22.52
$GdCl_3$	$\rho = 0.99707 + 0.2494\ C$	13.90

[*]C = molarity

Table XVII

Typical Transference Number Determination

Praseodymium Bromide - 0.090585 N.
Lithium Bromide - 0.06524 N.
Standard Resistance - 178.75 ohms

Data Obtained

Marks	Time sec.	Voltage volts
0	---	1.3396
0-1	273.7	1.3396
1-2	274.5	1.3396
2-3	276.9	1.3394
3-4	268.2	1.3395
4-5	277.6	1.3397
5-6	264.4	1.3396
6-7	272.4	1.3395
7-8	265.8	1.3393
8-9	269.8	1.3395
9-10	267.0	1.3395
10-11	275.6	1.3395
11-12	270.9	1.3395
12-13	278.0	1.3393
Av. Voltage		1.3395

Data Calculated

Marks	Volume cc.	Time sec.	T_+(obs.)
0-8	0.8077	2173.1	0.4336
0-9	0.9081	2442.9	0.4336
0-10	1.0071	2709.9	0.4335
0-11	1.1095	2985.5	0.4335
0-12	1.2114	3256.4	0.4339
0-13	1.3136	3534.4	0.4335
1-9	0.8066	2169.6	0.4337
1-10	0.9055	2436.6	0.4335
1-11	1.0079	2712.2	0.4335
1-12	1.1099	2983.1	0.4340
1-13	1.2120	3261.1	0.4335
2-10	0.8045	2162.1	0.4340
2-11	0.9069	2437.7	0.4340
2-12	1.0088	2708.6	0.4345
2-13	1.1110	2986.6	0.4339
3-11	0.8031	2160.8	0.4336
3-12	0.9050	2431.7	0.4341
3-13	1.0072	2709.7	0.4336
4-12	0.8054	2163.5	0.4343
4-13	0.9076	2441.5	0.4336
5-13	0.8050	2163.9	0.4340

Average: 0.4338

Average Deviation: 0.0003
Maximum Deviation: 0.0007

equations so obtained are listed in Table XVIII, along
with similar expressions for the rare earth chloride trans-
ference numbers previously reported by Spedding, Porter
and Wright (5). It should be pointed out that the in-
tercepts of these equations are not necessarily the true
limiting transference numbers, since these equations are
valid only in the concentration range investigated. The
limiting transference numbers, determined from the con-
ductance data in Table VIII, are also listed in the table.

D. Discussion and Conclusions

The transference numbers of lanthanum, praseodymium,
and neodymium bromides were found to be extremely close
together; this similarity was to be expected in view of
the similar nature of their equivalent conductances. This
same resemblance was observed in the case of the chlorides
of these same elements (5).

The data in Table XVIII show that the slopes of the
transference number versus concentration curves are fairly
constant for the first three rare earths listed. The
slopes for the last two rare earth bromides are slightly
higher. A similar trend is predicted from the theoretical
limiting law (equation (9)), although the theoretical and
experimental slopes are quite different in magnitude.
This difference between theory and experiment for rare

Table XVIII

Summary of Data on Transference Numbers

Salt[*]	Least-squares Line	$T_+^{\,o}$	$S(T_o)$[**]
$LaBr_3$	$T_+ = 0.4672 - 0.110\ N^{\frac{1}{2}}$	0.4707	-0.558
$PrBr_3$	$T_+ = 0.4697 - 0.120\ N^{\frac{1}{2}}$	0.4707	-0.558
$NdBr_3$	$T_+ = 0.4689 - 0.113\ N^{\frac{1}{2}}$	0.4707	-0.558
$GdBr_3$	$T_+ = 0.4689 - 0.132\ N^{\frac{1}{2}}$	0.4632	-0.581
$ErBr_3$	$T_+ = 0.4555 - 0.137\ N^{\frac{1}{2}}$	0.4573	-0.599
$LaCl_3$	$T_+ = 0.4730 - 0.108\ N^{\frac{1}{2}}$	0.4775	-0.550
$PrCl_3$	$T_+ = 0.4753 - 0.114\ N^{\frac{1}{2}}$	0.4772	-0.551
$NdCl_3$	$T_+ = 0.4744 - 0.112\ N^{\frac{1}{2}}$	0.4792	-0.545
$GdCl_3$	$T_+ = 0.4737 - 0.131\ N^{\frac{1}{2}}$	0.4687	-0.577
$ErCl_3$	$T_+ = 0.4600 - 0.118\ N^{\frac{1}{2}}$	0.4638	-0.591

[*] With the exception of $GdCl_3$, all of the chlorides listed are from the data of Spedding, Porter and Wright (5).

[**] $S(T_o)$ = theoretical slope as calculated from equation (9).

earth halide transference numbers was first reported by
Longsworth and MacInnes (3) and was confirmed by Spedding,
Porter and Wright (5). The data from this present work
further confirms this discrepancy.

There is also close agreement between the slopes of
the transference number curves between the bromide and
chloride of each cation, with the bromide slope being
slightly higher. Erbium appears to be an exception.
This similarity of slopes indicates that, except for
the higher mobility of the bromide ion over that of the
chloride ion, the influence of these anions upon the
rare earth cation is relatively the same.

Since transference numbers for only five or six
different concentrations of each salt were determined, a
statistical analysis of this limited number of data is
not strictly valid. However it is noticeable that the
intercepts of the least squares lines are quite close
to the limiting transference numbers as calculated
from conductance data.

The limits of error of these transference number
measurements are estimated to be within 0.1 per cent.
The volume of the measuring tube and the absolute value
of the current were known to within 0.05 per cent, while
the limits of error in the analyses of the solutions are

within 0.1 per cent. Duplicate determinations of a given transference number varied on an average of 0.06 per cent.

VI. ACTIVITY COEFFICIENTS

A. Apparatus

For the determination of the electromotive force of concentration cells with transference, the following equipment was used: a potentiometer, a galvanometer, standard cells, a constant temperature bath, suitable concentration cells, and silver, silver halide electrodes.

A Rubicon Type B High Precision potentiometer was employed for measuring the potentials developed in the cells. It was checked at intervals during the measurements against Epply-type standard cell which had been calibrated by the National Bureau of Standards. A Leeds and Northrup Type E galvanometer (catalog number 2430-d) with a sensitivity of 0.00042 microamperes per millimeter of scale deflection was used as the null-point indicator. The constant temperature bath was identical with that used for conductance measurements (see Section IV, Part A), except that water was used as the bath liquid. The bath was maintained at a temperature of 25.00 ± 0.02°C.

The cells and electrodes were of the same design as those used by Spedding, Porter and Wright (6). Each cell had two compartments, both of which were fitted with two standard taper glass joints to hold the electrodes. The compartments were joined by means of a hollow-bore

stopcock, with a trap between one compartment and the
stopcock to prevent rapid diffusion between the two solu-
tions. When used with bromide solutions, the exteriors
of the cells were painted black. A picture of the
assembled cell and of its component parts is shown in
Figure 12.

B. Procedure

Silver, silver bromide electrodes were used with
the rare earth bromide solutions; silver, silver chloride
electrodes were employed with the chloride solutions.

The silver, silver chloride electrodes were prepared
by the thermal-electrolytic method as described by Smith
and Taylor (135). The platinum wire spirals, sealed into
the ends of pyrex tubes containing 12/30 male standard
taper joints, were cleaned by alternately heating to a
red heat in a flame and plunging into a boiling nitric
acid solution. After cleaning, the spirals were rinsed
in conductivity water and coated with a paste of puri-
fied silver oxide. These coated electrodes were heated
to 400°C for about four hours to decompose the oxide to
metallic silver. The coating with oxide and heating were
repeated until the platinum was completely covered. These
silver electrodes were electrolyzed in a one normal solu-
tion of redistilled hydrochloric acid, with a platinum
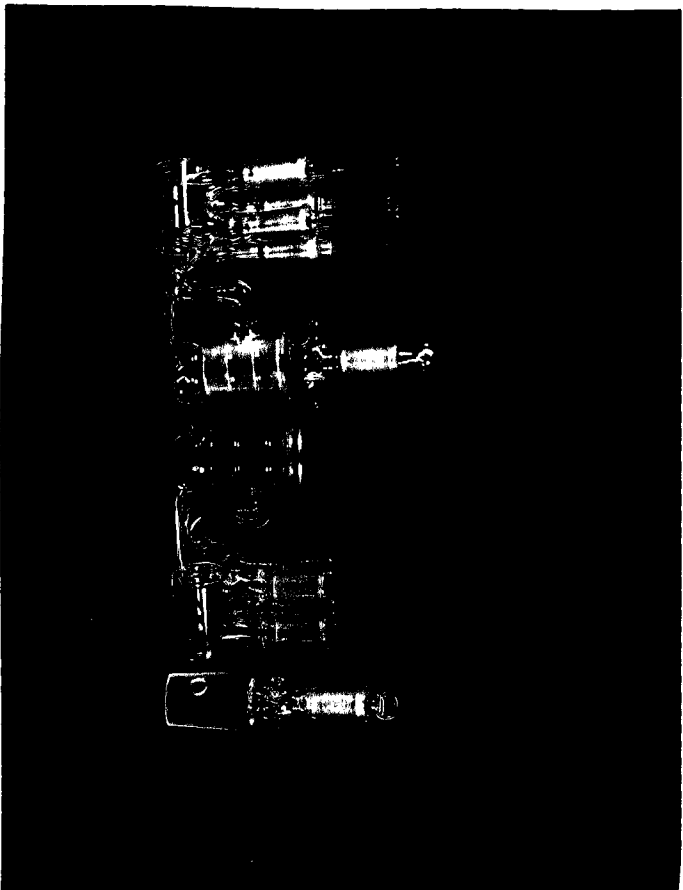
Figure 12 - Concentration cell with transference.

electrode as the cathode, for 45 minutes with a current
of eight milliamperes per anode.

After electrolysis, the electrodes were rinsed
several times with conductivity water to remove all traces
of the acid. They were then connected in parallel to
each other with copper wire, and soaked in a 0.1 normal
solution of potassium chloride for at least 24 hours in
order to remove strains in the silver and to come to a
common potential.

Silver, silver bromide electrodes were prepared by
the above method and also by the thermal method described
by Keston (118). The thermal method consisted of coating
the platinum spirals with a paste consisting of 90 per
cent silver oxide and 10 per cent silver bromate, and
heating the electrodes to $600^{\circ}C$ for eight minutes, to
reduce the mixture to silver and silver bromide. The
coating and heating were repeated several times to com-
pletely cover the platinum. Finally the electrodes,
connected to each other by copper wire, were soaked in
a 0.1 normal solution of potassium bromide for at least
five days before they reached a constant potential. The
silver, silver bromide electrodes were protected from
light while they were soaking. Since no differences
were detected in the behavior of the bromide electrodes

as prepared by the two methods, both types were used interchangeably.

Before being used in the rare earth halide solutions, the electrodes were soaked for one hour in conductivity water, followed by two one-hour soakings in the proper rare earth halide solution before being placed in the cell.

With the stopcock in the open position, the cell compartment connected to the center opening of the stopcock was rinsed and filled with the more dilute solution. The stopcock was closed and the second compartment was rinsed and filled with the more concentrated solution. After the electrodes were placed in their proper compartments, the cell was placed in the water bath. A period of one hour was allotted for the cell to attain thermal equilibrium with the bath. After this equilibration period the stopcock was opened and the potentials were measured. The potentials were found to be constant within experimental error for several hours after the stopcock was opened. No grease was used on the stopcock plug; the ground-glass joint was sufficiently tight so that diffusion was not observed to have occurred during the thermal equilibration period.

In order to eliminate the effects of the slight differences in potential among the electrodes, the electrodes

in the two compartments were switched. That is, the elec-
trodes in the more concentrated solution were placed in
the more dilute solution, and vice versa. This reversal
also included the soaking routine described above in order
to be sure that the electrodes were in complete equilibrium
with the desired concentration of rare earth halide. Fresh
solutions were used for the soakings and for both sets of
measurements.

The average of the two potential readings for each
pair of electrodes before and after switching was computed.
Since there were two electrodes in each compartment, four
such averages were obtained for each cell; these were
averaged to obtain the potential of the cell. All dilu-
tions of a rare earth halide solution were measured against
the same dilution, termed the reference concentration.

C. Data and Calculations

The potentials of cells with transference were measured
for solutions of lanthanum, praseodymium, neodymium, gado-
linium and erbium bromides, and for gadolinium chloride.
A typical set of data is shown in Table XIX.

For the special case of the rare earth halides, equa-
tion (46) takes the form:

$$dE = - \frac{4RT}{3F} \; T_+ \; d \, (\ln a_\pm) \; , \qquad (57)$$

Table XIX

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

Salt: Neodymium Bromide
Concentration: 0.002375 molar
Reference Concentration: 0.02375 molar

Electrodes	E.M.F. millivolts	Average E.M.F. millivolts
1 vs. 2	29.100	29.107
2 vs. 1	29.114	
1 vs. 3	29.125	29.103
3 vs. 1	29.080	
4 vs. 2	29.091	29.105
2 vs. 4	29.119	
4 vs. 3	29.110	29.105
3 vs. 4	29.100	

	Average:	29.105 mv.
	Average Deviation:	0.002 mv.
	Maximum Deviation:	0.002 mv.

in which $a_{\pm}$ is the mean activity of the rare earth halide.
From equations (36), (37) and (38), it follows that:

$$-F\ dE = \frac{4}{3}\ RTT_{+}(d\ \ln\ y_{\pm}) + \frac{4}{3}\ RTT_{+}(d\ \ln\ 27^{\frac{1}{2}}C)\ ,\qquad (58)$$

in which C is the concentration of the halide in equivalents
per liter. Since T_{+} varies with concentration, equation
(58) cannot be directly integrated. However, a function,
δ, can be defined as:

$$\delta = (1/T_{+}) - (1/T_{+_r}),\qquad (59)$$

in which T_{+_r} is the specific cation transference number of
the constant reference solution. Then, since $d\ \ln\ 27^{\frac{1}{2}}$
equals zero, equation (58) can be rearranged to yield:

$$d\ \ln\ y_{\pm} = -\ d\ \ln\ C - \frac{3F\ dE}{4RTT_{+_r}} - \frac{3F\ \delta\ dE}{4RT}\ .\qquad (60)$$

All but the last term can be integrated directly, and this
last term can be evaluated by graphical integration. After
converting to Briggsian logarithms, the equation becomes:

$$\log \frac{y_{\pm}}{y_{\pm_r}} = \log \frac{Cr}{C} - \frac{3FE}{2.303\ RTT_{+_r}} - \frac{3F}{9.212RT} \int_0^E \delta\ dE,\qquad (61)$$

in which the subscript r refers to the indicated quantities
of the reference solution. Thus, a ratio of activity coef-
ficients can be obtained directly from the experimental data.

These data are shown in Tables XX through XXV. For the graphical integration of $\int_0^E \delta \, dE$, graphs on the scale of 2500 mm. per unit of δ, and 10 mm. per millivolt were used. The listed transference numbers were computed from the equations in Table XVIII.

To obtain activity coefficients from this experimentally determined ratio, recourse was made to the Debye-Hückel equation (equation (40)) according to the method of Brown and MacInnes (103). For 3-1 electrolytes, this equation takes the form:

$$\log y_{\pm} = -A' \sqrt{C}/(1 + 2 B' \sqrt{C}), \tag{62}$$

in which $\underline{A'} = 3\sqrt{6} \, A/2.303$, and $\underline{B'} = \sqrt{6} \, B$. $\underline{A}$ and $\underline{B}$ have been previously defined by equations (41) and (42). By subtracting $\underline{\log y_{\pm_r}}$ from both sides of equation (62), the following is obtained:

$$\log(y_{\pm}/y_{\pm_r}) = -A' \sqrt{C}/(1 + 2B' \sqrt{C}) - \log y_{\pm_r} . \tag{63}$$

This equation can be rearranged to yield:

$$\log(y_{\pm}/y_{\pm_r}) + A' \sqrt{C} = - \log y_{\pm_r} - 2B'[\log(y_{\pm}/y_{\pm_r})$$
$$+ \log y_{\pm_r}] \sqrt{C} . \tag{64}$$

Since $\underline{A'}$ and $\underline{B'}$ are constants for a given solvent, solute and temperature, a graph of the left-hand side of this equation against $\underline{[\log(y_{\pm}/y_{\pm_r}) + \log y_{\pm_r}] \sqrt{C}}$ should be a

Table XX

E.M.F. Data of Lanthanum Bromide at 25°C

Molarity	E.M.F. millivolts (observed)	E.M.F. millivolts (average)	$\underline{T_+}$	$\text{Log}(y_\pm/y_{\pm r})$
0.03468	-3.8948 -3.8980 -3.8985 -3.9005	-3.8981	0.4318	-0.03228
0.02478*	0.0000	0.0000	0.4371	0.00000
0.01982	2.6450 2.6563 2.6448 2.6449	2.6452	0.4404	0.02041
0.009912	11.0379 11.0375 11.0404 11.0398	11.0389	0.4485	0.08188
0.004956	19.851 19.857 19.850 19.858	19.854	0.4541	0.13522
0.003469	24.561 24.584 24.568 24.589	24.576	0.4563	0.15862
0.002478	29.041 29.030 29.044 29.037	29.038	0.4582	0.18089
0.001982	32.052 32.052 32.053 32.052	32.052	0.4593	0.19453
0.0009912	41.871 41.875 41.871 41.875	41.873	0.4621	0.22526

*reference concentration

Table XXI

E.M.F. Data of Praseodymium Bromide at 25°C

Molarity	E.M.F. millivolts (observed)	E.M.F. millivolts (average)	T_+	$Log(y_\pm/y_{\pm r})$
0.03523	-1.7260 -1.7260 -1.7260 -1.7260	-1.7260	0.4307	-0.01630
0.03020*	0.0000	0.0000	0.4336	0.0000
0.02013	4.7698 4.7697 4.7698 4.7699	4.7698	0.4402	0.03768
0.01007	13.0286 13.0287 13.0286 13.0285	13.0286	0.4488	0.10318
0.005033	21.836 21.838 21.837 21.837	21.837	0.4549	0.15260
0.003523	26.610 26.611 26.615 26.616	26.613	0.4574	0.17472
0.002013	33.939 33.938 33.938 33.937	33.938	0.4604	0.21536
0.001007	43.754 43.755 43.753 43.754	43.754	0.4631	0.24682

*reference concentration

Table XXII

E.M.F. Data of Neodymium Bromide at 25°C

Molarity	E.M.F. millivolts (observed)	E.M.F. millivolts (average)	T_+	$\text{Log}(y_\pm/y_{\pm_r})$
0.03166	-3.3867 -3.3915 -3.3972 -3.3985	-3.3935	0.4338	-0.02626
0.02375*	0.0000	0.0000	0.4388	0.0000
0.01583	4.8469 4.8496 4.8477 4.8487	4.8482	0.4448	0.03693
0.007916	13.4225 13.4258 13.4198 13.4211	13.4223	0.4521	0.09558
0.003166	25.267 25.250 25.252 25.245	25.254	0.4595	0.16463
0.002375	29.107 29.103 29.105 29.105	29.105	0.4612	0.18344
0.001583	34.743 34.741 34.746 34.748	34.744	0.4633	0.20482
0.0007916	44.572 44.581 44.560 44.561	44.569	0.4647	0.23740

*reference concentration

Table XXIII

E.M.F. Data of Gadolinium Bromide at 25°C

Molarity	E.M.F. millivolts (observed)	E.M.F. millivolts (average)	T_+	$Log(y_\pm/y_{\pm r})$
0.03393	-3.2472 -3.2469 -3.2470 -3.2470	-3.2470	0.4269	-0.02907
0.02544*	0.0000	0.0000	0.4325	0.0000
0.01696	4.6552 4.6554 4.6552 4.6552	4.6552	0.4392	0.04070
0.008482	13.1131 13.1130 13.1131 13.1131	13.1131	0.4479	0.09991
0.004241	21.819 21.818 21.818 21.817	21.818	0.4541	0.15616
0.003393	24.636 24.636 24.635 24.636	24.636	0.4556	0.17424
0.002544	28.535 28.535 28.535 28.535	28.535	0.4574	0.19111
0.001696	34.072 34.074 34.074 34.073	34.073	0.4594	0.21400
0.0008481	43.752 43.753 43.753 43.752	43.752	0.4623	0.24856

*reference concentration

Table XXIV

E.M.F. Data of Erbium Bromide at 25°C

Molarity	E.M.F. millivolts (observed)	E.M.F. millivolts (average)	T_+	$Log(y_\pm/y_{\pm_r})$
0.03679	-3.1015 -3.1023 -3.1058 -3.1015	-3.1028	0.4100	-0.02967
0.02759*	0.0000	0.0000	0.4163	0.00000
0.01840	4.6204 4.6207 4.6201 4.6210	4.6205	0.4233	0.03648
0.009198	12.6457 12.6458 12.6457 12.6457	12.6457	0.4328	0.09584
0.004599	21.174 21.173 21.172 21.173	21.173	0.4394	0.15279
0.002759	27.538 27.537 27.538 27.539	27.538	0.4431	0.19179
0.001840	32.970 32.969 32.970 32.970	32.970	0.4453	0.21279
0.0009198	42.356 42.357 42.355 42.357	42.356	0.4483	0.24690

*reference concentration

Table XXV

E.M.F. Data of Gadolinium Chloride at 25°C

Molarity	E.M.F. millivolts (observed)	E.M.F. millivolts (average)	T_+	$Log(y_\pm/y_{\pm r})$
0.03503	-6.7271 -6.7270 -6.7271 -6.7271	-6.7271	0.4312	-0.05962
0.02725	-3.8902 -3.8901 -3.8901 -3.8901	-3.8901	0.4362	-0.03362
0.01946*	0.0000	0.0000	0.4420	0.0000
0.01168	6.1072 6.1070 6.1068 6.1070	6.1070	0.4492	0.04788
0.007785	11.0585 11.0586 11.0586 11.0587	11.0586	0.4537	0.08453
0.003892	19.924 19.918 19.919 19.914	19.919	0.4595	0.13754
0.002725	24.626 24.625 24.624 24.625	24.645	0.4618	0.16259
0.001168	36.573 36.573 36.573 36.573	36.573	0.4659	0.20793

*reference concentration

straight line with an intercept of $(-\log y_{\pm_r})$ and a slope of $(- \overset{o}{a}B')$. In practice, this calculation was carried out analytically by a method of successive approximations and of least squares (134). The data so obtained are listed in Tables XXVI through XXXI, and are plotted in Figures 13 and 14.

The molal quantities listed in these tables were computed from the molar quantities by use of equations (33) and (34). The densities were computed from the equations in Table XVI.

The values of $\overset{o}{a}$ are listed in Table XXXII. Using these values of $\overset{o}{a}$, the mean molal activity coefficients, as predicted by the Debye-Hückel limiting law (equation 62)), were calculated. For comparison purposes, these values are listed in Tables XXVI through XXXI next to the experimentally-determined values.

D. Discussion and Conclusions

Within the concentration range studied, from 0.001 molar to 0.035 molar, the activity coefficients of the various rare earth halide solutions investigated obey the Debye-Hückel limiting law. This agreement is in accord with previous investigations on other rare earth halides (1,6).

Table XXVI

Activity Coefficients of Lanthanum Bromide at 25°C

Molarity	Molality	$y_\pm$	$\gamma_\pm$	$\gamma_\pm$ (Debye-Hückel)
0.03468	0.03483	0.4345	0.4340	0.4345
0.02478	0.02487	0.4680	0.4676	0.4672
0.01982	0.01990	0.4905	0.4902	0.4899
0.009912	0.009945	0.5626	0.5624	0.5633
0.004956	0.004971	0.6390	0.6389	0.6380
0.003469	0.003480	0.6742	0.6741	0.6753
0.002478	0.002486	0.7098	0.7097	0.7090
0.001982	0.001988	0.7324	0.7324	0.7305
0.0009912	0.0009942	0.7962	0.7862	0.7909

Table XXVII

Activity Coefficients of Praseodymium Bromide at 25°C

Molarity	Molality	$y_\pm$	$\gamma_\pm$	$\gamma_\pm$ (Debye-Hückel)
0.03523	0.03535	0.4295	0.4293	0.4306
0.03020	0.03030	0.4459	0.4457	0.4452
0.02013	0.02020	0.4863	0.4861	0.4861
0.01007	0.01010	0.5655	0.5654	0.5600
0.005033	0.005048	0.6336	0.6335	0.6351
0.003523	0.003533	0.6667	0.6667	0.6728
0.002013	0.002019	0.7321	0.7321	0.7283
0.001007	0.001010	0.7872	0.7872	0.7882

Table XXVIII

Activity Coefficients of Neodymium Bromide at 25°C

Molarity	Molality	$y_\pm$	$\gamma_\pm$	$\gamma_\pm$ (Debye-Hückel)
0.03166	0.03178	0.4407	0.4403	0.4394
0.02375	0.02383	0.4681	0.4678	0.4680
0.01583	0.01587	0.5097	0.5095	0.5103
0.007916	0.007941	0.5834	0.5833	0.5869
0.003166	0.003175	0.6839	0.6838	0.6835
0.002375	0.002382	0.7142	0.7142	0.7122
0.001583	0.001588	0.7502	0.7502	0.7503
0.0007916	0.0007939	0.8087	0.8087	0.8079

Table XXIX

Activity Coefficients of Gadolinium Bromide at 25°C

Molarity	Molality	$y_{\pm}$	$\gamma_{\pm}$	$\gamma_{\pm}$ (Debye-Hückel)
0.03393	0.03505	0.4233	0.4229	0.4230
0.02544	0.02553	0.4526	0.4523	0.4522
0.01696	0.01702	0.4970	0.4968	0.4954
0.008482	0.008508	0.5696	0.5695	0.5725
0.004241	0.004255	0.6484	0.6483	0.6491
0.003393	0.003403	0.6760	0.6759	0.6729
0.002544	0.002552	0.7027	0.7027	0.7026
0.001696	0.001701	0.7408	0.7408	0.7419
0.0008482	0.0008507	0.8022	0.8022	0.8014

Table XXX

Activity Coefficients of Erbium Bromide at 25°C

Molarity	Molality	$y_{\pm}$	$\gamma_{\pm}$	$\gamma_{\pm}$ (Debye-Hückel)
0.03679	0.03693	0.4205	0.4204	0.4205
0.02759	0.02769	0.4502	0.4500	0.4487
0.01840	0.01846	0.4896	0.4894	0.4907
0.009198	0.009229	0.5666	0.5665	0.5664
0.004599	0.004613	0.6401	0.6400	0.6424
0.002759	0.002768	0.7002	0.7002	0.6948
0.001840	0.001845	0.7349	0.7349	0.7355
0.0009198	0.0009225	0.7949	0.7949	0.7957

Table XXXI

Activity Coefficients of Gadolinium Chloride at 25°C

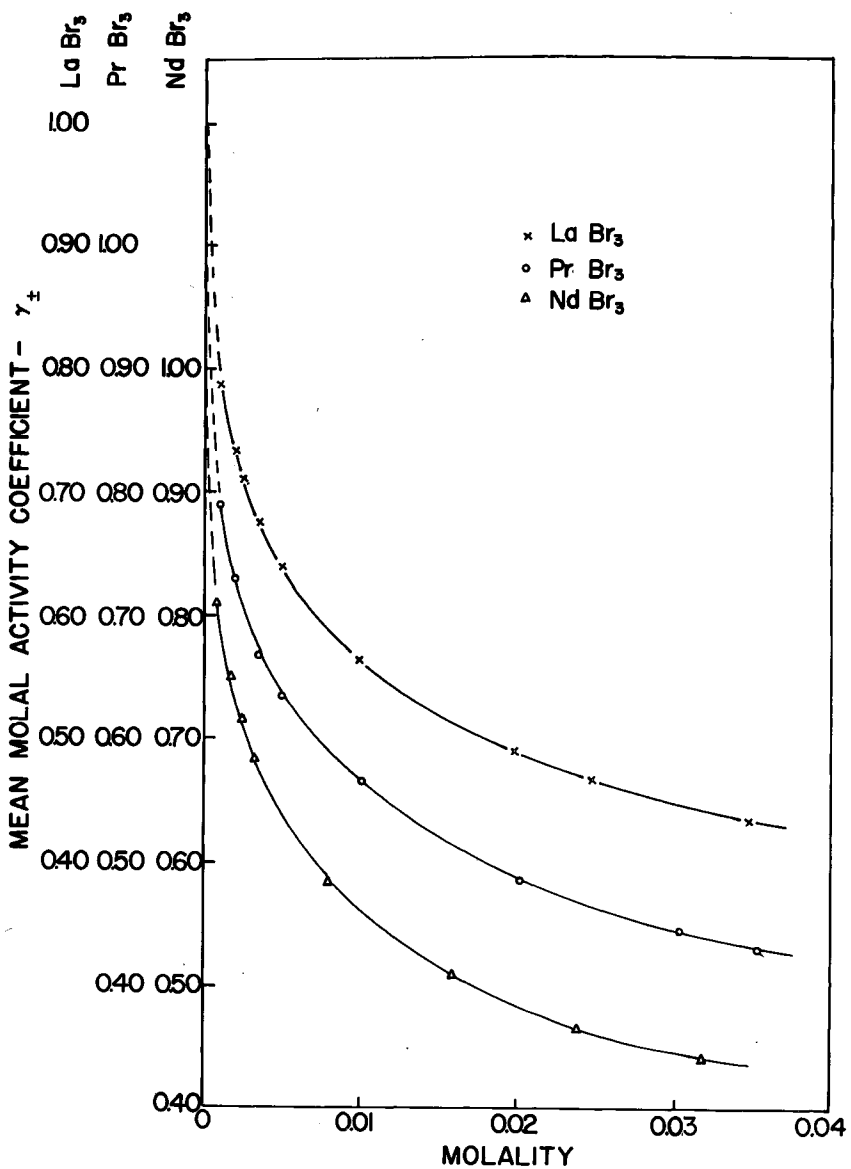| Molarity	Molality	$y_\pm$	$\gamma_\pm$	$\gamma_\pm$ (Debye-Hückel)
0.03503	0.03515	0.4174	0.4172	0.4174
0.02725	0.02734	0.4431	0.4429	0.4428
0.01946	0.01952	0.4788	0.4787	0.4785
0.01168	0.01171	0.5346	0.5345	0.5312
0.007785	0.007808	0.5817	0.5816	0.5806
0.003892	0.003904	0.6572	0.6572	0.6575
0.002725	0.002733	0.6962	0.6962	0.6949
0.001168	0.001171	0.7728	0.7728	0.7748

Figure 13 - Mean molal activity coefficients of
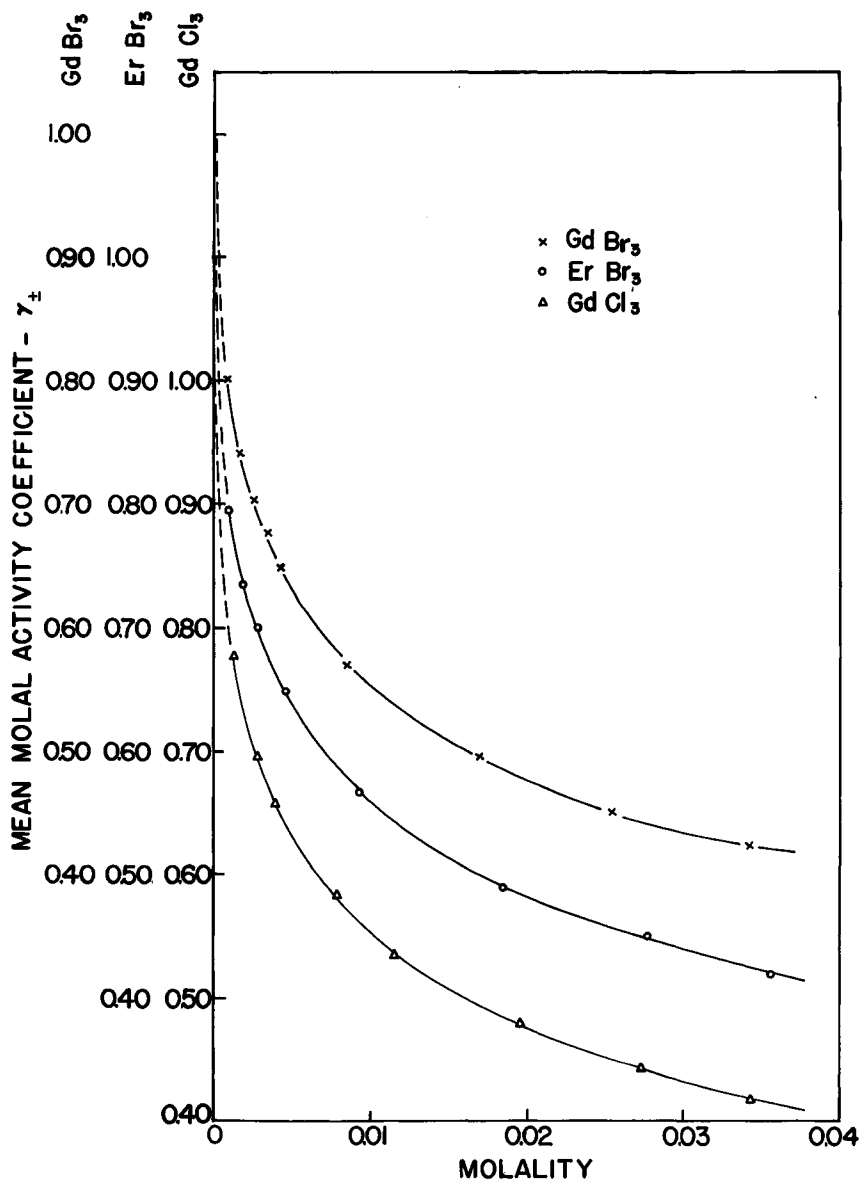lanthanum, praseodymium and neodymium
bromides at 25°C.

Figure 14 - Mean molal activity coefficients of
gadolinium and erbium bromides and of
gadolinium chloride at 25°C.

Table XXXII

Distances of Closest Approach for some
Rare Earth Halides

Rare Earth Ion	$\overset{o}{\underline{a}}$ (Angstrom Units)	
	Bromide	Chloride[*]
La(III)	6.20	5.75
Pr(III)	6.10	5.73
Nd(III)	6.06	5.92
Gd(III)	5.72	5.63
Er(III)	5.90	5.65

[*]With the exception of Gd(III), all chloride values are from data of Spedding, Porter and Wright (6).

The values of $\overset{o}{\underset{\sim}{a}}$ obtained are of an order of magnitude which indicates that a single layer of water molecules is held by the rare earth ions which is not displaced by the halide ions. There is no general order in the variations of these values, although the $\overset{o}{\underset{\sim}{a}}$ values for the rare earth bromides are higher than the corresponding values for the rare earth chlorides; this is to be expected since the bromide ion is larger than the chloride ion. Furthermore, the differences in $\overset{o}{\underset{\sim}{a}}$ values between the bromide and the chloride of the same rare earth are not constant. However, the method of calculating these values of $\overset{o}{\underset{\sim}{a}}$ is not sufficiently sensitive to determine whether the variation in the $\overset{o}{\underset{\sim}{a}}$ values is real. These experimentally determined values are probably not the true mean distances of closest approach, but are rather parameters of each salt which are somewhat affected by the approximations inherent in the Debye-Hückel theory which may not be valid for these 3-1 electrolytes.

The errors in the determination of the activity coefficients include both the errors in the transference numbers and in the potential measurements. The former are known to an accuracy within 0.1 per cent; the latter are limited by the accuracy with which the molarities of the solutions are known. The average deviation among the potential readings was of an order of 0.002 millivolts,

which was less than 0.1 per cent of the smallest potential
measured. According to the manufacturer, the error in
the potentiometer readings were of an order of 0.01 per
cent in the range of voltages measured. The temperature
fluctuation of $\pm$ 0.02°C contributed no noticeable error.
Therefore, the over-all error in the determination of
the activity coefficients is estimated to be within 0.1
per cent.

VII. GENERAL SUMMARY

The conductances, transference numbers and activity coefficients of aqueous solutions at $25.0^{\circ}C$ of lanthanum, praseodymium, neodymium, gadolinium and erbium bromides and of gadolinium chloride have been determined for concentrations up to 0.1 normal. The accuracy for all determinations was within 0.1 per cent.

The Onsager limiting law for conductance is obeyed for all salts studied up to a concentration of approximately 0.001 normal. The equivalent conductances of the first three salts mentioned are identical within experimental error. As the atomic number increases beyond neodymium, there is a regular decrease in the conductances of the rare earth bromides investigated. This same general behavior has been previously observed for rare earth chlorides (4). The identical conductances for lanthanum, praseodymium and neodymium bromides may be explained by assuming that a second coordination number is available for these rare earth ions as the atomic radius increases with decreasing atomic number. There is crystallographic evidence for hydrated rare earth sulfates at $25^{\circ}C$ which indicates that while neodymium (131) has only one stable coordination number for oxygen at that temperature, lanthanum (130) has two. Thus, for lanthanum, and possibly for praseodymium, an equilibrium might be established

between the two types of hydrated ions which would be expected to materially affect their mean ionic radii and should greatly influence their conductances.

For the heavier rare earths beyond neodymium, there is a decrease in conductance with a decrease in atomic radius. This decrease in conductivity is probably due to the hydration of the ions as in the case of the alkali metal ions. This decrease has been observed in the series of the rare earth chlorides (4) as well as the bromides.

The Onsager limiting law for transference numbers predicts for the rare earth halides that their cation transference numbers should be linear functions of the square root of the normality and that the slopes of these functions should be approximately -0.5. Also, these slopes should increase with decreasing Λ_o. It was found for all of the rare earth halides investigated that the transference numbers were linear functions of the square root of the normality as predicted. Although negative slopes were obtained which increased with decreasing Λ_o, the magnitudes of these experimental slopes were approximately one-fifth of the theoretical values. This same discrepancy between experiment and theory for rare earth halides has been previously observed (3,5).

The transference numbers of lanthanum, praseodymium and neodymium bromides were quite close together. In view

of the similarity of their conductances, this similarity
of their transference numbers was not unexpected. The
transference numbers of the other rare earth bromides
studied decreased with increasing atomic number in the
same manner as did their conductances.

The activity coefficients of all six halides studied
agreed with those predicted by the Debye-Hückel law pro-
viding that the experimentally determined $\overset{\circ}{\text{a}}$ values are
used to calculate the theoretical coefficients. This
same agreement between experiment and theory was obtained
in previous investigations of the rare earth chlorides
(1,6).

The distances of closest approach, $\overset{\circ}{\text{a}}$, for all rare
earth halides studied were found to be larger than the
sum of the crystal radii of the rare earth ions and the
halide ions by approximately the diameter of one water
molecule. If any physical significance may be attached
to the magnitude of $\overset{\circ}{\text{a}}$, the values obtained would indicate
that there is a mono-molecular layer of water about each
rare earth ion which is not displaced by the anion.

However, the difference between the $\overset{\circ}{\text{a}}$ value of the
chloride and of the bromide of the same rare earth ion
was not, in general, equal to the difference in ionic
radii of the two anions. Unfortunately, the method used

for the calculation of these $\overset{\circ}{\underline{a}}$ values is not sufficiently
sensitive to determine whether the variations of these
values are real. Also, the values of $\overset{\circ}{\underline{a}}$ would be in-
fluenced by the assumptions of the Debye-Hückel theory
which may not be valid for these poly-valent electrolytes.
Therefore, the correct interpretation of the experimentally
determined $\overset{\circ}{\underline{a}}$ values will have to be postponed until these
values can be more accurately determined and can be
correlated to such properties as the crystallographic
radii of the hydrated rare earth halides and their partial
molal volumes.

Before any more definite conclusions may be made con-
cerning the behavior of solutions of rare earth halides,
data on the rare earth elements not yet investigated should
be obtained. It is hoped that when the complete rare earth
series is investigated, the data so obtained will permit
the further development of satisfactory theories to explain
the behavior of poly-valent electrolytes in concentrated
solutions. However, the data already obtained further
confirm the validity of the Debye-Hückel and of the
Onsager limiting laws for activities and conductances.

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IX. ACKNOWLEDGMENTS

X. APPENDICES

APPENDIX A. GLOSSARY OF SYMBOLS

Only those symbols which are repeatedly used in the
text of this thesis are included in this list. Other
symbols are defined in the text.

Symbol	Quantity
a	Activity of an electrolyte
$\mathring{a}$	Mean distance of closest approach of ions
A	Debye-Hückel Constant (equation 41)
A'	Modified Debye-Hückel Constant (equation 62)
B	Debye-Hückel Constant (equation 42)
B'	Modified Debye-Hückel Constant (equation 62)
c	Concentration in equivalents per liter
C	Concentration in moles per liter
D	Dielectric Constant
E	Electromotive Force
F	Faraday
$\mathcal{F}$	Free Energy (Gibbs)
f	Rational Activity Coefficient
k	Boltzman Constant
L	Specific Conductance
M	Molecular Weight
m	Concentration in moles per 1000 grams of solvent

Symbol	Quantity
n	Number of Equivalents
N	Avogadro Number
N	Mole Fraction
p	Partial Pressure
R	Gas Constant per mole
R	Resistance
S(T)	Theoretical Limiting Slope of Transference Number
T	Absolute Temperature
T	Transference Number
t	Time in Seconds
V, v	Volume
$\bar{V}$	Partial Molal Volume
w	Ionic Strength
y	Molar Activity Coefficient
z	Ionic Charge or Valence
γ	Molal Activity Coefficient
ϵ	Electronic Charge
η	Viscosity
Λ	Equivalent Conductance
λ	Ionic Equivalent Conductance
μ	Chemical Potential
ν	Total Number of Ions Formed From The Dissociation of One Molecule
ν_i	Number of ith Ions Formed From the Dissociation of One Molecule

Symbol	Quantity
$\prod$	Product
π	Pi
ρ	Density
$\sum$	Summation

Symbol	Subscript
$\pm$	Mean Quantity
i	Indicated Quantity of an Ion
+	Indicated Quantity of a Positive Ion
-	Indicated Quantity of a Negative Ion
o	Limiting Quantity (May also be a superscript)
f	Indicated Quantity of a Following Solution
r	Indicated Quantity of a Reference Solution

APPENDIX B.   VALUES OF NUMERICAL CONSTANTS[*]

Constant	Symbol	Value
Electronic Charge	$\in$	4.8025×10^{-10} abs. e.s.u.
Faraday Constant	$\underline{F}$	9.650×10^{4} int.-coul. per gram-equivalent 2.306×10^{4} calories per volt per gram-equivalent
Gas Constant	$\underline{R}$	1.986 calories per degree per mole
Boltzman Constant	$\underline{k}$	1.3805×10^{-16} ergs per degree
Avogadro Number	$\underline{N}$	6.0228×10^{23} molecules per mole
Dielectric Constant of water at 25°C	$\underline{D}$	78.54
Viscosity of water at 25°C	η	8.949×10^{-3} poise
Absolute Temperature	$\underline{T}$	273.16 + Centigrade Temperature
Pi	$\underline{\pi}$	3.14159
Atomic Weight		The 1951 international atomic weight table was used.
Debye-Hückel Modified Constant	$\underline{A'}$	3.7446
Debye-Hückel Modified	$\underline{B'}$	0.8049

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[*]The values of the basic constants listed are those recommended by Birge (10,136), and Wyman and Ingalls (137).