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The electrical conductances of some aqueous rare earth electrolyte solutions from five hundredths molal to saturation at 25°C

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The electrical conductances of some aqueous
rare earth electrolyte solutions from five
hundredths molal to saturation at 25°C

by

Joseph Antoine Rard

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

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I. A HISTORICAL REVIEW OF THE EXPERIMENTAL METHOD

A. Introduction

The electrical conductance of a salt in solution depends on the concentration of all the ionic species present, the charges on these species, and their mobilities. If the conductances of rare earth salt solutions are studied as a function of concentration and as a function of different anions, then large amounts of qualitative information can be obtained about the nature of the ionic interactions occurring in such solutions.

The rare earths form an excellent series for the study of the aqueous solution properties of higher valence salts. The rare earths form a series of 15 elements which exist as the trivalent cation in aqueous solutions. These cations are not extensively hydrolyzed although they are strongly hydrated. The occurrence of the lanthanide contraction allows one to study the effects of cation size and hydration on the chemistry of the various salts.

The rare earth perchlorate, chloride and nitrate salts are highly soluble in water. The perchlorate ion is believed to undergo outer sphere ion-pairing with the rare earth ion in concentrated solutions while the rare earth chlorides do so at much lower concentrations. The rare earth nitrates are believed to undergo inner sphere complexation by moderate concentrations. Since these three anion series exhibit very

different complexing behavior, a study of their conductivities at various isomolal concentrations will give qualitative information about the nature and extent of the complexing which occurs in such solutions.

The measurement of electrolyte solution resistivities is not a simple straight-forward procedure. As will be shown later, accurate data generally cannot be obtained by direct current methods. Alternating current measurements of resistance are therefore used. These alternating current methods are subject to many experimental problems so that none should be undertaken without a detailed knowledge of the characteristics of an alternating current bridge. Perhaps the best way to approach these problems is through a study of the historical development of the alternating current bridge method.

One could almost say that the measurement of accurate electrolytic conductance was begun by Kohlrausch and perfected by Grinnell Jones. Kohlrausch did most of his work over a forty year period beginning in 1869. The essence of his results can be found in his famous book (1) "Leitvermögen der Elektrolyte" and in one of his papers (2). Most developments in electrolyte conductance measurement are merely improvements on the basic methods developed by Kohlrausch. His original method involved a direct current circuit, but, because of electrode problems, he soon rejected this in favor of an alternating current method.

Kohlrausch's alternating current method, with improvements, has been used for nearly all the accurate conductance measurements reported in the literature. These improvements were due to a large number of workers, but, by far, the most important contributions on the subject were made by Grinnell Jones and co-workers (3-11).

An apparatus for electrolytic conductance measurements usually consists of a modified Wheatstone Bridge, a power source, a null detector and a conductance cell. A simple Wheatstone Bridge diagram is given in Figure 1. R_3 is a

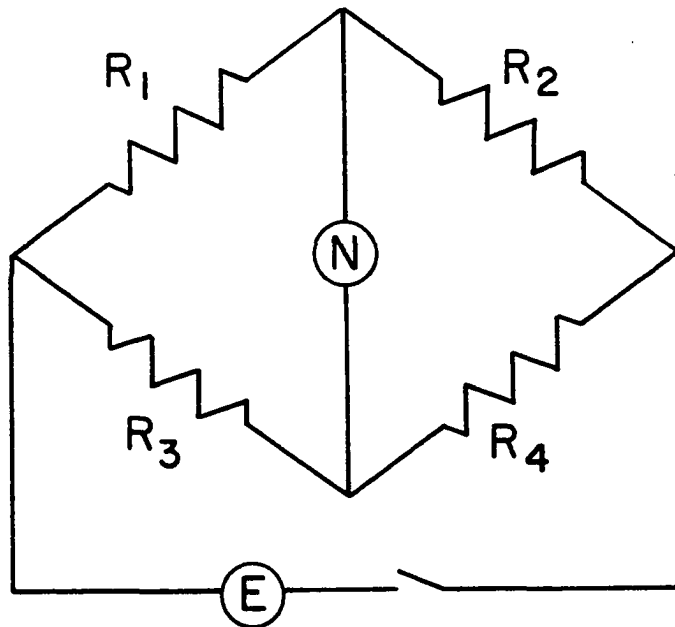


Figure 1. Wheatstone Bridge schematic

standard resistor, R_4 is an unknown resistor to be measured, R_1 and R_2 are variable bridge resistors, N is a null detector and E is a power source. At bridge balance, $R_4 = \frac{R_2 R_3}{R_1}$ so the resistance of the unknown resistor can be calculated from the bridge readings. R_1 and R_2 may be the two portions of a uniform slide wire. Alternately, R_1 may be a fixed resistance and the circuit is adjusted so that $R_3 = R_1$. In this case, R_2 becomes a decade box used to balance the bridge. Then, the measured decade box resistance reading is equal to the unknown resistance. This is the case for most modern bridges.

Some direct current measurements of electrolyte conductance are still being made. This approach requires the measurement of an electrical potential between two points, in an electrolyte solution, using a known current. To relate this voltage to resistance, the current through the cell must be accurately measured. A pair of reversible electrodes is required in order that no loss of electricity occurs in the circuit due to side reactions, such as the electrolysis of water. This insures that the measured current corresponds to the current due to the electrolytic conductance only. Electrodes that are reversible to a particular ion are not available in many cases, considerably restricting the application of this method. The reversible electrodes are sometimes also used as voltage probes. If the reversible electrodes are used as the current source

only, then a pair of inert electrodes are required as the voltage probes. Gunning and Gordon (12) have pointed out that if the reversible electrodes serve as a current source, they must be non-polarizable. That is, there should be no contribution to the measured potential from ionic absorption on the electrode surface, or from concentration gradients caused by electrolysis. If the reversible electrodes function as probes, they should theoretically be point size so that no potential drop occurs across them. Using silver-silver chloride electrodes supported by platinum, Gunning and Gordon obtained data for sodium chloride and potassium chloride which agreed quite well with Shedlovsky's (13) alternating current data. Newberry (14) used calomel electrodes for sodium chloride and silver nitrate; and, while he obtained reproducible results, some of his data does not agree with other data measured by direct or alternating current methods. He also found that mercurous sulfate electrodes gradually dissolve in sulfuric acid solutions. Electrode leaching can become a major problem in some cases, but can usually be controlled by restricting the electrode-solution contact time. Even if electrode leaching is kept to a minimum, the direct current method still involves small amounts of electrolysis. This produces small concentration changes and sets up concentration gradients near the electrodes. Eastman (15)

measured direct current and alternating current electrolyte conductivities of several aqueous solutions. In some cases the two methods agreed to .02%, but typically obtained about a .1% agreement. In one case he differs from Newberry's direct current value by .7%. Most of the error appears to be due to Newberry, but direct current methods seem to be susceptible to larger errors than the alternating current methods. Graham and Maass (16) have pointed out one major advantage that direct current measurements have over alternating current measurements -- the necessary equipment is cheaper.

A modern alternative to the Kohlrausch alternating current method involves the use of a transformer ratio-arm bridge operating at audio frequencies. This method has been described in detail by Calvert, Cornelius, Griffiths and Stock (17) and by Kotter (18). This bridge can be used with a conductance cell containing metal electrodes, or it can be used with an electrodeless system (19). In the electrodeless case, the windings of a transformer are linked by a tube of insulating material (glass) containing a conducting solution. The resistance of the solution can be balanced against a standard resistor by performing an impedance balance. At balance, the solution resistance is equal to the resistance of the standard resistor times a constant dependent only on the ratio of the transformer

windings. Although this method is generally in good agreement with the Kohlrausch method (Griffiths (19) obtained .1% agreement or better), its reliability is not yet fully established. Electrodeless conductance measurements may some day become a major experimental method, since they avoid electrode complications such as reactions and polarization.

The Kohlrausch alternating current method (henceforth to be called the Kohlrausch method) has received the largest amount of attention of all the methods. This method is well understood and is the method used for almost all accurate electrolyte conductance measurement. This method will now be described in detail.

B. Conductivity Bridge

Kohlrausch and Nippoldt (20) made their first alternating current measurements in 1869 using an induction coil and a telephone earpiece detector. His bridge contained an ordinary resistance box. To reduce the problem of electrode polarization, he connected a condenser in parallel with his resistance box. Electrode polarization introduces an additional resistance and capacitance which, coupled with the true solution resistance, may lead to errors in the measured resistance. His use of a compensating condenser reduced the polarization capacitance problem somewhat. Nernst (21) attacked the problem in a similar manner by

using an inductor in his bridge arm. He also replaced the resistance box with a slide wire of uniform resistance.

The bridge resistors should be free of capacitance and inductance for accurate measurements to be made. Washburn and Bell (22) prepared resistors, made with a thin film of platinum on glass, which were almost free of this problem. These resistors, however, had a rather large temperature coefficient which was undesirable. Washburn and Bell also used an expanded slide wire on their bridge which gave bridge readings reproducible to .002%. Taylor and Acree (23) substituted Curtis type coils (24) (wire wound on porcelain spools) on the bridge. They found that these were nearly free of inductance and capacitance. However, Livingston, Morgan and Lammert (25) found that Curtis type coils were not stable over long periods of time and required frequent recalibration. This made them unsuitable for accurate work.

The next major advance in bridge design occurred with the publication of Jones and Josephs' (3) detailed paper on this subject. They studied the problems of alternating current circuitry. The main problem is electrostatic and electromagnetic couplings (stray couplings) with the surroundings. These include the capacity of the bridge with the ground, capacities between circuit parts, and capacities and inductances between the bridge parts and any other equipment in the laboratory. They recommend against

shielding the bridge from stray capacitances and inductances since the shield itself, if not properly placed, may cause capacitance effects. They theoretically analyzed the grounding of the bridge and concluded that the grounding should be done at the endpoints of the bridge, in parallel with the bridge proper and the oscillator. They recommended a modified Wagner ground which, when properly connected, gave bridge readings independent of the direction of current flow. Improper grounding can cause poor nulls.

The bridge balance condition for a true null is $R_1R_4 = R_2R_3$. For alternating current circuits, this holds only if the phase angles between the current and voltage are equal in the adjacent bridge arms. To achieve this Jones and Josephs recommended that the bridge arms be as identical as possible in resistance and construction. Likewise, their reactances should be as low as possible. Since the cell has a reactance, one must also provide a reactance in one of the bridge arms to balance it out, usually in parallel with R_2 .

They also considered the construction of the resistors and concluded that most resistors are unsuitable due to dielectric loss in the insulators. Likewise, if the resistors were not properly connected, appended coils not in use could give rise to an energy loss. They described an improved resistance box without these defects. They found that the resistor spacing was important and

recommended that the resistors be separated at least $.04\sqrt{R}$ (in cm) where R is in ohms and is the total resistance of the two resistors being considered. They concluded that careful reactance balance is important.

Shedlovsky (26) reanalyzed the problem of shielding of the bridge. His theoretical analysis of the problem indicated that shielding could be used as long as adequate precautions were taken (shielding is desirable so that bridge readings are unaffected by the experimenter). He concluded that the only parts of the circuit capable of significant coupling are the oscillator and detector and recommended spacing them as far apart as is convenient. He agreed with Jones and Josephs' grounding procedure.

Dike (27) described an accurate Leeds and Northrup conductivity bridge based mostly on the recommendations of Jones and Josephs. A small amount of shielding was used, following the ideas of Shedlovsky. This bridge set-up was used by Jones and co-workers for determination of cell constant standards (7,10). The ground assembly and the capacitors used to balance out cell reactance were shielded. The front of the bridge was shielded to reduce capacitance with the experimenter's body. The resistance dials were of the exposed stud variety, to facilitate cleaning and calibration, and were spaced according to Jones' recommendations. The larger resistors (100 to 10,000 ohms) were of

woven construction mounted on isolantite spools. The resistors had a very low residual inductance and were very stable with time. The modified Wagner ground, recommended by Jones and Shedlovsky, was used. This ground consisted of a variable resistance and a variable air capacitor in series with each other. This type of bridge is known as a Jones Bridge and was used in this present research.

Hague (28) has written a review on alternating current bridge methods. This is a good reference not only for bridges and grounding, but also for amplifiers and oscillators. This work is written on level suitable for most chemists.

C. The Alternating Current Source and Amplifiers

In his early work, Kohlrausch used a 1000 cycle per second "alternating current" produced by an induction coil. He generated this current by rotating a coil of wire in a uniform magnetic field at a "constant" rate.

Taylor and Acree (23) studied the use of the induction coil and recommended against its use for various reasons. The current produced was pulsating, rather than truly sinusoidal, and possessed a large number of overtones. The frequency of the resulting current drifted with time, due to motor problems, for any fixed frequency setting. For this apparatus, it was inconvenient to change the frequency

setting large amounts for variable frequency measurements. The induction coil method produced unsymmetric polarization at the electrodes which, in turn, made null detection less sensitive for the telephones then in use. This unsymmetric polarization also made it hard to reproduce current and voltage phases at the detector. The polarization capacitance then depended slightly on the polarity of the electrode and made a proper capacitance balance difficult.

In 1913 Washburn and Bell (22) abandoned the induction coil in favor of the "Small High-Frequency Machine" manufactured by Siemens and Halske. This machine utilized a rapidly rotating, motor driven, toothed wheel. The "teeth" consisted of fixed magnetic poles of alternating polarity. The current produced was fairly free of overtones and was of nearly one frequency. This instrument was noisy, both electromagnetically and audibly, and was placed in a room away from the one in which the conductance measurements were being made. It was also difficult to change frequencies on this oscillator.

In 1916 Taylor and Acree (23) studied induction coils, high frequency generators, and various types of oscillators as sources of alternating current. They made oscillograms of the current from each of these sources, and visually compared the purity of the sine waves. They recommended the Vreeland-B oscillator, manufactured by Leeds and

Northrup, as the best one on the market at the time. This oscillator was placed in another room, due to its electromagnetic noise, when being used for conductance measurements.

The Vreeland oscillator series were early triode tube oscillators (28,29). The triode consisted of an evacuated tube containing a mercury cathode and two carbon anodes in a triangular arrangement. This was placed between two inductors in a resonating circuit. The circuit potential caused a current flow via the resulting double mercury vapor arc. The magnetic fields around the coil deflected the arcs until a condenser in the circuit discharged and reversed the current. These oscillators were widely used until the 1920's. Livingston, Morgan and Lammert (25) studied the Vreeland oscillators and found that the frequency drifted rather badly for the first hour of use, a rather long warm up period, and was not really constant until after four hours. This was rather inconvenient for an operational viewpoint.

In 1919 Hall and Adams (30) introduced a vacuum tube oscillator with a sensitive amplifier. The voltage through the bridge and cell was kept low to reduce heating effects. To regain sensitivity, the amplifier became necessary. Jones and Bollinger (4) recommended an amplifier for this reason, but cautioned the experimenter against the possibility of mutual induction arising between the

oscillator and the detector. They recommended spacing the oscillator and detector as far apart as was convenient.

The vacuum tube amplifiers presently used for accurate work are tuned to the oscillator frequencies and contain a wave filter. The oscillator and amplifier are connected to the bridge through shielded and grounded transformers. These transformers prevent indirect coupling between the oscillator and detector circuits.

Jones and Christian (8) studied the measurement of electrolyte solution resistance when two different current frequencies passed through the same cell simultaneously. They found no change in the resistance and concluded that overtones did not cause any error as long as they were not intense enough to cause heating effects.

Solid state equipment is gaining increased favor due to the increased stability and reliability over the conventional equipment. However, no dramatic improvement is obtained, when used in conjunction with the Kohlrausch method, for the measurement of most electrolytic conductances. Therefore, their use will not be described.

D. The Detector Circuit

Kohlrausch used a telephone earpiece for null detection in his conductance measurements. Washburn and Bell (22) and Washburn and Parker (31) discussed the use of a tuned

telephone to increase the sensitivity of the null detection. The tuning consisted of adjusting the period vibration of the telephone diaphragm until it equaled that of the alternating current. Washburn and Parker also studied the audibility current and its relationship to the sensitivity of the telephone.

In 1945, Buck and Smith (32) introduced a glorified cathode ray tube called the "magic eye", as a null detector. This instrument contained a cathode ray coupled to a triode tube by a common, and indirectly heated, cathode. A fluorescent screen surrounded the glowing (indirectly heated) cathode whose light was screened by a cap. By properly adjusting the various voltages, the fluorescent screen "eye" could be made to wink as an electrical null was reached in the circuit. Its advantage over previous detectors was that it gave a visual rather than an audio signal. It was soon replaced by the cathode ray oscilloscope which had been introduced slightly earlier.

Although the cathode ray oscilloscopy had previously been used in alternating current circuits, Jones, Mysels and Juda (11) in 1940 first described its detailed use in conjunction with the Kohlrausch method. The horizontal deflecting plates were connected to the oscillator via a transformer, and the vertical deflecting plates were connected to the output terminal of the amplifier. The

oscilloscope was adjusted so that a horizontal straight line appeared when no voltage difference occurred at the midpoint of the bridge. When the bridge was out of balance, an ellipse appeared. If the capacitance of the cell was unbalanced, a phase shift occurred between the voltage and current, and the major axis of the ellipse was tilted from the horizontal. The resistive and capacitance balances could then be performed separately. Balances could be achieved to .002% and could be done rapidly. Stray couplings and harmonics were seen as such and offered no problem.

Haszeldine and Woolf (33) also studied the oscilloscope and found that the presence of other electrical and mechanical equipment in the surrounding area had no effect on the trace. They found that poor electrical contacts and improper grounds caused a blurred or unsteady trace, and that "cell polarization" caused the trace to thicken.

The null detection procedure is now accurate and reliable. By using an oscilloscope, the detector problems can be eliminated or analyzed into their components.

E. The Conductivity Cell and Its Associated Apparatus

The word polarization has been, and still is, used to lump together a number of widely different phenomena. Duncan MacInnes (34) observed that polarization was indiscriminately used to refer to the concentration and chemical

changes due to electrolysis, and to the potentials resulting from these changes. The measured resistance of a solution in a cell consists of the pure resistance of the solution together with several sources of impedance arising from the interaction of the measuring electrodes with the solution. These other impedences are considered to be due to "polarization". Attempts are now made, in the literature, to analyze the various contributions to the "polarization" and these will be discussed later. Non-polarization problems also affect the cell. The cell problems are sufficiently complicated to warrant their division into polarization and non-polarization phenomena. The cell calibration problem will also be considered.

1. Non-polarization problems

If water is used as the temperature bath liquid, the walls of the cell may act as a dielectric in a condenser, allowing the alternating current to leak out into the water. This causes the observed resistance of the cell to decrease. The more dilute the solution in the cell, the higher its resistance and the more important this bypath becomes. Mineral oil, or some similar hydrocarbon mixture, is presently used as the standard bath liquid to reduce this effect. Mineral oil, however, has a low heat capacity, so precise temperature control is more difficult to maintain. With sufficient care this problem can be overcome.

The electrolytic conductances of most aqueous inorganic ions, except for the hydrogen ion, have about two percent per degree centigrade temperature coefficients. Robinson and Stokes (35) have pointed out that most solutions, whose conductances are being measured, generally have a temperature coefficient of conductance similar to the standard solutions used for the calibration of the cell. Therefore, if the bath temperature is set slightly different than the desired temperature, no serious errors will result as long as the temperature is held constant for the series of measurements and calibration. This is true as long as the bath temperature is both constant and within a few hundredths of a degree of the desired temperature. To obtain conductivities good to $\pm 0.01\%$, it becomes necessary to control the bath temperature to $\pm 0.005\%$ degrees. The periodic variations of the bath temperature may be larger than this as long as the measurements are consistently made at a fixed position in this heating cycle.

Washburn (36) recommended the use of a sizable pair of mercury filled cups, dipping into the oil bath containing the cell. If the temperature of the laboratory is different than the temperature of the oil bath, then heat will flow along the leads towards, or away from, the cell. These mercury cups act as a ballast to reduce heat exchange between the cell and the laboratory. The entire temperature

bath is frequently enclosed in a plastic cover to reduce direct heat transfer with the laboratory.

Taylor and Acree (37) studied various cell designs and found that no variation of inductance and resistance occurs with variable low voltages, as long as the cell is kept quite clean. These authors set up a criteria for accurate conductance work. This criteria is that the ratio of the resistances of several solutions in one cell should be the same for any cell to within .01% or some other acceptable limit. This should insure that true resistances are being measured. This criteria is applied mainly to dilute solution work where cell problems become more pronounced in their effect on the accuracy of the measurements.

Washburn (36) made a very detailed study of the theory of conductance cells in a conductance bridge circuit. He derived, in detail, the current distribution in the cell and bridge. He used his results to design several cells. He also derived equations for the temperature coefficient of the cell constant in terms of the coefficients of expansion of the glass used to make the cell body and the metal used to make the electrodes. Let ρ be the resistivity of the solution in the cell and L be its conductivity. By definition $\rho L = 1$. The resistivity, ρ , can be related to the measured resistance, \bar{R} , by a geometric proportionality factor, k , known as the cell

constant. Then, $\rho k = R$ and $LR = k$. The error of the measured resistance is then given by equation 1.1

$$\delta R = \sum_{x_1} \left| \frac{\partial R}{\partial x_1} \right| \delta x_1 = R \left(\frac{\delta k}{k} + \frac{\delta L}{L} \right) . \quad (1.1)$$

We are interested in temperature dependence, so

$$\delta k = \frac{\partial k}{\partial T} \delta T \quad \text{and} \quad \delta L = \frac{\partial L}{\partial T} \delta T . \quad (1.2)$$

Then,

$$\frac{\delta R}{R} = \delta T \left\{ \frac{1}{k} \frac{\partial k}{\partial T} + \frac{1}{L} \frac{\partial L}{\partial T} \right\} \quad (1.3)$$

and

$$\frac{1}{R} \left(\frac{\delta R}{\delta T} \right) = \frac{1}{k} \frac{\partial k}{\partial T} + \frac{1}{L} \frac{\partial L}{\partial T} . \quad (1.4)$$

We know that $\frac{1}{L} \frac{\partial L}{\partial T} \sim 2 \times 10^{-2}$ per degree centigrade. The cell dimensions and the material from which the cell is made influence the values of $\frac{1}{k} \frac{\partial k}{\partial T}$. Washburn (36) has tabulated values of $\frac{1}{k} \frac{\partial k}{\partial T}$ for various cell geometries. For capillary cells of the type used in this research, the value of $-\frac{1}{k} \frac{\partial k}{\partial T}$ is essentially equal to $\frac{1}{3V} \frac{\partial V}{\partial T}$ for the glass used to make the cell. For most glasses, $-\frac{1}{3V} \frac{\partial V}{\partial T} \sim 10^{-5}$. Then, the temperature variation of the cell constant will make no detectible error contribution to measured resistances under normal experimental conditions. In general, Washburn found that short electrode stems and long cell dimensions tend to

lower the temperature coefficient of the cell constant. Washburn also stated that if cells are properly aged and annealed, and are not subjected to large temperature variations, then they will exhibit no thermal volume hysteresis and the cell constant will not drift with time.

Parker (38) found that the "cell constant" varied with the resistance being measured. This phenomena is now called the "Parker effect". He thought that it was due to an adsorbed layer of ions at the surface of the electrodes. He found that the further the electrodes are separated, the more constant the "cell constant" becomes.

Shedlovsky (26) felt that this problem was due to some form of polarization and set out to design a cell to avoid this problem. He designed cells with multiple electrodes which could be connected to the bridge in several different ways. The results could be combined to subtract out electrode effects in a manner similar to operating a four terminal resistor.

Jones and Bollinger (5) then tackled the problem. They chose a bridge in which the phase angle displacement was essentially zero so that the measured phase displacement was due to the cell only. Let the phase angle displacement angle be θ , the polarization capacitance C_p , the cell resistance R and the current frequency ν . Then, $\tan \theta = 2\pi\nu C_p R$ for their circuit. They found that a plot of $\tan \theta$

versus $\log R$ goes through a minimum. The high R portion of the curve corresponds to the Parker effect and the low R portion to "polarization".

Jones and Bollinger then varied the amount of platinization on the electrodes and found no change in the Parker effect. This showed that the effect is not due to adsorption on the electrodes. The error is always in the negative direction. This suggested that a shunt path was present for the current which was electrically parallel with the solution resistance. They showed that this effect arose because the cell leads passed close to the cell solution for the cells then in use. This produces a capacitive shunt. They found that proper placing of the electrode leads, and long cell dimensions, can eliminate this effect. If short cells are used, it may be necessary to calibrate them with several standards of different resistances.

Another problem of interest is the range of conditions over which Ohm's law applies for electrolyte solutions. That is, the circumstances are sought under which the measured resistance is independent of the current and voltage used.

Malsch and Wien (39) and Wien (40,41) studied electrolytic conductance in very strong fields. They found that the measured resistance of the solution decreases with increasing electrical field strength at high field values.

They found the effect in some cases with fields as low as 3,000 volts per centimeter. This is about 1,000 times the maximum voltage used in the Kohlrausch method. This field effect was proportional to the valence of the ions and increased with solution concentration. It appeared that the ionic velocities were approaching a maximum at very high fields. Wien concluded that "It is probably the case that the great velocity which the high fields imparts to the ions completely or partially abolishes the cause for the change in equivalent conductance with concentration" (5). This is known to be the case and the phenomena is known as the Wien effect.

A similar effect is the Debye and Falkenhagen effect. This phenomena is a decrease in resistance with frequency at high frequencies. This effect was predicted by Debye and Falkenhagen (42) and established experimentally by Sack (43). It has been studied in more detail by Arnold and Williams (44). This effect is detectable at about 10^6 cycles per second and higher. Measurements by Kohlrausch's method are seldom done above 10,000 cycles per second, so this effect can be ignored.

2. Polarization problems

Kohlrausch discovered the electrode polarization problem in alternating current conductance measurements. He thought that it was due to reversible deposition of hydrogen and

oxygen at the platinum electrodes. He reasoned that this electrolysis should give rise to a capacitance in series with the solution resistance. He used a compensating capacitor in his bridge arm to compensate for this capacitance. He observed that this did not completely solve the problem of polarization and that platinization of the electrodes greatly reduced the remaining polarization effects (45). He platinized his electrodes by electrolysis of chloroplatinic acid containing a trace of lead acetate.

Wien (46) believed that the polarization phenomena arose from the incomplete reversibility of the electrode processes. He found that nickel, silver, mercury and smooth platinum electrodes possessed an excess resistance which is not compensated for by the bridge arm capacitor. This indicated that polarization produced both a resistive and a capacitive effect. He found that the resistance due to polarization was inversely proportional to electrode surface area, independent of current density (up to .0025 amps/cm²) and independent of frequency at low frequency. He concluded that the capacitance due to polarization should be in parallel with the cell resistance, and this capacitance effect should vary inversely with the square root of the measuring frequency. Neumann (47) tested mercury and silver electrodes and found that the measured resistance had a frequency dependence in approximate agreement with Wien's prediction.

Taylor and Acree (37) found that different solutions with the same resistance have approximately the same frequency dependence in the same cell. To obtain a frequency independent resistance, they recommended an extrapolation of resistance values to infinite frequency. Jones and Bollinger (5) concluded that proper platinization, large electrodes, high frequency and high resistances tended to reduce the frequency dependence of the measured resistance.

Miller (48) investigated a cell with movable electrodes. He considered the intercept on the curve of the measured resistance versus the electrode separation (at infinite electrode separation) as being the polarization resistance. His results were not accurate enough for any definite conclusions to be drawn. Jones and Christian (8) followed this same approach. They tested movable electrodes of nickle, silver and platinum. Slight differences were found for the different metals, but the general behavior was the same. By assuming that the polarization resistance, ΔR , is independent of electrode separation, S , they obtained $R_s = R_t + \Delta R = \frac{S}{AL} + \Delta R$ where A is the (uniform) cross sectional area of the cell, R_s is the measured resistance and R_t the true resistance of the solution. They plotted R_s versus S for their data and found that it was indeed linear. This showed that the polarization resistance

occurred in the electrode region of the cell and not in the bulk solution. They found that, almost within experimental error, ΔR was inversely proportional to the square root of frequency. This confirmed Warburg's law (49) that $R_s = R_t + \frac{k'}{\sqrt{\nu}}$. Jones and Bollinger also showed that the polarization capacitance of the cell decreased with increasing frequency and was in series with the solution resistance. By proper platinizing of platinum electrodes, the frequency dependence of the resistance can usually be reduced to .01%, or less, of the total resistance. Because of its small frequency dependence, platinized platinum is the preferred electrode material.

Warburg's law is now known to be only approximately correct. The reason for this lies in the fairly complex nature of the electrode-solution interaction. The major capacitance effect is due to the existence of a diffuse electrical double layer at the electrode surface. This double layer consists of the charged electrode surface and a diffuse layer of ions, of equal and opposite charge, located in the solution near the electrode surface (50, 51, 52). This double layer is quite thin and leads to a fairly large capacitance in series with the solution resistance. This capacitance may be as high as several microfarads per square centimeter of electrode surface in some cases. The resulting impedance is proportional to

$(\nu c)^{-1}$ and so has almost no effect on the measured resistance. The cell electrodes, with the solution as a dielectric, have a small capacitance. This parallel capacitance, along with the capacitance between the cell leads, is balanced out by the bridge arm capacitors.

At the electrode surfaces small amounts of electrolysis occurs. This usually consists of solvent electrolysis (H_2 and O_2 formation if the solvent is water) and the reduction of dissolved oxygen. This electrolysis gives rise to a "faradaic leakage" electrically in parallel with the diffuse double layer capacitance. This faradaic leakage consists of a resistance part, independent of frequency, and an impedance part known as the "Warburg impedance". This Warburg impedance is equivalent to a resistance and capacitance in series, each having the same impedance, and each varying inversely with the square root of frequency. This effect is discussed in detail by Grahame (53) and is summarized by Robinson and Stokes (35, p. 93-5).

The schematic diagram of the conductance cell and its associated polarization effects is given in Figure 2. R_t is the pure resistance of the bulk solution, C_0 is the electrode capacitance with the solution as a dielectric, C_1 is the double layer capacitance, R_1 is the purely resistive part of the faradaic leakage, and W is the Warburg

impedence. This diagram can be found in Robinson and Stokes (35, p. 53) and is similar to the model proposed by Feates, Ives and Pryor (54). Under the usual conditions of the Kohlrausch method, the major sources of current transport is through ionic migration and by the building up and discharging of the double layer capacitance. Very little current is (usually) carried through faradaic processes. This is desirable since faradaic processes give rise to errors in the measured resistance.

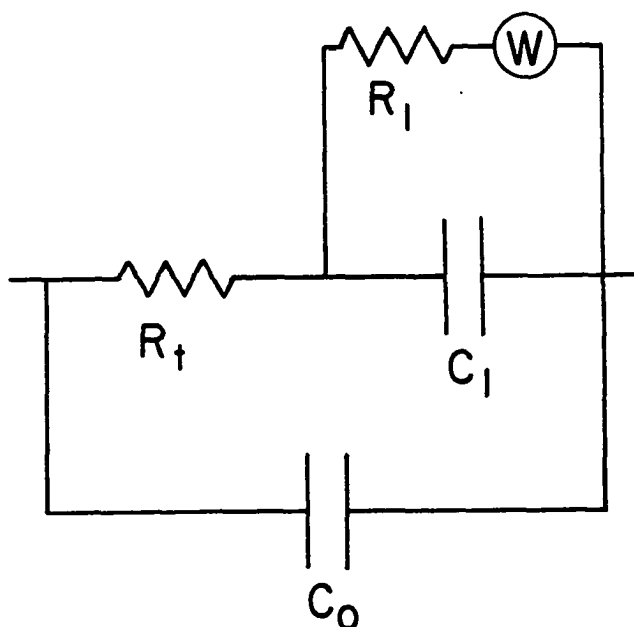


Figure 2. Conductance cell schematic

A disadvantage of platinized platinum electrodes is the susceptibility of platinum black to surface adsorption. Some organic compounds are strongly adsorbed on the electrode surface and tend to destroy the double layer current path. This causes an increase in faradaic processes and neutralizes the beneficial properties of platinum black. The presence of absorbing organic species should be avoided whenever possible. Any electrode with adsorbed organic impurities can generally be cleaned by application of a sufficiently high voltage to oxidize off these adsorbed species or by careful chemical oxidization.

A more fundamental problem lies in the nature of the electrode surface reactions. The standard potential for the oxidation of Pt to Pt^{+2} is 1.2 volts. This potential is reduced to .7 volts by complexing agents such as the halide ions (55, p. 270). This potential is also pH dependent and is usually estimated to be .5 volts in neutral solution (56-58) with acidic solutions having a higher potential. In contact with an aqueous solution, a platinum electrode would form a surface coating of PtO (and PtO_2) if the external potential is sufficiently high. This oxide coating encourages faradaic processes and is undesirable. Anson and Lingance (59) found that high potentials produced a surface film containing PtO and PtO_2 (or hydroxides). They stripped off this film with a HCl-NaCl solution and

identified the platinum ions by their absorption spectra. By keeping the potential below .5 volts in neutral and acid solutions, the problem of electrolytic oxidation of the platinum electrode surface can be avoided during the course of conductance measurements. By further restricting this potential to .4 volts or less, water electrolysis should be avoided (reduction of hydrogen ions).

Another similar problem is the chemical oxidation of the platinum surface. Kolthoff and Tanaka (58) showed that acidic solutions of $K_2Cr_2O_7$, Ce(IV) and $KMnO_4$ could cause oxidation of platinum electrodes. Similarly, concentrated HNO_3 and dilute bromine water produced the same effect while acidic $FeSO_4$ and $AsCl_3$ reduced the oxide film back to metallic platinum. It becomes clear that prolonged contact between the electrode and oxidizing solutions should not be allowed without a thorough knowledge of the chemistry and kinetics of the species involved.

In most cases the solution being measured will not attack the electrodes and the platinum black becomes a definite advantage. Then, the catalytic effect of the finely divided platinum helps to make the small amounts of electrolysis more nearly reversible. It thereby reduces the faradaic leakage and, thus, the Warburg impedance. Platinization increases the electrode surface area and consequently reduces the surface charge density. This

causes some reduction in the double layer capacitance, but never enough that a compensating capacitor in series with the bridge arm becomes necessary. Increasing the surface area by sandblasting has been tried (60), but platinization is the only method in general use.

Platinized electrodes also cannot be used when kinetics is being studied since many reactions are catalyzed by platinum black. Likewise, mixtures of concentrated HCl and HNO₃ cannot be studied since their combination readily dissolves platinum. Although bulk platinum is moderately inert to nitric acid, platinum black is not, so concentrated nitric acid should be avoided. Also, strongly basic solutions should be avoided if the cell body is constructed out of glass.

Jones and Bollinger (9) systematically studied platinization. They found that if lead acetate was not present in the chloroplatinic acid, then the platinum black was of inferior quality and tended to chip off. They found that even small amounts of platinization greatly reduced ΔR and C_p , and an optimum value of ΔR was reached when approximately six coulombs of platinum per square centimeter of electrode surface was deposited. They used a direct current of .010 amperes and reversed polarity every ten seconds in their platinization process. They were able to reduce ΔR to .005% of the total resistance and eliminated

it as a significant source of error. They found that excessive platinization increased ΔR slightly above its minimum value.

F. Cell Calibration

Consider a cell made of glass, with metal electrodes, and filled with solution. The resistance of the solution will depend on its volume and the cell geometry. If the cell has a uniform cross section A , a length S , and a solution resistivity of ρ , then the total resistance is given by $R = \rho(S/A)$.

The quantity S/A is constant for any particular cell and is known as the cell constant, k . Its dimensions are cm^{-1} . If one has a solution of known specific conductance, then one can use this solution to determine the cell constant of any cell. This is useful if the cell is not of uniform cross sectional area since the cell constant is no longer a simple function of S and A .

Kohlrausch (reviewed in (1)) approached the cell constant problem by measuring the dimensions of his cells. He prepared solutions of potassium chloride diluted to certain volumes and measured them in his cells for use as secondary standards. His standards were accepted until the 1920's. He did not correct his weights to vacuum.

In 1922, Kraus and Parker (61) noted that Kohlrausch defined his standards in several different ways which were not always mutually consistent. In some cases, his definitions differ by several tenths of a percent. Kraus and Parker recommended that a certain one of Kohlrausch's values be chosen as "the" standard.

Parker and Parker (62) returned to the cell constant problem and redetermined the conductance of some of Kohlrausch's standards. They did not correct their weights to vacuum but did define their standards in terms of weight rather than volume dilutions. They measured their cell dimensions and differed from Kohlrausch's standards by .03% to .23%.

Shedlovsky (13) used one of Parker and Parker's standards to calibrate his cell and measured potassium chloride conductances as a function of concentration. Although his data was not meant to be used in place of the standard solutions, many experimentors have done so. These standards are easier to make and their conductances are obtained by interpolation of Shedlovsky's data.

Jones and Bradshaw (7) then tackled this problem of standard solutions. They used mercury as a primary standard and obtained their cell-constants by filling the cells with mercury. They measured the resistances with a Kelvin Bridge (28) using standards calibrated by the

National Bureau of Standards. The potassium chloride solutions were so much less conducting than mercury that two cells were necessary in order to obtain optimum resistance values. The primary cells were calibrated with mercury and then used to measure the conductance of some sulfuric acid dilutions. These dilutions were used to calibrate secondary cells which were then used to measure the potassium chloride standards. Their potassium chloride standards were prepared by weight and corrected to vacuum. The potassium chloride was fused in a platinum dish. Their cell designs were influenced by the suggestions of Dr. Frank Wenner. He pointed out that the resistivity of mercury was approximately eight times that of the electrode platinum while that of the sulfuric acid was about 200,000 times as great. If the cells were not properly designed, there would be a slightly different current distribution when the cell was filled with mercury than when it is filled with sulfuric acid. Jones and Bradshaw took this into account when designing their cells. They measured the standards using the equipment described by Dike (27). They differed from Parker and Parker's values by .02 to .12%.

Jones and Prendergast (10) measured several more standards in the same manner. The standards of Jones and co-workers are generally accepted today as the best. Gunning and Gordon (12) have shown a slight discrepancy

between Jones and Prendergast's and Jones and Bradshaw's values. They preferred Jones and Prendergast's values for their own work. For the sake of self consistency, one set of values should be chosen as absolute standards. When using these standard values, one should correct them to absolute ohms (absolute ohms = 1.000495 international ohms).

The water used for all accurate conductance work is conductivity water. Kendall (63) reviewed the various methods of preparing conductivity water. The method generally used is the distillation of water from a solution of potassium hydroxide and potassium permanganate. Pinching and Bates (64) describe several methods for the purification of potassium chloride. Recrystallization from conductance water is the most commonly used method. Fusion of the potassium chloride is usually done under vacuum since the presence of moisture allows the formation of some basic products (64,65,66).

II. EXPERIMENTAL METHODS

The resistivities of 24 different aqueous rare earth electrolytes were measured at 25°C. The resistivities of the various salts were measured at 31 to 36 different concentrations ranging from .002 molal to saturation. From this data, the specific and equivalent conductivities for each salt have been calculated as a function of concentration. In this research, data was obtained for various rare earth chloride, nitrate and perchlorate solutions.

A. Solution Preparation and Analyses

The pure rare earth oxides, used to prepare these electrolyte solutions, were obtained from the rare earth separation group of the Ames Laboratory. The purity of the various oxides was determined from their emission spectra. The results are listed in Table 1 in terms of weight %.

A primary stock was prepared for each rare earth salt studied. These stocks consisted of approximately two liters of almost saturated solution. Rare earth oxide samples of 1200 to 1500 grams were used to prepare each stock solution. The less concentrated solutions were then prepared from these stocks by weight dilution.

The stock solutions were prepared by dissolving the rare earth oxides in C.P. grade acid corresponding to the desired anion. In each case a slight excess of oxide was

Table 1. Results of spectrographic analyses of rare earth oxides for impurities

OXIDES	ANALYSES IN PERCENT ^a			
La ₂ O ₃	Ca: < .002 Fe: < .004	Ce: < .035 Pr: < .015		
Pr ₆ O ₁₁	Ca: < .020 Fe: < .010 Si: < .025	La: < .005 Ce: < .075 Nd: < .060	Sm: < .010	
Nd ₂ O ₃	Ca: < .020 Fe: < .009	Pr: < .100 Sm: < .010		
Sm ₂ O ₃	Ca: < .002 Fe: < .004 Si: .004	Y : < .005 Pr: .020 Nd: .020	Eu: .010 Gd: < .030	
Eu ₂ O ₃	Ca: .002 Si: .006	Gd: < .010 Tb: < .010		
Gd ₂ O ₃	Ca: < .005 Fe: .001 Y : < .002	Sm: < .020 Eu: < .001 Tb: < .020	Dy: < .010	

^aThe less than sign, <, indicates that the element was detected but was present in concentrations somewhat below the analytical detection limit listed immediately afterwards. The < indicates that the element was undetected. The Nd₂O₃ and Pr₆O₁₁ samples are not less pure than the other oxides, interference makes the trace element detection less accurate for these two. If several stocks were prepared from different oxide samples of the same rare earth, then average analyses results are listed. Different samples of the same oxide did not generally differ significantly in purity.

Table 1 (continued)

OXIDES	ANALYSES IN PERCENT ^a		
Tb ₄ O ₇	Ca: $\bar{<}$.002 Fe: $\bar{<}$.005	Si: $<$.005 Gd: $\bar{<}$.020	Dy: $<$.010
Dy ₂ O ₃	Er: $<$.02 Ho: $<$.05	Y : $\bar{<}$.007	
Ho ₂ O ₃	Ca: .005 Fe: $\bar{<}$.003 Si: $\bar{<}$.003	Y : $\bar{<}$.001 Dy: $<$.015 Er: $\bar{<}$.050	Tm: $<$.020
Er ₂ O ₃	Ca: .002 Fe: .002 Si: .006	Y : $\bar{<}$.001 Dy: $\bar{<}$.010 Ho: $<$.005	Tm: $<$.010 Yb: $<$.005
Tm ₂ O ₃	Ca: .003 Si: $<$.006 Y : $\bar{<}$.001	Ho: $\bar{<}$.020 Er: $\bar{<}$.003 Yb: .008	Lu: $\bar{<}$.030
Lu ₂ O ₃	Ca: $<$.002 Fe: $\bar{<}$.003	Y : $<$.005 Er: $\bar{<}$.001	Tm: $\bar{<}$.001 Yb: $\bar{<}$.001

used and the solution was boiled, after visible reaction ceased, for at least 24 hours. The excess oxide was removed by filtration through a sintered glass filter. The resulting solutions usually had a pH of 3 to 5, which is basic relative to the equivalence pH. These solutions are

"basic" due to the presence of colloidal rare earth oxide and because of the existence of various basic species produced by the hydrolysis of the rare earth cations. One type of hydrolysis expected for the rare earth ions is given in equation 2.1.



There is also the possibility that some of the basic species exist as polymers in solution, further complicating the chemistry involved.

In each case a 20 ml sample of the stock solution was titrated with dilute acid to determine whether the solution was basic enough to obtain a complete titration curve. If not, more oxide was added and the solution was reheated and refiltered. It was found that .1 N HCl was a suitable acid strength for titration of the ReCl_3 samples. For $\text{Re}(\text{NO}_3)_3$'s and $\text{Re}(\text{ClO}_4)_3$'s an acid concentration of .5 N was necessary.

The solution samples were titrated with acid using a Sargeant model D recording titrator. The strip chart speed on this instrument is proportional to the rate at which acid is added to the sample. A continuous plot of pH versus volume of acid added is thereby obtained.

Two samples of the stock were titrated and the average of their equivalent points used for the adjustment of the stock. These two equivalent point determinations generally

agreed to .1 pH unit or better. Values of the pH were graphically determined at equal intervals of acid addition. From this data, values of $\frac{\Delta \text{pH}}{\Delta V}$ and $\frac{\Delta^2 \text{pH}}{\Delta V^2} = \frac{\Delta}{\Delta V} \left(\frac{\Delta \text{pH}}{\Delta V} \right)$ were calculated. The titration curves were typical strong acid-strong base titration curves so the equivalence points correspond to the inflection points in the resulting curves. At the inflection points, $\frac{\Delta^2 \text{pH}}{\Delta V^2} = 0$ so the equivalence points are easily obtained. The bulk solutions were then adjusted to this value with acid of the same concentration as that used in the equivalence point titrations. The chloride stocks were heated overnight, below their boiling point (some HCl would boil off otherwise), and then cooled and rediluted to their original volume. The nitrate and perchlorate stocks were treated in the same manner except that they were heated to their boiling points. Fresh samples of the solution were titrated and the stock solution pH readjusted. This procedure was repeated until the overnight heating no longer caused the stock solution pH to change. The solutions were then bottled until ready for use as the primary stocks. Under these conditions of preparation, no colloidal oxide remained (no Tyndall cone) and the correct ratio of rare earth cation to anion had been insured. The perchlorates were filtered through a .25 micron filter to remove solid silica particles produced by the dehydrating action of HClO_4 (67).

All glassware and filters used in the solution preparation were boiled overnight in a 1 N acid solution corresponding to the desired anion. That is, if a rare earth nitrate stock was being prepared all the necessary glassware was boiled in a nitric acid solution. All glassware used in the stock solution storage and in dilution preparations was cleaned by soaking overnight in alcoholic KOH. This glassware was then rinsed with tap distilled water followed by overnight soaking in 1 N HCl. Finally, the glassware was rinsed with conductivity water and oven dried at 110°C.

All water used in solution and dilution preparation was conductivity water of specific conductance less than 1×10^{-6} mho/cm and pH of approximately 6. This acidic pH was due to the dissociation of dissolved carbon dioxide. The conductivity water was prepared by distillation from a KOH-KMnO₄ mixture in a modified Barnsted E-1 tin lined conductivity still.

The dilutions were prepared by weighing fixed amounts of stock solution and conductivity water from separate weight burettes into clean flasks. Approximately 250 gram samples of each dilution were prepared. The weights were corrected to vacuum. The dilution concentrations were calculated from the weight data and from the stock solution

analyses. A secondary stock of approximately .3 molality was prepared and was used in making the more dilute solutions.

The saturated solutions were prepared by evaporation of a sample of each primary stock, in an evacuated dessicator, by the action of anhydrous magnesium perchlorate. When sufficient crystals had formed, the solution and crystals were transferred to a flask which was positioned in a constant temperature bath at 25°C. This solution was shaken several times daily over a three week equilibrium period. The solution was then decanted from the crystals into another flask. This new flask was examined for mechanical carry-over of crystals and, if any were present, the decantation was repeated. The saturated solution was then stored until ready for use. The laboratory temperature occasionally dropped below 25°C and crystals would sometimes form in these solutions. If any crystals were present, they were redissolved by warming the solution, before the solution was used.

The various stock solutions were analyzed by several different methods. These methods, the chloride, EDTA, and sulfate methods, will be discussed in more detail later. The various stocks were analyzed in the following manner:

- 1) The rare earth chloride primary stock solutions were analyzed by EDTA and, in some cases, by

sulfate analyses. The saturated solution concentrations were previously measured by various members of our group.

- 2) The rare earth chloride secondary stock solutions were all analyzed for chloride, and by EDTA, or sulfate, or both. The separate analyses agreed with each other to .1% or better. The value calculated from the primary stock analyses and the dilution data agreed with the direct analysis result to .05% or better in all cases.
- 3) All rare earth nitrate and perchlorate primary stocks and most saturated solutions were analyzed both by EDTA and sulfate methods. Some of the saturated solution concentrations had been previously measured by various members of our group.
- 4) All rare earth nitrate and perchlorate secondary stocks were analyzed by EDTA and nearly all by sulfate also. The concentrations calculated from the primary stock analyses and dilution data agreed to within .07% of the value obtained by direct analyses for the perchlorates and to within .06% for the nitrates.

a. Chloride method Samples of the rare earth chloride secondary stock (approximately 60 grams each) were weighed into empty beakers. To each was added .1 g of dextrin and sufficient water to obtain a total volume of 125 ml. Approximately 8 drops of .1% dichlorofluorescein was added to each sample, which was then titrated with .1 N AgNO_3 solution to the pale pink end point. The silver nitrate solution was standardized against a .04 N KCl solution prepared from vacuum fused, triply recrystallized KCl. Samples were run in triplicate and a precision of $\pm .05\%$ was generally obtained.

b. EDTA method for rare earth ions Samples of the rare earth electrolyte solutions were weighed into empty beakers. Rare earth solution sample sizes were chosen so the weight of EDTA solution required for the titrations fell between 50 and 80 grams. To each rare earth sample was added 250 ml of pH=5 buffer. This buffer was prepared by dissolving 109 grams of sodium acetate and 25 ml of acetic acid in two liters of conductance water. The EDTA was prepared by dissolving the analytical reagent solid in conductance water. The EDTA solutions used in these titrations had concentrations between 1.4×10^{-4} and 2.0×10^{-4} moles of EDTA per gram of solution. To each sample several drops of .1% xylenol orange were added and the solution titrated with EDTA to the yellow end point. During the course of the titration, sufficient pyridine was added to produce a stable end point.

The EDTA solutions were standardized against rare earth electrolyte solutions prepared from the pure metals. These rare earth standards were prepared by dissolving the weighed metal samples in a slight excess of acid. Mass spectra analyses were used to correct the weight of the rare earth metals for the impurities present. The quality of the EDTA end point changed across the rare earth series, so La^{+3} , Gd^{+3} , and Lu^{+3} standards were used to compensate for this variation. Samples were run in at least triplicate, and usually quadruplicate, and results generally had a precision of better than $\pm .05\%$.

c. Sulfate method for rare earth ions Empty
porcelain crucibles were fired in a furnace at 550°C and allowed to cool in a desiccator over anhydrous $\text{Mg}(\text{ClO}_4)_2$. This procedure was repeated until a constant weight was obtained.

To each weighed crucible was added sufficient rare earth stock to produce 3-5 grams of anhydrous sulfate. Excess 1 molar H_2SO_4 solution was added to each crucible, which was then dried on a hot plate at low heat (approximately 150°C). The heat was gradually raised to 325°C and held at this temperature until all evolution of SO_3 ceased. The samples were then placed in a furnace and fired to 550°C . The samples were then allowed to cool and the H_2SO_4 treatment repeated. Finally, the crucibles were

fired to a constant weight by the same procedure used for the empty crucibles. This treatment is adequate for rare earth chloride stock solutions.

The rare earth nitrate stock samples were predecomposed, in the crucibles, with excess HCl to destroy the nitrate ions. This treatment was performed twice before the sulfuric acid additions. By decomposing the nitrate ion, the co-precipitation of $\text{Re}(\text{NO}_3)_3$ with the $\text{Re}(\text{SO}_4)_{1.5}$ was avoided.

Rare earth perchlorates also showed some tendency to co-precipitate with the sulfate. By using the hot plate temperatures recommended for the H_2SO_4 treatment, this problem was usually avoided. In a few cases co-precipitation occurred and it was necessary to heat the rare earth sulfate with NH_4Cl to destroy the trapped perchlorate ions. After all excess NH_4Cl had sublimed from the samples, an additional sulfuric acid treatment was performed and the samples weighed as previously mentioned.

Pr and Tb tend to form "abnormal" oxidation states in solid compounds. These "abnormal" compounds sometimes formed when rare earth chlorides were being converted to sulfates (rare earth nitrates decomposed with HCl also equal rare earth chlorides). Their presence was obvious due to the dark color they impart to the sulfate. The second addition of H_2SO_4 eliminated this problem.

Tare crucibles were used and all weights were corrected to vacuum. The stock concentrations were calculated from the weights of anhydrous sulfate and the weights of stock solution used. Sulfates were performed in at least duplicate and usually triplicate with a general precision of $\pm .05\%$ or better.

When independent analyses were performed on stocks by different methods, no results were accepted unless they agreed to $.2\%$ or better in terms of molality. If analyses results disagreed by more than $.2\%$, they were repeated. In most cases the independent analyses agreed to $.1\%$. The molal concentrations of the stock solutions are therefore known with an absolute precision of at least $\pm .1\%$. The average molality obtained from the independent analyses was used to calculate the concentration of all dilutions from that stock. The atomic weights used in the calculations of concentrations were the IUPAC values of July, 1969.

B. Electrical Equipment and Cells

The resistance measurements of the aqueous rare earth electrolyte solutions were performed with a Jones conductivity bridge and its associated electronics. A description of this bridge and its operation is given by Dike (27). This bridge was purchased from Leeds and Northrup and was designed according to the recommendations of Jones and Josephs (3).

A small amount of shielding was used according to the recommendations of Shedlovsky (26). The alternating current source was an audio-frequency, vacuum tube, electronic oscillator which was adjustable to frequencies of 500, 1000, and 2000 cycles per second. A narrow-band, audio-frequency amplifier was used which was adjusted and tuned to the above three frequencies. The amplification gain was 8000 at 2000 c.p.s., 12,000 at 1000 c.p.s., and 35,000 at 500 c.p.s. The oscillator and amplifier were connected to the bridge through shielded and grounded transformers. The oscillator and amplifier were built by the Ames Laboratory Instrumentation Group. Their schematic diagrams can be found in Saeger and Spedding (68, p. 112). A Dumont type 303 Cathode Ray Oscilloscope was used as a null detector.

The bridge resistors were calibrated against Leeds and Northrup-type 4020-B, 4025-B, 4030-B and 4035-B standard resistors. These standards are manufactured according to National Bureau of Standards design and are stress relieved and aged for accuracy. In these resistors, the resistance element is sealed in a metal container filled with moisture free oil. Each standard is supplied with its report of calibration and its temperature coefficient data and is reported to be accurate to .001%.

The Jones Bridge contains resistors from .1 ohm to 10,000 ohms and can measure resistance directly to 60,000

ohms. Higher resistances can be measured by connecting them in parallel with 30,000 ohms of the bridge resistors. The 10, 100, 1000 and 10,000 ohm resistors were calibrated before and after all the conductance measurements were performed. The two measured resistance values of these bridge resistors agreed to at least .004% in all cases. The resistors were calibrated to .01 ohms and these values were used in all calculations to avoid round off errors since the actual solution resistances were only measured to .1 ohm. The .1 and 1 ohm resistors were calibrated only once since they are designed for stability and would require a huge change (at least 1% for the 1 ohm case) in their resistance in order to affect results. Resistor calibrations were reproducible to $\pm .0003\%$ from day to day.

The bridge ratio was reset every two dilution series, approximately 66 runs, since a very slight drift would occur over long periods of time. The total resistance of the leads and of the mercury pools used to connect the bridge to the conductance cell was measured on a Mueller Bridge. Their total resistance was applied as a correction to all readings. Capacitors were present in the bridge arms to balance out the electrode capacitance of the cell.

The conductance apparatus was operated in a thermostated room. The room temperature was constant to $25 \pm 4^\circ\text{C}$ (at worse) and the humidity was constant to $40 \pm 15\%$. Dike (27) lists the

probable errors from all sources for this bridge design. His values are listed in Table 2. My experimental error was therefore $\pm 0.01\%$ or less for each resistance measurement. Because of this limiting factor, the solution resistances were measured only to this accuracy.

Table 2. Measurement errors for resistances

SOURCE OF ERROR	ERROR
Equality of ratio arms	$\pm 0.0002\%$
Calibration error	$\pm 0.001\%$
Temperature coefficient of bridge resistors ($\pm 1^\circ$)	$\pm 0.0005\%$
Humidity effect on resistors ($\pm 5\%$)	$\pm 0.001\%$
Difference between D.C. and A.C. resistance values	$\pm 0.0006\%$

The constant temperature bath was filled with mineral oil and heated with an electrical resistor element controlled by an electronic relay. This relay was activated by a mercury thermoregulator consisting of an expanding mercury column contacting a movable platinum wire. The bath was cooled with tap water flowing through a copper coil. The water flow rate was held constant by use of a constant head

water tower. The bath oil was stirred with a propeller type stirrer.

The bridge to cell connection was made through two mercury filled cups dipping into the oil. These eliminate heat transfer between the room and cell via the leads connecting the cell to the bridge. If these mercury cups were removed from the bath oil, the scatter in data approximately doubled.

The bath temperature was measured with an Emerson calorimeter thermometer which had been calibrated against two different platinum resistance thermometers before and after all the conductance measurements were made. The bath temperature was controlled to $24.99 \pm 0.01^\circ\text{C}$. All the runs were made at the midpoint of the heating cycle, and the reproducibility of this temperature is to $.003^\circ\text{C}$ or better. As mentioned previously, most aqueous electrolytes have similar temperature coefficients so the temperature error should be less than .01%. All my resistances were measured to at least .01%.

A few of the very dilute chloride solutions were run in commercially available Leeds and Northrup cells. Nearly all of the conductances were measured in capillary cells of the type recommended by Jones and Bollinger (5). These cells were constructed from Pyrex glass and possessed a total volume of about 35 cm^3 . The electrode chambers were constructed from 30 mm glass tubing, and the capillary

portion was made from 3 mm tubing. The overall length of the cell was about 25 cm, that of the capillary portion was about 15 cm. This electrode separation is sufficient to eliminate the Parker effect. Saeger and Spedding (68, p.114) give a detailed drawing of this cell.

The solution filling tubes were made from 10/30 standard tapers and the cell was filled with solution using an eye dropper. These filling tubes were sealed during runs with rubber tubing containing a glass plug.

Electrical contact with the cell was made with mercury filled sidearms. These were connected to the mercury cups in the temperature bath by platinum leads. The cell electrodes consisted of platinum discs .25 mm thick and 1.6 cm in diameter. A short length of platinum wire was welded to these electrodes, and this wire was sealed into the glass wall of the electrode compartment and extended into the mercury filled sidearms. The electrodes were platinized according to the recommendations of Jones and Bollinger (9).

The KCl used to prepare the conductance standards was purified in the following manner. "Baker Analyzed" KCl was triple recrystallized from conductance water (with cooling) with about an 80% recovery of KCl at each step. This KCl was then oven dried at 110°C and placed in a platinum crucible. This crucible was then positioned in an induction

furnace under vacuum. The KCl was slowly heated and continuous pumping applied to keep the vapor pressure inside the inductance furnace at about 10^{-5} torr until the temperature was near the fusion point of KCl. The salt was then fused about 20 minutes and allowed to cool for about $\frac{1}{2}$ hour. The induction furnace was then back filled with argon and the crucible allowed to cool to room temperature. This sample was then placed in a desiccator and stored over anhydrous $\text{Mg}(\text{ClO}_4)_2$.

Two separate .1 N and two separate 1 N KCl standards were prepared according to the directions of Jones and Prendergast (10). Their conductances were corrected to absolute ohms. Two capillary cells were used in this research and one was calibrated with all four standards to obtain a cell constant of $274.89 \pm 0.02 \text{ cm}^{-1}$. A second cell was calibrated with four solutions previously measured in the other capillary cell and $253.50 \pm 0.02 \text{ cm}^{-1}$ was obtained for this cell constant. No Parker effect was observed for these cells.

C. Operational Procedure

The cell was thoroughly rinsed with the solution to be run, and then filled with this solution and placed in the constant temperature bath. The solution in the cell was allowed to equilibrate for at least 30 minutes before the

resistance was measured. No systematic variation of resistance with time could then be observed, indicating that thermal equilibrium had been established. At least two samples, and usually four samples, of each solution were run. When calibrating the cell, four or five samples of each standard were run. The average deviation of the resistance readings from the mean was generally less than .01% and almost always less than .02%. All resistances were measured at 500, 1000 and 2000 c.p.s. The average resistance value obtained for these three frequencies was used in all calculations and it differed by .005% or less from the resistance at infinite frequency as obtained from Warburg's law. The frequency dependence of the resistance was small enough and similar enough for solutions and standards so that no correction to infinite frequency was necessary.

The voltages used in measuring the resistances ranged from .24 to .32 volts. This is low enough to avoid reduction of H^+ and oxidation of the platinum electrodes.

Freshly prepared rare earth perchlorate solutions show some tendency to chemically attack the platinum electrodes. When this occurred the frequency dependence of the resistance changed from .005% to several tenths of a percent. Resistance readings were unreliable when the electrodes were in this state. It was found that prolonged soaking of the cell electrodes with concentrated HCl, followed by soaking

in conductance water, would control this problem. Most of the $\text{Er}(\text{ClO}_4)_3$ dilutions and some of the $\text{La}(\text{ClO}_4)_3$ dilutions were run using this treatment.

A sample of the HCl used to soak the electrodes was analyzed by emission spectroscopy, and the presence of platinum ions ascertained. The presence of this platinum was to be expected if the perchlorate solutions were oxidizing the electrode surface to form a thin film of platinum oxides. It was found that treatment of the electrodes with acidified FeSO_4 for 30 minutes would reduce these oxides back to metallic platinum. The FeSO_4 treatment was followed by soaking the cell with 5 normal HCl, followed by soaking with conductance water. If this procedure was followed after each perchlorate solution was run, then the electrode attack problem could be completely controlled and had no effect on the resistance measurement. This treatment was used for the remaining perchlorate solutions.

It was possible that the repeated HCl extractions had altered the cell constant of one of the cells by removing small amounts of electrode platinum. This cell was therefore recalibrated after 25 perchlorate solutions had been run with HCl extractions. No detectable change was observed in the value of the cell constant. This was not too surprising since the cell constant of a capillary cell is dependent mostly on the capillary dimensions, and only slightly dependent on the electrode geometry.

This perchlorate solution attack on electrodes was general for freshly prepared solutions, less than two years old or so, but was absent in the well aged $\text{Gd}(\text{ClO}_4)_3$ and $\text{Lu}(\text{ClO}_4)_3$ solutions. If small amounts of perchlorate ion reduction had occurred in these older solutions (five years of age or more) then the presence of Cl^- ions would be expected. No trace of Cl^- was found. At present, no convincing reason can be given for the "passive nature" of the well aged perchlorate solutions. It is possible, however, that the electrode oxidation is catalyzed by the initial presence of a chemical species occurring in very small amounts and which transforms after prolonged aging into a non-catalyzing chemical species.

III. CALCULATIONS, ERRORS AND DATA TABLES

Consider an alternating current flowing through an electrolyte solution and obeying Ohm's law. The conductivity of this solution is $L_m = \frac{k}{R}$. Except for the double layer charging and discharging, which is compensated for, nearly all the electrical current is carried by the migration of ions in solution. A small amount of current is carried by the conductivity of the solvent used to dissolve the electrolyte. Let the actual specific conductivity of the electrolyte in solution be L , the measured specific conductance L_m , the weight fraction of solvent in the solution X , and the solvent conductivity L_s . Then,

$$L = L_m - X \cdot L_s \quad (3.1)$$

This correction is quite small for aqueous solutions and does not effect the conductivity values except for very dilute solutions.

Due to hydrolysis, the rare earth electrolyte solutions are somewhat acid. For very dilute solutions, this hydrogen ion contribution to the conductivity may become important, but for solutions at the concentrations studied in this research, this contribution can be neglected. The mobility of the hydrogen ion is quite large in dilute solutions but decreases rapidly with increasing

concentration. In concentrated solutions, any correction for this effect would be small and highly arbitrary since little is known of the hydrogen ion mobility in concentrated electrolyte solutions.

The equivalent conductance, Λ , of a solution is defined as the conductance of this solution due to the presence of one gram equivalent of electrolyte. The normality, N , of a solution is its concentration in terms of gram equivalents of electrolyte per liter of solution. For rare earth electrolyte solutions, a gram equivalent is one-third of a gram mole of the electrolyte.

Consider a function Y which is not measured directly but which is calculated from a set of measured quantities $\{Y_i\}$ which possess errors $\{\delta Y_i\}$. If each error is small relative to its corresponding Y_i , then

$$\delta Y = \sum_{i=1}^N \frac{\partial Y}{\partial Y_i} \delta Y_i \quad (3.2)$$

If these errors are uncorrelated and random, then

$$(\delta Y)^2 = \sum_{i=1}^N \left(\frac{\partial Y}{\partial Y_i}\right)^2 \delta Y_i^2 \quad (3.3)$$

and the root mean square relative error is

$$\sqrt{\left(\frac{\delta Y}{Y}\right)^2} = \frac{1}{Y} \sqrt{\sum_{i=1}^N \left(\frac{\partial Y}{\partial Y_i}\right)^2 \delta Y_i^2} \quad (3.4)$$

If the errors δY_1 are the standard deviations σ_{Y_1} , then the standard deviation in Y is obtained. This approach discussed in more detail in Bevington (69).

Consider a function of the form

$$Y = Y_1^\alpha Y_2^\beta Y_3^\gamma \dots$$

where $\alpha, \beta, \gamma \dots$ are real numbers, then

$$\ln Y = \alpha \ln Y_1 + \beta \ln Y_2 + \gamma \ln Y_3 + \dots \quad (3.5)$$

Differentiating gives

$$\frac{\delta Y}{Y} = \alpha \frac{\delta Y_1}{Y_1} + \beta \frac{\delta Y_2}{Y_2} + \gamma \frac{\delta Y_3}{Y_3} + \dots \quad (3.6)$$

and

$$\sqrt{\left(\frac{\delta Y}{Y}\right)^2} = \sqrt{\alpha^2 \left(\frac{\delta Y_1}{Y_1}\right)^2 + \beta^2 \left(\frac{\delta Y_2}{Y_2}\right)^2 + \gamma^2 \left(\frac{\delta Y_3}{Y_3}\right)^2 + \dots} \quad (3.7)$$

Now consider a dilution being prepared by adding A grams of stock solution of molality m_s to B grams of conductance water, with both weights corrected to vacuum. Let m be the molality of this dilution and M be the molecular weight of the electrolyte being studied. Then,

$$m = \frac{10^3 A \left(\frac{m_s}{10^3 + m_s M}\right)}{B + A \left(\frac{10^3}{10^3 + m_s M}\right)} = \frac{10^3 A m_s}{10^3 (A + B) + m_s M B} \quad (3.8)$$

The error in each dilution molality, δm , depends on the weighing errors δA and δB , the stock solution analysis error δm_s and the molecular weight error δM . Thus,

$$\ln m = 3 \ln 10 + \ln A + \ln m_s - \ln\{10^3(A+B) + m_s MB\} \quad (3.9)$$

and

$$\frac{\delta m}{m} = \frac{\delta A}{A} + \frac{\delta m_s}{m_s} - \frac{\delta\{10^3(A+B) + m_s MB\}}{\{10^3(A+B) + m_s MB\}} \quad (3.10)$$

Expanding gives

$$\delta\{10^3(A+B) + m_s MB\} = 10^3(\delta A + \delta B) + m_s M \delta B + m_s B \delta M + MB \delta m_s \quad (3.11)$$

If the weighing errors δA and δB are assumed to be equal, then

$$\delta\{10^3(A+B) + m_s MB\} = (2 \times 10^3 + m_s M) \delta A + m_s B \delta M + MB \delta m_s \quad (3.12)$$

After substituting this into equation 3.10 and squaring, one obtains

$$\sqrt{\left(\frac{\delta m}{m}\right)^2} = \frac{\sqrt{(B-A)^2(10^3 + m_s M)^2\left(\frac{\delta A}{A}\right)^2 + 10^6(A+B)^2\left(\frac{\delta m_s}{m_s}\right)^2 + m_s^2 B^2(\delta M)^2}}{\{10^3(A+B) + m_s MB\}^2} \quad (3.13)$$

A computer program was written to evaluate this function for all of my dilutions. The values of M and δM used were those adopted by the IUPAC in July, 1969. The values of δm_s used were the average deviations from the mean of the independent analyses of the stocks. As stated previously, $\% \delta m_s = .1\%$ or less in all cases. By letting $\delta m_s = 0$, the self-consistence of the dilution data, relative to the stock solution, could be obtained. Except for the two or three most dilute solutions of each electrolyte, the weighing errors make a negligible contribution to the total error.

Now consider a solution of molality m possessing an equivalent conductance Λ ($\text{cm}^2\text{-ohms}^{-1}$) and again let the corrected specific conductance be L and the molecular weight of the salt M (g/mole). Let N be the normality of the solution and d be its density (g/cm^3). Since $N = \frac{3md}{1+10^{-3}mM}$ and $\Lambda = \frac{10^3 L}{N}$, then

$$\Lambda = \frac{L(10^3+mM)}{3md} . \quad (3.14)$$

$$\ln \Lambda = \ln L + \ln(10^3+mM) - \ln 3 - \ln(md) \quad (3.15)$$

and

$$\frac{\delta \Lambda}{\Lambda} = \frac{\delta L}{L} + \frac{\delta(10^3+mM)}{10^3+mM} - \frac{\delta(md)}{md} . \quad (3.16)$$

However,

$$\delta(10^3 + mM) = \delta(mM) = m\delta M + M\delta m \quad (3.17)$$

so

$$\frac{\delta\Lambda}{\Lambda} = \frac{\delta L}{L} + \frac{m\delta M + M\delta m}{10^3 + mM} - \frac{\delta(md)}{md} \quad (3.18)$$

Density data of Spedding and co-workers¹ (average of 18-20 concentrations per salt) were fitted to fifth order polynomials in terms of molality using equal weights for all points. This is sufficiently accurate for the calculations of equivalent conductances since it is not necessary to use the full accuracy of their data. The mean absolute deviation was typically less than 10^{-4} g/cm³ for this type of fit. These fifth order density fits were used to calculate the densities needed in obtaining the equivalent conductances of all the dilutions. For the time being, it shall be assumed that there is no error in the density coefficients. Then,

$$\delta(md) = \delta\left(\sum_{i=0}^5 A_i m^{i+1}\right) = \delta m \sum_{i=0}^5 A_i (i+1) m^i \quad (3.19)$$

so

$$\frac{\delta\Lambda}{\Lambda} = \frac{\delta L}{L} + \frac{m\delta M + M\delta m}{10^3 + mM} - \frac{\delta m \sum_{i=0}^5 A_i (i+1) m^i}{\sum_{i=0}^5 A_i m^{i+1}} \quad (3.20)$$

¹F. H. Spedding and co-workers, Iowa State University, Ames, Iowa. Private communication. 1972.

Our root mean square relative error is therefore

$$\sqrt{\left(\frac{\delta\Lambda}{\Lambda}\right)^2} = \sqrt{\left(\frac{\delta L}{L}\right)^2 + \left(\frac{m\delta M + M\delta m}{10^3 + mM}\right)^2 + \left(\frac{\delta m \sum_{i=0}^5 A_i (i+1)m^i}{\sum_{i=0}^5 A_i m^{i+1}}\right)^2} \quad (3.21)$$

The assumption of $\{\delta A_i = 0\}$ is a good approximation if the densities and conductances were measured with the same set of dilutions. If this is indeed the case, then the conductances and densities are self-consistent. For most cases it was necessary to use density data measured on independently prepared solutions. The errors in the A_i 's were then assumed to be due to a stock solution analysis error equal in magnitude to that obtained for the solutions used in measuring the conductance. This is equivalent to letting $\sum A_i (i+1)m^i$ in equation 3.21 be replaced by $\sum A_i (2i+1)m^i$. This approximation should cause no serious errors and the results for $\delta\Lambda$ will be ordered in the same manner as if a rigorous treatment were used. The values of δm used in this calculation were those obtained from equation 3.13. The values used for δL were the experimental average deviations from the experimental mean and were not corrected for the uncertainty of the cell constant k . The contribution of δL to $\delta\Lambda$ is .1% or less

(obtained by letting $\delta L=0$), and the approximations used in obtaining $\delta(\text{md})$ would not warrant the use of more accurate δL values. A computer program was written to evaluate $\sqrt{\left(\frac{\delta \Lambda}{\Lambda}\right)^2}$ for all of the solutions. The rare earth electrolyte solutions above .05 molal in concentration have mean deviations in δL of .02% or less for nearly all solutions. The solutions below .05 molal in concentration have very high resistivities, causing the sensitivity of the bridge measurements to decrease. By .015 molal, it was necessary to measure the resistance of the solutions by placing the cell in parallel with 30,000 ohms of the bridge resistors. This results in a loss of a significant figure in L which is therefore reliable only to $\pm .2\%$ for these very dilute solutions. The dilute solution conductivities were measured only to compare this work with previously measured accurate dilute solution conductivities.

Electrical conductivities for dilute solutions (.04 molal or less) of most of the rare earth electrolytes measured in this research can be found in Spedding and Atkinson's review article in "The Structure of Electrolyte Solutions" (70, p. 322). This research's very dilute data is good only to .2% while the data of Spedding and Atkinson is reported good to .1%; therefore, agreement of .3% or better should be expected between all the sets of dilute data. Graphical comparison of the dilute data indicated that, except for

the $\text{La}(\text{ClO}_4)_3$ data, all sets agreed within this limit. The $\text{La}(\text{ClO}_4)_3$ data disagreed by about .4%. An additional EDTA was performed on the secondary stock and the results agreed well with the previous EDTA and sulfate analyses. This indicated that the major error probably lies in the other dilute work.

The conductivity data for all the solutions is reported in Tables 3 through 25 where Λ is in terms of $\text{cm}^2\text{-}(\text{absolute-ohms})^{-1}$. Some typical values of δm and δL are listed in Table 26 at various experimental concentrations. The error values for $\text{Sm}(\text{ClO}_4)_3$ are some of the largest obtained and are probably an overestimation. The ultimate aim in obtaining the $\delta\Lambda$ values is to use them in obtaining empirical fits for my data and this will be done in the section on Discussion of Results.

Table 3. PrCl₃ conductivities

m	N	L	Λ
3.8940	10.217	.075990	7.438
3.6143	9.5926	.090570	9.442
3.2936	8.8562	.10920	12.331
2.7610	7.5826	.13966	18.419
2.4905	6.9112	.15350	22.211
2.2371	6.2672	.16419	26.199
2.0048	5.6641	.17119	30.223
1.7701	5.0426	.17477	34.658
1.5714	4.5071	.17451	38.718
1.4376	4.1417	.17235	41.614
1.2731	3.6873	.16734	45.385
1.1636	3.3817	.16234	48.006
.94244	2.7572	.14792	53.649
.85263	2.5009	.14011	56.024
.71524	2.1059	.12635	60.001
.64509	1.9029	.11825	62.142
.56677	1.6752	.10833	64.666
.48051	1.4233	.096280	67.645
.41007	1.2167	.085516	70.287
.31827	.94627	.070152	74.135
.29774	.88563	.066475	75.061
.24692	.73526	.057089	77.645
.18443	.54988	.044618	81.141
.12385	.36969	.031639	85.582
.096413	.28794	.025416	88.270
.069136	.20658	.018929	91.632
.049715	.14860	.014105	94.920
.030497	.091185	.0090919	99.708
.017169	.051346	.0054201	105.56
.002293	.006859	.0008563	124.9
.001612	.004822	.0006152	127.6
.0009702	.002902	.0003805	131.1

Table 4. EuCl_3 conductivities

m	N	L	Λ
3.5864	9.5429	.091096	9.547
3.2418	8.7488	.10950	12.516
2.9119	7.9614	.12743	16.007
2.7272	7.5094	.13711	18.260
2.4974	6.9360	.14816	21.362
2.2385	6.2758	.15862	25.277
2.0476	5.7794	.16436	28.439
1.8485	5.2534	.16827	32.032
1.5733	4.5125	.16893	37.437
1.3765	3.9731	.16546	41.646
1.2467	3.6130	.16132	44.652
1.1021	3.2080	.15424	48.080
1.0080	2.9423	.14863	50.516
.96379	2.8169	.14572	51.731
.76294	2.2425	.12859	57.345
.74885	2.2019	.12717	57.759
.66193	1.9509	.11800	60.485
.56349	1.6650	.10605	63.700
.52213	1.5444	.10056	65.113
.42273	1.2534	.086265	68.823
.35437	1.0524	.075370	71.616
.29797	.88605	.065767	74.225
.24953	.74280	.056942	76.659
.20697	.61666	.048719	79.004
.16329	.48696	.039856	81.846
.12768	.38103	.032224	84.612
.098231	.29332	.025639	87.409
.071575	.21383	.019392	90.688
.050366	.15053	.014183	94.222
.030682	.091732	.0090977	99.177
.007747	.02317	.002617	113.0
.002471	.007392	.0009117	123.3
.001577	.004717	.0005987	126.9

Table 5. $TbCl_3$ conductivities

m	N	L	Λ
3.5727	9.4846	.086175	9.086
3.3716	9.0225	.096418	10.686
2.9214	7.9576	.11951	15.019
2.6335	7.2536	.11352	18.404
2.3097	6.4400	.14731	22.875
2.0407	5.7465	.15587	27.124
1.7923	5.0919	.16048	31.517
1.5943	4.5605	.16124	35.356
1.3913	4.0071	.15883	39.638
1.2291	3.5586	.15426	43.347
1.1300	3.2820	.15016	45.753
1.0295	2.9995	.14484	48.287
.94148	2.7504	.13924	50.627
.81353	2.3856	.12937	54.231
.68389	2.0128	.11708	58.169
.58546	1.7278	.10611	61.417
.51801	1.5315	.097713	63.804
.46428	1.3745	.090433	65.793
.37683	1.1181	.077517	69.332
.33109	.98343	.070134	71.315
.31856	.94650	.068099	71.948
.28125	.83637	.061639	73.697
.23356	.69531	.052986	76.205
.19211	.57244	.045071	78.734
.15731	.46910	.038061	81.137
.12290	.36675	.030778	83.918
.095844	.28617	.024790	86.627
.067065	.20036	.018096	90.320
.048459	.14483	.013559	93.615
.026771	.080043	.0079698	99.569
.018592	.055597	.0057392	103.23
.007590	.02270	.002545	112.1

Table 6. HoCl_3 conductivities

m	N	L	Λ
3.6965	9.7856	.075071	7.671
3.2283	8.7094	.098631	11.325
2.9675	8.0885	.11178	13.819
2.3863	6.6497	.13892	20.891
2.2545	6.3129	.14397	22.805
1.9208	5.4430	.15367	28.231
1.7083	4.8765	.15665	32.125
1.5230	4.3746	.15674	35.832
1.3584	3.9228	.15449	39.382
1.0341	3.0164	.14234	47.186
1.0264	2.9947	.14193	47.393
.87327	2.5593	.13194	51.551
.68301	2.0123	.11526	57.275
.63570	1.8753	.11027	58.804
.52824	1.5626	.097669	62.505
.47059	1.3940	.090206	64.709
.37286	1.1071	.076047	68.691
.37141	1.1028	.075759	68.696
.35063	1.0416	.072565	69.666
.31781	.94481	.067248	71.178
.25632	.76303	.056672	74.272
.20827	.62061	.047808	77.034
.17576	.52408	.041474	79.137
.13615	.40629	.033364	82.119
.10408	.31077	.026432	85.051
.073847	.22062	.019564	88.674
.055137	.16478	.015101	91.642
.032382	.096814	.0093867	96.956
.018763	.056110	.0057491	102.46
.008768	.02622	.002891	110.3
.002782	.008322	.001005	120.8

Table 7. TmCl_3 conductivities

m	N	L	A
3.8794	10.253	.063031	6.148
3.7390	9.9384	.069443	6.987
3.1922	8.6702	.095871	11.057
2.9236	8.0223	.10938	13.635
2.4650	6.8787	.13175	19.152
2.2823	6.4103	.13955	21.769
1.7935	5.1218	.15349	29.967
1.7888	5.1091	.15355	30.054
1.4854	4.2839	.15481	36.137
1.3449	3.8955	.15281	39.226
1.2476	3.6242	.15039	41.496
1.0319	3.0163	.14141	46.882
.98391	2.8799	.13871	48.168
.91452	2.6818	.13429	50.074
.83074	2.4416	.12807	52.455
.70100	2.0671	.11666	56.438
.60106	1.7768	.10613	59.733
.52951	1.5679	.097624	62.264
.44371	1.3164	.086266	65.532
.36289	1.0785	.074328	68.920
.32967	.98042	.069044	70.422
.32303	.96081	.067932	70.702
.27634	.82270	.060113	73.068
.22684	.67598	.051187	75.724
.15323	.45724	.036849	80.590
.11868	.35435	.029575	83.459
.090174	.26937	.023281	86.427
.065896	.19692	.017662	89.687
.047256	.14126	.013143	93.040
.028584	.085471	.0083843	98.094
.015853	.047413	.0049304	104.00
.007927	.02371	.002628	110.8
.002130	.006372	.0007818	122.7

Table 8. LuCl_3 conductivities

m	N	L	Λ
4.1202	10.840	.050257	4.636
3.3136	8.9954	.086593	9.626
3.1706	8.6539	.094073	10.870
2.6389	7.3445	.12131	16.517
2.4863	6.9571	.12864	18.491
2.1924	6.1967	.14107	22.766
1.9364	5.5193	.14913	27.020
1.7013	4.8853	.15339	31.397
1.5051	4.3478	.15401	35.422
1.3348	3.8751	.15190	39.198
1.1805	3.4421	.14760	42.882
1.0677	3.1228	.14282	45.735
1.0016	2.9346	.13936	47.490
.93824	2.7535	.13552	49.216
.76013	2.2408	.12196	54.427
.63309	1.8719	.10953	58.514
.54650	1.6190	.099618	61.532
.48677	1.4439	.092044	63.748
.43335	1.2868	.084736	65.848
.33647	1.0011	.070109	70.034
.31540	.93876	.066663	71.012
.29284	.87197	.062904	72.140
.26665	.79437	.058371	73.481
.22308	.66508	.050497	75.927
.18442	.55018	.043103	78.344
.15081	.45015	.036362	80.778
.11652	.34799	.029126	83.700
.090910	.27161	.023466	86.396
.064182	.19183	.017274	90.047
.048749	.14573	.013526	92.813
.028326	.084703	.0083269	98.308
.016256	.048618	.0050545	103.97
.007168	.02144	.002403	112.1

Table 9. $\text{La}(\text{ClO}_4)_3$ conductivities

m	N	L	Λ
4.7601	9.0839	.031627	3.482
4.1325	8.3136	.051900	6.243
3.7787	7.8392	.067334	8.589
3.3414	7.2084	.089973	12.482
2.9588	6.6119	.11196	16.933
2.4797	5.7985	.13893	23.960
2.1110	5.1160	.15563	30.419
1.8072	4.5126	.16426	36.399
1.5541	3.9794	.16643	41.821
1.3627	3.5567	.16422	46.172
1.1545	3.0768	.15755	51.204
1.0522	2.8332	.15239	53.789
.99194	2.6871	.14873	55.350
.90266	2.4673	.14240	57.714
.72170	2.0089	.12606	62.747
.58850	1.6602	.11074	66.703
.51504	1.4637	.10108	69.054
.44558	1.2752	.090984	71.351
.39624	1.1396	.083269	73.070
.30897	.89637	.068448	76.362
.28647	.83297	.064367	77.275
.26246	.76498	.059898	78.299
.24192	.70656	.055965	79.207
.20045	.58787	.047734	81.198
.16508	.48584	.040380	83.113
.13609	.40168	.034096	84.884
.10416	.30841	.026898	87.215
.077773	.23089	.020702	89.661
.054750	.16291	.015066	92.481
.041848	.12468	.011803	94.670
.024851	.074164	.0073262	98.783
.014288	.042685	.0044098	103.31
.006586	.01969	.002165	109.9
.002463	.007367	.0008623	117.0

Table 10a. Pr(CIO₄)_s conductivities

m	N	L	A
4.6955	9.1010	.030515	3.353
4.2554	8.5521	.044460	5.199
3.8618	8.0271	.061252	7.630
3.3977	7.3580	.085298	11.593
2.9300	6.6202	.11271	17.025
2.5083	5.8934	.13688	23.227
2.1498	5.2247	.15379	29.434
1.7729	4.4667	.16467	36.864
1.5207	3.9258	.16619	42.332
1.3410	3.5229	.16374	46.479
1.1192	3.0045	.15595	51.904
1.0165	2.7564	.15033	54.541
.95288	2.6000	.14616	56.215
.87329	2.4014	.14017	58.369
.70958	1.9827	.12489	62.987
.57260	1.6215	.10883	67.117
.50424	1.4374	.099638	69.316
.45232	1.2959	.092069	71.045
.38204	1.1020	.081025	73.523
.31537	.91557	.069642	76.064
.27798	.80992	.062847	77.596
.25640	.74859	.058788	78.532
.23516	.68797	.054681	79.482
.19507	.57287	.046630	81.398
.16068	.47341	.039442	83.314
.13103	.38714	.032987	85.209
.099670	.29535	.025865	87.575
.079351	.23559	.021097	89.551
.055838	.16614	.015346	92.364
.041697	.12423	.011758	94.648
.023947	.071465	.0070866	99.161
.013848	.041366	.004288	103.66
.007391	.02209	.002406	108.9
.002443	.007305	.0008590	117.6

Table 10b. Nd(ClO₄)₃ conductivities

m	N	L	A
4.6851	9.1154	.029970	3.288
4.2395	8.5589	.043844	5.123
3.9530	8.1762	.055559	6.795
3.7491	7.8914	.065162	8.257
3.5328	7.5774	.076433	10.087
3.1215	6.9442	.10005	14.408
2.5811	6.0329	.13195	21.872
2.0850	5.1058	.15562	30.478
1.6785	4.2732	.16544	38.715
1.4542	3.7830	.16535	43.708
1.1903	3.1765	.15892	50.029
1.0720	2.8937	.15339	53.009
.99606	2.7086	.14891	54.977
.92506	2.5328	.14404	56.867
.76329	2.1228	.13024	61.350
.58948	1.6672	.11092	66.534
.51453	1.4657	.10100	68.908
.45384	1.3004	.092275	70.960
.40874	1.1762	.085301	72.521
.30097	.87508	.067038	76.609
.28681	.83503	.064503	77.246
.27150	.79161	.061644	77.872
.20048	.58851	.047824	81.263
.16545	.48730	.040530	83.174
.13471	.39792	.033840	85.042
.10355	.30678	.026797	87.348
.079608	.23638	.021173	89.572
.058692	.17462	.016067	92.011
.042463	.12653	.011970	94.600
.027730	.082745	.0081108	98.022
.016545	.049422	.0050574	102.3
.008163	.02440	.002641	108.2
.003460	.01035	.001191	115.1

Table 11. $\text{Sm}(\text{ClO}_4)_3$ conductivities

m	N	L	A
4.6401	9.1042	.032558	3.576
4.3237	8.7167	.042140	4.834
4.0056	8.2975	.054820	6.606
3.4331	7.4701	.083502	11.178
3.0512	6.8649	.10570	15.396
2.5596	6.0181	.13367	22.211
2.2444	5.4312	.14902	27.439
1.9425	4.8341	.15967	33.030
1.6935	4.3139	.16404	38.026
1.4443	3.7667	.16371	43.461
1.2863	3.4052	.16054	47.144
1.1070	2.9809	.15361	51.530
.94681	2.5888	.14419	55.698
.87587	2.4110	.13910	57.695
.74740	2.0827	.12762	61.279
.61162	1.7265	.11277	65.315
.49806	1.4212	.097999	68.953
.44158	1.2669	.089762	70.854
.37525	1.0834	.079361	73.253
.34002	.98496	.073459	74.581
.27571	.80356	.062042	77.208
.24968	.72950	.057162	78.359
.22746	.66598	.052881	79.403
.21194	.62145	.049777	80.098
.14363	.42389	.035580	83.936
.11625	.34398	.029530	85.849
.092447	.27416	.024067	87.786
.074189	.22040	.019752	89.623
.048855	.14549	.013531	93.001
.037135	.11071	.010539	95.191
.021629	.064575	.0064278	99.539
.013142	.039268	.004071	103.7
.006148	.01838	.002020	109.9
.001892	.005659	.0006714	118.7

Table 12. $Gd(ClO_4)_3$ conductivities

m	N	L	Λ
4.6089	9.0860	.034784	3.828
4.2847	8.6759	.045363	5.229
3.4541	7.4998	.082843	11.046
2.7879	6.4153	.11953	18.633
2.4762	5.8594	.13562	23.145
2.1764	5.2926	.14851	28.060
1.8131	4.5601	.15857	34.776
1.5518	3.9999	.16055	40.138
1.3695	3.5915	.15862	44.166
1.1561	3.0942	.15227	49.210
1.0517	2.8431	.14734	51.827
.98816	2.6877	.14369	53.463
.90761	2.4878	.13831	55.596
.72293	2.0171	.12260	60.777
.58365	1.6506	.10730	65.010
.51002	1.4526	.097884	67.384
.44433	1.2736	.088674	69.626
.36636	1.0580	.076675	72.469
.30523	.88670	.066408	74.893
.24973	.72937	.056397	77.323
.24299	.71014	.055109	77.604
.20812	.61028	.048406	79.317
.17076	.50253	.040876	81.339
.13991	.41297	.034366	83.219
.11426	.33809	.028755	85.052
.089119	.26457	.023071	87.202
.070281	.20884	.018624	89.178
.048503	.14443	.013310	92.156
.037602	.11208	.010560	94.214
.021050	.062845	.0062144	98.883
.013309	.039764	.004081	102.6
.005762	.01723	.001884	109.4
.001909	.005710	.0006713	117.6

Table 13. $\text{Dy}(\text{ClO}_4)_3$ conductivities

m	N	L	Λ
4.6016	9.0712	.035101	3.870
4.3166	8.7042	.043854	5.038
4.0445	8.3377	.054040	6.481
3.7833	7.9696	.065208	8.182
3.5372	7.6072	.076794	10.095
3.1416	6.9900	.096972	13.873
2.5615	5.9997	.12670	21.118
2.0865	5.1040	.14607	28.618
1.6799	4.2691	.15471	36.240
1.4556	3.7790	.15480	40.964
1.1902	3.1702	.14932	47.101
1.1006	2.9571	.14579	49.300
1.0686	2.8801	.14428	50.095
.92387	2.5255	.13610	53.891
.74582	2.0747	.12219	58.895
.58852	1.6626	.10591	63.704
.50903	1.4493	.096106	66.313
.44582	1.2772	.087497	68.507
.40207	1.1568	.081078	70.087
.30968	.89907	.066308	73.751
.28378	.82596	.061795	74.816
.26267	.76609	.058072	75.803
.24411	.71324	.054650	76.622
.20005	.58701	.046289	78.855
.16316	.48047	.038887	80.934
.13304	.39292	.032578	82.914
.10450	.30948	.026326	85.067
.080631	.23933	.020892	87.293
.058400	.17372	.015546	89.489
.040460	.12056	.011202	92.921
.025323	.075563	.0073069	96.700
.015589	.046560	.004691	100.7
.006224	.01861	.002018	108.5
.002541	.007599	.0008750	115.2

Table 14. $\text{Ho}(\text{ClO}_4)_3$ conductivities

m	N	L	A
4.6241	9.1064	.033091	3.633
4.1273	8.4618	.049541	5.854
3.7836	7.9820	.063798	7.993
3.5263	7.6029	.075755	9.964
3.0797	6.9013	.098394	14.257
2.5258	5.9459	.12611	21.208
2.2180	5.3699	.13918	25.919
1.8111	4.5537	.15064	33.080
1.5396	3.9716	.15303	38.530
1.3653	3.5809	.15158	42.331
1.1299	3.0313	.14521	47.904
1.0319	2.7947	.14080	50.380
.96045	2.6192	.13686	52.254
.88744	2.4372	.13210	54.202
.72021	2.0103	.11857	58.984
.56522	1.6016	.10214	63.774
.50131	1.4293	.094186	65.898
.43328	1.2435	.084972	68.334
.30245	.87901	.064546	73.429
.27521	.80194	.059865	74.649
.25818	.75354	.056808	75.387
.23700	.69313	.052972	76.423
.19319	.56738	.044627	78.655
.15797	.46550	.037584	80.739
.12819	.37881	.031344	82.742
.099953	.29616	.025152	84.926
.076742	.22789	.019869	87.186
.054083	.16095	.014493	90.048
.038407	.11446	.010625	92.825
.023936	.071433	.0069038	96.647
.016198	.048376	.0048292	99.827
.005787	.017300	.001874	108.3
.002712	.008110	.0009241	113.9

Table 15. $\text{Er}(\text{ClO}_4)_3$ conductivities

m	N	L	A
4.6185	9.1195	.031250	3.427
3.9158	8.1838	.056215	6.869
3.5742	7.6872	.071617	9.317
3.1769	7.0700	.091481	12.939
2.7546	6.3622	.11333	17.813
2.3065	5.5465	.13418	24.191
2.0137	4.9743	.14462	29.073
1.7258	4.3789	.15080	34.438
1.4729	3.8273	.15194	39.699
1.2861	3.4018	.14938	43.913
1.0795	2.9123	.14259	48.959
1.0047	2.7301	.13889	50.875
.91766	2.5145	.13377	53.199
.85285	2.3516	.12936	55.010
.68041	1.9076	.11452	60.035
.54537	1.5490	.099639	64.325
.47511	1.3586	.090659	66.731
.42387	1.2180	.083550	68.594
.38810	1.1191	.078205	69.884
.27227	.79381	.059269	74.664
.26836	.78270	.058565	74.824
.23406	.68489	.052356	76.444
.22952	.67190	.051501	76.650
.18754	.55119	.043474	78.872
.15399	.45402	.036708	80.851
.12728	.37621	.031093	82.647
.096027	.28467	.024243	85.162
.074917	.22253	.019417	87.255
.053719	.15988	.014389	89.996
.038499	.11474	.010636	92.698
.023496	.070125	.0067802	96.687
.013958	.041695	.004208	100.9
.006354	.01899	.002039	107.4
.002245	.006714	.0007721	115.0

Table 16. $\text{Lu}(\text{ClO}_4)_3$ conductivities

m	N	L	Λ
4.6335	9.1856	.027201	2.961
4.3003	8.7614	.037404	4.269
3.9583	8.2949	.050228	6.055
3.5666	7.7217	.067492	8.740
3.2179	7.1754	.084869	11.828
2.7787	6.4358	.10778	16.747
2.3356	5.6263	.12915	22.954
2.0230	5.0130	.14096	28.119
1.6980	4.3351	.14841	34.234
1.4753	3.8452	.14962	38.911
1.2922	3.4261	.14759	43.079
1.1042	2.9797	.14209	47.687
1.0037	2.7342	.13752	50.299
.89928	2.4739	.13145	53.133
.81701	2.2650	.12564	55.466
.68867	1.9324	.11455	59.278
.54296	1.5445	.098776	63.953
.47633	1.3635	.090324	66.246
.45625	1.3084	.087605	66.955
.41197	1.1863	.081379	68.597
.35869	1.0381	.073344	70.655
.31048	.90257	.065563	72.641
.26317	.76841	.057420	74.726
.23785	.69611	.052861	75.938
.19617	.57634	.045000	78.079
.15965	.47063	.037750	80.212
.13150	.38865	.031904	82.091
.099270	.29427	.024906	84.637
.076265	.22655	.019686	86.892
.054738	.16292	.014607	89.653
.040281	.12005	.011067	92.187
.022335	.066676	.0064656	96.971
.013977	.041757	.004208	100.8
.005954	.01780	.001917	107.7
.002228	.006663	.0007670	115.1

Table 17. $\text{La}(\text{NO}_3)_3$ conductivities

m	N	L	A
4.6100	10.020	.020369	2.033
4.3745	9.6632	.023665	2.449
4.0664	9.1768	.028622	3.119
3.8371	8.7994	.032865	3.735
3.2723	7.8108	.045238	5.791
2.8333	6.9797	.056739	8.129
2.3930	6.0858	.069494	11.419
2.1015	5.4584	.078080	14.305
1.8216	4.8278	.085818	17.775
1.5524	4.1944	.091984	21.930
1.4026	3.8301	.094466	24.665
1.3339	3.6601	.095298	26.036
1.1991	3.3214	.096206	28.965
.96157	2.7074	.094816	35.020
.78516	2.2372	.090441	40.427
.68959	1.9773	.086522	43.757
.60440	1.7428	.081932	47.012
.52852	1.5314	.076846	50.178
.40486	1.1824	.066240	56.024
.37800	1.1058	.063501	57.426
.34397	1.0084	.059820	59.324
.32162	.94414	.057215	60.600
.26710	.78671	.050352	64.004
.21865	.64589	.043550	67.426
.17782	.52656	.037233	70.709
.13833	.41058	.030552	74.411
.10891	.32382	.025161	77.701
.073456	.21885	.018113	82.766
.055283	.16488	.014216	86.222
.032618	.097408	.0089968	92.363
.019070	.056993	.005610	98.44
.009506	.02843	.003013	106.0
.003213	.009611	.001124	116.9

Table 18. Pr(NO₃)₃ conductivities

m	N	L	Λ
5.0166	10.663	.015705	1.473
4.8330	10.400	.017883	1.719
4.5344	9.9567	.021845	2.194
4.0025	9.1163	.030635	3.361
3.4437	8.1561	.042591	5.222
2.9776	7.2883	.054715	7.508
2.5642	6.4635	.066752	10.328
2.2005	5.6919	.077708	13.652
1.9222	5.0710	.085635	16.887
1.6838	4.5172	.091476	20.251
1.4480	3.9490	.095688	24.231
1.2912	3.5598	.097194	27.304
1.2262	3.3956	.097434	28.694
1.1060	3.0880	.097098	31.444
.91740	2.5940	.094276	36.343
.74053	2.1184	.088371	41.717
.64297	1.8510	.083430	45.074
.55861	1.6168	.078043	48.271
.50006	1.4526	.073619	50.679
.38312	1.1210	.062866	56.079
.35824	1.0498	.060234	57.376
.31954	.93858	.055819	59.471
.30602	.89960	.054210	60.260
.25339	.74722	.047459	63.514
.20612	.60951	.040749	66.855
.16930	.50170	.035042	69.846
.13081	.38849	.028562	73.518
.099968	.29741	.022952	77.174
.070139	.20902	.017081	81.720
.051275	.15296	.013090	85.579
.033209	.099167	.0089995	90.750
.019274	.057599	.0055949	97.135
.008388	.02508	.002673	106.6
.002780	.008315	.001008	121.2

Table 19. $\text{Nd}(\text{NO}_3)_3$ conductivities

m	N	L	A
4.6184	10.096	.021295	2.109
4.4850	9.8957	.023160	2.341
4.1238	9.3306	.029250	3.135
3.7528	8.7136	.036727	4.215
3.2481	7.8131	.048964	6.267
2.8288	7.0084	.060759	8.669
2.4525	6.2398	.072113	11.557
2.1272	5.5378	.081839	14.778
1.8489	4.9082	.089338	18.202
1.5994	4.3203	.094690	21.917
1.3906	3.8107	.097471	25.579
1.2566	3.4751	.098196	28.257
1.1775	3.2738	.098053	29.950
1.0862	3.0386	.097379	32.047
.87432	2.4804	.093077	37.525
.69958	2.0072	.086001	42.846
.61642	1.7780	.081255	45.701
.54592	1.5816	.076446	48.334
.47354	1.3781	.070649	51.265
.38378	1.1230	.062147	55.339
.34846	1.0218	.058353	57.106
.30857	.90703	.053750	59.259
.29551	.86931	.052164	60.007
.24481	.72233	.045597	63.124
.20106	.59476	.039377	66.206
.16498	.48905	.033812	69.138
.12739	.37843	.027539	72.772
.099610	.29638	.022544	76.066
.068537	.20428	.016517	80.852
.050770	.15147	.012808	84.557
.030079	.089845	.0081649	90.878
.019306	.057700	.0055487	96.165
.010038	.030016	.003115	103.8
.004242	.01269	.001437	113.2

Table 20. $\text{Sm}(\text{NO}_3)_3$ conductivities

m	N	L	Λ
4.2811	9.6155	.029531	3.071
3.8271	8.8731	.039016	4.397
3.4372	8.1880	.048614	5.937
3.2278	7.8019	.054317	6.962
2.8661	7.1042	.064827	9.125
2.4569	6.2659	.077183	12.318
2.1250	5.5457	.086748	15.643
1.8563	4.9351	.093407	18.926
1.6469	4.4416	.097380	21.924
1.4277	3.9080	.099825	25.544
1.2480	3.4574	.10005	28.939
1.1240	3.1395	.099038	31.547
1.0386	2.9172	.097672	33.482
.97806	2.7580	.096340	34.931
.80449	2.2939	.090599	39.496
.65320	1.8803	.082891	44.083
.57159	1.6537	.077537	46.887
.49511	1.4392	.071558	49.722
.44016	1.2837	.066703	51.961
.34502	1.0120	.056993	56.318
.31726	.93208	.053853	57.777
.31064	.91299	.053040	58.095
.26552	.78245	.047485	60.688
.22280	.65819	.041733	63.404
.18143	.53726	.035706	66.459
.14955	.44366	.030705	69.205
.11402	.33894	.024706	72.891
.099226	.29521	.022057	74.716
.063046	.18795	.015132	80.508
.046691	.13932	.011738	84.242
.028524	.085201	.0076892	90.248
.016622	.049682	.0048088	96.792
.007381	.02207	.002347	106.3

Table 21. $\text{Gd}(\text{NO}_3)_3$ conductivities

m	N	L	Λ
4.3766	9.8149	.029735	3.030
4.2095	9.5482	.033096	3.467
3.8619	8.9709	.040796	4.547
3.5302	8.3899	.049120	5.854
3.0994	7.5883	.061312	8.080
2.6373	6.6657	.075448	11.319
2.3179	5.9879	.085141	14.219
1.9915	5.2599	.094173	17.904
1.7277	4.6447	.10000	21.531
1.4962	4.0846	.10324	25.276
1.3117	3.6244	.10407	28.713
1.1804	3.2895	.10342	31.440
1.0930	3.0631	.10233	33.406
1.0245	2.8837	.10103	35.036
.80932	2.3091	.094144	40.772
.67337	1.9374	.087142	44.979
.57604	1.6672	.080627	48.362
.50491	1.4676	.074943	51.065
.44951	1.3109	.069938	53.352
.37002	1.0841	.061774	56.981
.32976	.96843	.057151	59.015
.30265	.89021	.053837	60.477
.27829	.81971	.050704	61.856
.23347	.68946	.044574	64.651
.18926	.56030	.037991	67.806
.15641	.46391	.032713	70.516
.12043	.35791	.026504	74.052
.093185	.27736	.021448	77.330
.067240	.20042	.016306	81.356
.048000	.14322	.012224	85.351
.030974	.092506	.0083675	90.453
.016764	.050106	.004885	97.493
.007698	.02302	.002443	106.1
.002926	.008752	.001012	115.7

Table 22. $Tb(NO_3)_3$ conductivities

m	N	L	Λ
4.5395	10.083	.027639	2.741
4.3234	9.7431	.031729	3.257
3.9249	9.0878	.040284	4.433
3.6250	8.5681	.047738	5.571
3.1932	7.7757	.059837	7.695
2.7500	6.9042	.073564	10.654
2.3845	6.1382	.085193	13.879
2.0198	5.3295	.095995	18.012
1.7525	4.7077	.10251	21.774
1.5350	4.1832	.10619	25.388
1.3090	3.6203	.10769	29.749
1.2095	3.3666	.10740	31.902
1.1362	3.1775	.10676	33.601
1.0453	2.9402	.10531	35.816
.86019	2.4478	.10000	40.852
.67485	1.9424	.090717	46.704
.59663	1.7254	.085398	49.495
.51732	1.5031	.079009	52.563
.46609	1.3584	.074297	54.695
.35715	1.0475	.062590	59.751
.33539	.98491	.059935	60.853
.30945	.91009	.056655	62.252
.28617	.84273	.053555	63.549
.23503	.69413	.046279	66.672
.19383	.57377	.039903	69.547
.15741	.46689	.033830	72.456
.12277	.36484	.027634	75.743
.094733	.28195	.022268	78.980
.065018	.19382	.016169	83.425
.048035	.14332	.012449	86.858
.034537	.10312	.0093347	90.520
.016848	.050352	.0049487	98.282
.008601	.02572	.002710	105.4
.002625	.007851	.0009166	116.8

Table 23. $\text{Ho}(\text{NO}_3)_3$ conductivities

m	N	L	A
5.0183	10.817	.020598	1.904
4.8078	10.508	.023823	2.267
4.3767	9.8460	.031467	3.196
3.9829	9.2037	.040079	4.355
3.4389	8.2499	.054572	6.614
2.8861	7.1931	.072222	10.040
2.5677	6.5411	.083248	12.728
2.1696	5.6787	.096914	17.066
1.8734	5.0019	.10595	21.181
1.6441	4.4568	.11140	24.996
1.3935	3.8396	.11480	29.898
1.2470	3.4683	.11506	33.172
1.1528	3.2255	.11439	35.463
1.0838	3.0456	.11336	37.218
.85909	2.4479	.10668	43.576
.69733	2.0065	.098008	48.846
.59994	1.7362	.090883	52.345
.51517	1.4983	.083385	55.653
.46466	1.3553	.078295	57.769
.37486	1.0990	.067966	61.844
.30569	.89967	.058789	65.344
.27839	.82056	.054868	66.866
.25432	.75060	.051241	68.267
.20188	.59753	.042801	71.629
.16863	.50001	.037031	74.059
.13657	.40564	.031130	76.739
.10120	.30115	.024182	80.299
.077661	.23139	.019270	83.280
.060713	.18105	.015560	85.937
.038924	.11621	.010528	90.596
.024222	.072369	.0069112	95.499
.016773	.050133	.0049748	99.232
.006726	.02011	.002177	108.2
.003000	.008973	.001037	115.6

Table 24. $\text{Er}(\text{NO}_3)_3$ conductivities

m	N	L	Λ
5.4348	11.395	.015798	1.387
5.2485	11.146	.017883	1.604
5.1587	11.023	.018979	1.722
4.4596	9.9923	.030367	3.039
4.1626	9.5174	.036739	3.860
3.8766	9.0387	.043563	4.819
3.6219	8.5938	.050604	5.888
3.1044	7.6335	.066833	8.755
2.6121	6.6444	.084389	12.700
2.2614	5.8917	.097145	16.489
1.9732	5.2417	.10680	20.377
1.6931	4.5818	.11437	24.962
1.4615	4.0150	.11823	29.449
1.3205	3.6604	.11906	32.526
1.2112	3.3806	.11870	35.113
1.1302	3.1705	.11777	37.145
.91143	2.5912	.11194	43.199
.74847	2.1486	.10381	48.315
.64136	1.8527	.096377	52.019
.55711	1.6171	.089218	55.171
.49713	1.4479	.083338	57.558
.38036	1.1151	.069837	62.630
.35621	1.0457	.066687	63.775
.32279	.94929	.062128	65.447
.30023	.88403	.058888	66.613
.24913	.73560	.051109	69.479
.20632	.61060	.044059	72.159
.16773	.49741	.037255	74.898
.12978	.38564	.030103	78.059
.10323	.30718	.024783	80.682
.070063	.20884	.017731	84.903
.053765	.16040	.014064	87.684
.032690	.097631	.0090548	92.745
.020061	.059953	.0058544	97.652
.008369	.02503	.002660	106.3
.002805	.008390	.0009740	116.1

Table 25. $\text{Lu}(\text{NO}_3)_3$ conductivities

m	N	L	A
6.8219	13.141	.005660	.431
6.0372	12.231	.010592	.866
5.6592	11.753	.014156	1.205
5.4481	11.474	.016473	1.436
5.0089	10.864	.022586	2.079
4.7112	10.428	.027638	2.650
4.1052	9.4724	.040909	4.319
3.4556	8.3398	.059994	7.194
2.9112	7.2941	.079627	10.916
2.4596	6.3543	.097199	15.297
2.1268	5.6176	.10950	19.493
1.8423	4.9572	.11832	23.869
1.5343	4.2102	.12443	29.554
1.4006	3.8754	.12540	32.358
1.3120	3.6510	.12537	34.345
1.1849	3.3220	.12417	37.378
.95921	2.7255	.11812	43.338
.76686	2.2033	.10821	49.116
.67010	1.9358	.10125	52.305
.59036	1.7130	.094400	55.109
.51123	1.4898	.086540	58.089
.40262	1.1801	.073859	62.586
.37418	1.0984	.070156	63.870
.33684	.99074	.065005	65.613
.31601	.93048	.062007	66.640
.25982	.76726	.053424	69.630
.21540	.63753	.046055	72.240
.17354	.51472	.038620	75.030
.13407	.39844	.031142	78.160
.10621	.31608	.025535	80.786
.071667	.21365	.018162	85.011
.053429	.15942	.014027	87.991
.032297	.096466	.008974	93.028
.018657	.055762	.0054903	98.460
.007703	.02303	.002466	107.1
.002993	.008952	.001035	115.6

Table 26. Typical error values

	m	% δ m	% δ A
PrCl ₃ :	3.9840	.077	.13
	2.4905	.033	.054
	1.5714	.028	.043
	.71524	.040	.051
	.24692	.037	.041
	.049714	.035	.036
Sm(ClO ₄) ₃ :	4.6401	.097	.17
	3.0512	.097	.17
	1.9425	.078	.13
	1.1070	.062	.094
	.49805	.051	.066
	.048855	.026	.028
Dy(ClO ₄) ₃ :	4.6016	.070	.12
	3.1416	.038	.068
	2.0865	.030	.053
	1.0686	.023	.039
	.50903	.020	.027
	.058400	.011	.020
Nd(NO ₃) ₃ :	4.4850	.060	.11
	3.2481	.050	.088
	2.1272	.041	.067
	1.0862	.033	.048
	.54592	.029	.038
	.050770	.013	.018
Lu(NO ₃) ₃ :	6.8219	.054	.10
	5.4481	.053	.098
	3.4556	.040	.070
	2.1268	.031	.053
	.95921	.024	.036
	.25982	.023	.027
	.053429	.022	.024

IV. A QUALITATIVE THEORETICAL DISCUSSION

The theoretical treatment of dilute ionic solution conductance is due mainly to the school of Onsager and Fuoss. A fairly extensive treatment of this complex theory can be found in Harned and Owen (71). This theory and its various extensions are dilute solution theories. Many of the assumptions made in deriving this theory have broken down by a concentration of .05 molar for one to one electrolytes and much sooner for higher valence salts. These theories of conductance, which are based on the Debye-Hückle approach, have not been extended to the concentration range studied in this research, so a detailed theoretical discussion of this approach would not be warranted. However, a qualitative discussion of the basic Onsager-Fuoss theory and the physical and mathematical approximations inherent in its derivation may aid in a partial understanding of the various contributions to electrical conductance in more concentrated solutions. This discussion will be qualitative because mathematical details of the derivations will not be provided and because no numerical estimates of the relative importance of the various approximations will be given.

There is some feeling among theoreticians that a better approach to concentrated electrolyte solutions would be to treat them as fused salts being diluted by a solvent. No

significant progress has yet been made from this direction, so only the dilute solution theories will be considered. Likewise, only aqueous solutions will be considered.

The transport of electricity in an electrolyte solution occurs by the migration of ions, with their associated solvent molecules, under the influence of an external electrical field. The total equivalent conductance, Λ , of an electrolyte in solution may be decomposed into contributions due to the various ionic species present. If n_i is the number of ions of type i in a solution containing a total of one equivalent of electrolyte, v_i is the average velocity of the type i ions due to a one volt/cm potential gradient, z_i is the charge on the type i ions, and e is the electronic charge, then

$$\Lambda = \sum_i n_i v_i z_i e \quad (4.1)$$

This summation is over all the ionic species present in solution and thus depends on any complexation and ion pairing that may be occurring. The v_i 's will, in general, be a function of solution composition and concentration.

An ion in solution possesses a definite electrical conductance, in the absence of other ions, due solely to the characteristics of the ion itself and to the nature of the ion-solvent interactions. This conductance is known as the limiting conductance Λ_0 , and is obtained by some suitable extrapolation of experimental data to zero concentration.

The velocities of the ions in solution are not strictly linear in the direction of the electrical field due to the presence of the thermal motions of the ions and solvent. Only the net drift of the ions along the direction of the electrical field makes a contribution to the electrical conductance. In deriving ionic distribution functions this thermal motion must be considered.

The starting point of the Onsager-Fuoss theory is the Debye-Hückle treatment of the interionic electrostatic potential in solution. The limitations of the Debye-Hückle theory will therefore be present in the Onsager-Fuoss theory. Vaslow (72, p. 465) has summarized some of these limitations in a review paper, and Frank and Thomas (73) have discussed the limitations of the charge cloud model. The only major problem of theoretical electrical conductance calculations that will be considered here is the concentration dependence of conductance.

Consider a liquid solution containing a number of electrical charges (ions). The total electrostatic potential $\phi(r)$, at a point of distance r , relative to a central ion, is given by Poisson's equation

$$\nabla^2\phi(r) = -\frac{4\pi\rho(r)}{D} \quad (4.2)$$

where D is the dielectric constant of the solvent and $\rho(r)$ is the charge density at the point being considered. This

equation involves the assumption of a dielectric continuum around the central ion. Poisson's equation holds exactly only if the ions around the central ion are completely motionless. If the positions of the charges are changing, as will be the case in any real electrolyte solution, then a solution of this equation using the average charge density will give an average potential. This average, $\rho(r)$, will be spherically symmetric.

The close presence of the individual neighboring ions will distort the local "ionic atmospheric" charge density from its spherically symmetric average. Likewise, the possession of internal degrees of freedom by the ions, if any, will give rise to a non-spherical charge distribution for the ion itself. For dilute solutions the neglect of distortion polarization and the structure of the ions, along with short range van der Waals type forces, will lead to no serious errors in the charge distribution. To this approximation the contributions to the total electrostatic potential are additive and are given by Coulomb's law

$$\phi(r) = \sum_i z_i e / r_i D \quad (4.3)$$

where r_i is the distance from the central ion to the i^{th} ion being considered. This sum is over all ions in the solution and an average potential can be obtained by averaging over all positions that the ions can take. For any realistic

number of ions this equation cannot be evaluated exactly, so the use of some sort of radial distribution function for the ions becomes necessary.

The Debye-Hückle approach assumes that the appropriate radial distribution function for the ions in solution is the Boltzman equation

$$\rho(r) = \rho_0 e^{-w(r)/kT} \quad (4.4)$$

where ρ_0 is the bulk charge density in solution, $\rho(r)$ is the charge density at a point of distance r relative to the central ion, and $w(r)$ is a type of average potential. Kirkwood (74) showed, in considerable detail, that $w(r)$ is not exactly equal to the true average potential but differs from this average by a third order fluctuation in the potential arising from microscopic fluctuations in concentration from the average concentration. Kirkwood concluded that "this fluctuation term depends entirely upon the screening action of the statistical space charge and therefore its influence on the distribution function at small distances from the central ion is small compared with that of the Coulomb term, $\frac{e_k}{Dr}$, at low ionic concentrations." For very dilute solutions the use of $w(r)$ (called the potential of the average force) rather than the average potential should cause no serious error.

The relationship between potential and charge is linear in the Poisson equation but becomes non-linear when the

Boltzman distribution is assumed. The resulting Poisson-Boltzman equation is therefore mathematically inconsistent. This inconsistency can be removed for very dilute solutions where

$$e^{-w(r)/kT} \approx 1 - \frac{w(r)}{kT} \quad (4.5)$$

since $\frac{w(r)}{kT} \ll 1$. This linear approximation to the Boltzman equation makes the resulting Poisson-Boltzman equation internally consistent. The Poisson-Boltzman equation then becomes

$$\nabla^2 w(r) = K^2 w(r) \quad (4.6)$$

where $K = \frac{4\pi \sum_i N_i z_i^2 e^2}{VDkT}$. In this case N_i is the number of ions of type i and V is the total volume of the solution. The initial breakdown of equation 4.6, as ionic concentration increases, is not due to the truncated series expansion but is due to approximating $\phi(r)$ by $w(r)$ (72, p. 468). At greater concentrations the neglect of higher order terms in the series expansion also becomes important.

The assumption of a dielectric continuum in the "simple theory" neglects changes in the water molecules in the neighborhood of the central ion. The actual dielectric constant change is dependent on the central ion's charge and size and this effect diminishes with distance from the central ion. For very dilute solutions most of the water molecules are not close to any ion so the use of the

solvent dielectric constant is a good approximation. At higher ionic concentrations the dielectric constant of water adjacent to the central ion becomes a complicated function of the "ionic co-sphere" structure and of the distance of the neighboring ions. This problem is further complicated by the experimental difficulty involved in obtaining meaningful dielectric constants for ionic solutions. Some recent theoretical progress in this area can be found in a paper by Bahe (75).

Ions moving in the presence of an external electrical field have the spherical symmetry of their ionic atmosphere disturbed due to the motion of the central ion relative to the ionic atmosphere. This ionic atmosphere dysymmetry gives rise to a restoring force between the central ion and the ionic atmosphere which tends to slow down the velocity of the central ion. This restoring force diminishes as the thermal motions of the ions and solvent rearrange the perturbed ionic atmosphere. This effect consequently involves the concept of a relaxation time for ionic atmospheric disturbances. The equation of continuity of hydrodynamics is used in the treatment of this effect and the mathematical details are quite complex. The calculated results for this concentration dependent effect are valid only for extremely dilute solutions due to the oversimplification of the physical model and the mathematical approximations used.

The ions are also moving through a viscous medium and tend to drag solvent molecules along. The neighboring ions do not, therefore, move in a stationary fluid but move with or against the solvent motion. The frictional force is calculated from Stoke's law

$$F = 6\pi\eta Rv \quad (4.7)$$

where R is the effective radius of the central ion and η is the viscosity coefficient of the solvent. The calculation of this electrophoresis effect involves the assumption of a hydrodynamic continuum and does not readily lead to a detailed inclusion of solvent effects except in an approximate and somewhat arbitrary fashion. The effect of the highly structured nature of water on conductance, along with the disruption of this structure by the presence of ions, is neglected. The reduction of the ionic velocities due to the increasing viscosity of the solution caused by the increasing concentration of ions is also not treated in a rigorous fashion. This electrophoresis calculation is therefore valid only for very dilute solutions.

The physical nature of the ions requires that there be a distance of closest approach for ionic interactions. For any real situation there will be several different distances of closest approach corresponding to cation-cation, anion-anion, and anion-cation interactions. The Onsager-Fuoss

approach utilizes only one distance of closest approach obtained by curve fitting. This distance of closest approach is an empirical parameter and is not directly related to any one of the real distances of closest approach. This "average" distance of closest approach may be interpreted as including the ions along with some adjacent solvent and therefore includes hydration and electrostriction effects in a rather loose fashion. Fuoss and Accascina (76, p. 165) also assumed that this distance of closest approach was equal to the hydrodynamic radius obtained from Stoke's law.

Bjerrum (77) introduced the concept of ion-pairs occurring in solution due to purely electrostatic attractions between ions. All ions of opposite charge, closer than a certain critical distance, were assumed to be associated as ion-pairs. For symmetrical electrolytes this ion-pair would be neutral and therefore not contribute to conductance. This approach has been somewhat successful in the treatment of solvents of low dielectric constants but this effect is not significantly large for most dilute aqueous solutions. In more concentrated aqueous solutions, ion-pairing may become important but the application of this concept is limited since most of the dilute solution approximations have already broken down.

Pitts (78) has extended the Onsager-Fuoss treatment using higher terms in the Boltzman equation and different

application of the ionic-atmospheric concept and boundary conditions. The distance of closest approach is not equated to the hydrodynamic radius of the ion and the physically unreasonable distances of closest approach, sometimes obtained in the Fuoss treatment, are avoided. The effect of using higher terms in the distribution function results in an inconsistent Poisson-Boltzmann equation. The consequence of building a theory on this mathematically non-self-consistent equation is not fully understood although the improvement over the Onsager-Fuoss treatment is encouraging (79,80). Pitts and Tabor (80) have shown that the negative equilibrium constants for ion-pairing, frequently obtained by curve fitting the Onsager-Fuoss theory (81) to experimental data, no longer appear in their extended theory.

The use of purely coulombic effects is equivalent to assuming 100% ionization of the electrolyte subject to the restriction of coulombic ion-pairing. The effect of covalent complexes on conductance has not been rigorously treated. A general treatment would require the use of mixed electrolyte theory which is far behind simple electrolyte theory in development.

Another non-coulombic effect which has not been treated adequately is hydration of the ions in solution. The assumptions of a hydrodynamic and a dielectric continuum

precludes the use of a detailed microscopic model. For very dilute solutions, hydration effects should be similar in magnitude to the effects at infinite dilution so a net cancellation will occur when taking differences. At higher solution concentrations, hydration changes may occur as the concentration increases and the effect of this on conductance is not easily treated theoretically.

The effect of ions on the structure of water is also difficult to treat. The dilute solutions are usually treated as a pure solvent with the ions inserted into the solvent structure. The success of quasi-lattice models in calculations of some thermodynamic properties (70, pp. 97-134; 82) indicates that a quasi-lattice approach to conductance in concentrated electrolyte solutions may be worth developing.

It is known that lower valence type salts obey the limiting laws to greater concentrations than higher valence salts and that symmetrical valence salts obey the limiting laws better than unsymmetrical valence salts. This is mainly due to the approximation to the Boltzman distribution used in the Debye-Hückle approach. It turns out that to this approximation $w(r)$ is proportional to $z_1 e$ so $w(r) = z_1 e w^1(r)$. Then, expanding $\rho = \rho_0 e^{-w(r)/kT}$ gives

$$\rho = \sum_i n_i \alpha_i - \sum_i n_i \alpha_i^2 \beta + \sum_i \frac{n_i}{2!} \alpha_i^3 \beta^2 - \sum_i \frac{n_i}{3!} \alpha_i^4 \beta^3 + \dots \quad (4.8)$$

where $n_i = N_i/V$; $\alpha_i = z_i e$ and $\beta = w^1(r)/kT$. Electroneutrality

requires that $\sum_1 n_1 z_1 e = 0$ so, to third order,

$$\rho = - \sum_1 n_1 \alpha_1^2 \beta + \sum_1 \frac{n_1}{2!} \alpha_1^3 \beta^2 - \sum_1 \frac{n_1}{3!} \alpha_1^4 \beta^3. \quad (4.9)$$

For symmetrical electrolytes, $\sum_1 \frac{n_1}{2!} \alpha_1^3 \beta^2 = 0$ so the series is correct to second order in β for the Debye-Hückle approximation. For unsymmetrical electrolytes this term does not vanish so the Debye-Hückle approximation is correct only to first order in β , hence the poorer agreement with the limiting law. The higher order terms are proportional to z_1^p where p is an interger greater than 2. These higher order terms are therefore larger for higher valence salts so the errors involved in truncating the series become larger for this case.

The rare earth salts studied in this research are three to one electrolytes and are thus both unsymmetrical and of higher valence type. Their conductances follow the Onsager-Fuoss theory only in the limit of extreme dilution, but Dye and Spedding (83) have extended the theory using graphical integrals evaluated with distance of closest approach values obtained from activity coefficient measurements. This extended treatment agrees with experimental rare earth chloride conductance data up to .008 normal which is about the dilute limit studied in this research.

The deficiencies of the "simple" theories of electrical conductance arise from the oversimplification of the physical model and because of the mathematical approximations used. All the weaknesses of the Debye-Hückle approach are present along with many new approximations. These new approximations arise from the perturbation of the static ionic distribution function by the electrical field and from the greater mathematical complexity and approximations involved in treating charge flow systems. However, the conductance theories have had considerable success in predicting and explaining the dilute solution behaviour of aqueous, non-aqueous and mixed solvent electrolyte solutions and are able to explain the Wien and Debye-Falkenhagen effects. The criticisms I have made are to indicate why the simple theories are not applicable to the electrolyte solution concentrations studied in this research and by no means constitute a criticism of the theoretical limiting laws or of the more refined theoretical calculations. The theoretical laws all predict that the conductance should initially decrease with the square root of normality. That is,

$$\Lambda = \Lambda_0 - G\sqrt{N} + \dots \quad (4.10)$$

where the higher order terms depend on the degree of approximation used. The square root of normality dependence

is a fully established experimental fact and its explanation in terms of a microscopic model is the most important success of these theories.

V. DISCUSSION AND CONCLUSIONS

A. Objectives of the Research

The conductance of an electrolyte in solution is known to be related to interionic interactions such as ion pairing and complexation, and to ion-solvent interactions. The conductance is directly related to the concentration, charge, and mobility of each chemical species in solution. The exact dependence is given by equation 4.1, $\Lambda = \sum_i n_i v_i z_i e$. The measurement of the concentration dependence of conductance can give considerable information about ionic interactions in solution.

A considerable amount of data exists for the electrical conductances of one to one electrolytes in concentrated aqueous solution, and a small amount for two to one electrolytes. A survey of this data up to 1958 can be found in Robinson and Stokes (35, Appendix 6.3). Conductance data for three to one electrolytes is almost completely restricted to dilute solutions. One important exception is the data of Saeger and Spedding (68) for the aqueous solution conductivities at 25°C for LaCl_3 , NdCl_3 , SmCl_3 , GdCl_3 , DyCl_3 , ErCl_3 , and YbCl_3 . This data is limited to seven cations and one anion, so it was felt that measurements on other cations and anions would add considerably to the understanding of the electrical conductance behavior of higher valence salts.

Some stable or relatively stable cations such as Al(III), Fe(III) and Cr(III) exist among the lighter elements, but these are extensively hydrolyzed in aqueous solution and tend to precipitate out from all but highly acid media. The properties of these highly acid solutions may be measured, but these solutions are really mixed electrolyte solutions and the individual electrolyte contributions cannot presently be separated from the total result. The actinides also form a number of trivalent cations in aqueous solution. However, some of these actinides form several different oxidation states which can exist simultaneously in aqueous solution, and can further complicate the chemistry. In addition, the actinides are all highly radioactive which makes the experimental measurement of their properties more complicated. Some of the heavier actinides are available only in trace amounts. The rare earths form the only extensive series of trivalent cations which is virtually free of all the above defects.

The rare earths with atomic numbers between 57 and 71 form a regular series of salts with the most stable oxidation state in aqueous solution being the trivalent cation. For most of the rare earths, this is the only oxidation state found in aqueous solution. The rare earths form highly soluble salts with the chloride, perchlorate and nitrate

anions that are highly ionized in aqueous solution and which are only slightly hydrolyzed. These salts were chosen for this research.

The rare earth trivalent cations are formed by the transfer of the 5d and 6s² (or 6s² and a 4f) electrons from the atoms. These rare earths differ from each other in the number of electrons present in the 4f subshell which are almost completely shielded from outside interactions by the electrons in the (outer) filled 5s and 5p subshells. The increasing nuclear charge causes all the electronic shells to be pulled in closer to the nucleus with the major effect occurring for the 4f subshell. The 4f electrons, due to their spatial arrangement, poorly shield other 4f electrons from the nucleus, allowing this subshell to shrink in size. This in turn allows the outer subshells to contract, causing a net decrease in the ionic radius with increasing atomic number. According to Templeton and Dauben (84), this lanthanide contraction is from 1.06 Å to 0.85 Å in going from La(III) to Lu(III).

Highly pure rare earths have become available in kilogram quantities due to improved ion-exchange separation methods (85, pp. 55-73) and recently, for a few cases, to liquid extraction techniques. Promethium is highly radioactive and Ce(III) is highly unstable with respect to partial oxidation to Ce(IV) by atmosphere oxygen.

Measurements on these two rare earths requires special precautions. The other thirteen rare earths do not possess these disadvantages and were consequently chosen for this study.

The rare earth cations undergo principally electrostatic interactions in solution with all but the strongest complexing agents. Unlike the transition metals which form strong complexes with suitable ligands using their d orbital electrons, the rare earths have no low energy orbitals available for overlap with ligand orbitals (86). Consequently, at concentrations at which complexation occurs, ligands such as the chloride, perchlorate and nitrate ions would be expected to form predominantly electrostatic "ion-pair" complexes with rare earth cations in aqueous solutions. Ion-dipole interactions between the rare earth ions and adjacent water molecules produces a hydration sheath around the cation which discourages ionic interactions at close distances. The bulky perchlorate ions are believed to be essentially uncomplexed with the rare earth cations except in very concentrated solutions. The chloride ions are believed to form weak outer sphere complexes in moderately concentrated solutions but may possibly displace inner sphere water in highly concentrated solutions. The nitrate ion may penetrate this hydration sheath, and is believed to form outer and possibly inner

sphere complexes in dilute solutions. In concentrated solutions, several nitrate ions may penetrate into the inner coordination sphere and displace additional water.

The decrease in the rare earth cation radii across the rare earth series allows one to study the role of the increasing surface charge density in ionic interactions. There is much evidence to suggest that the number of water molecules in the cation inner sphere changes in the rare earth cation series due to the decrease in the cation surface area. This effect has been observed in dilute apparent and partial molal volume data (87,88), in heat capacity data (89-91), and in many other properties. The mobility of the ions does not depend solely on inner sphere hydration but mainly on overall hydration. The concentration dependence of conductance, the role of cation size and hydration, and the effect of anion and cation substitution can all be studied using the data obtained in this research.

To completely analyze conductance data, high quality equilibrium constant and transference number data is needed. A small amount of equilibrium constant data is available and this will be discussed later. Transference numbers cannot presently be measured for most concentrated electrolyte solutions and are not available for the salts studied in this research, except for extremely dilute solutions (70, p. 319). Even without these properties, large amounts of

qualitative information can be extracted from conductance data.

In this research the conductances of 24 rare earth salts were accurately measured from 0.05 molal to saturation. The measurements were made on 6 chlorides, 9 perchlorates and 9 nitrates and the salts were chosen to cover the rare earth series. Together with the data of Saeger and Spedding (68), 13 chlorides have now been measured. Sufficient data is now available to show all the major trends influencing rare earth electrolytic conductance in aqueous solution for these series at 25°C.

B. Least Square Polynomial Fit

In order to facilitate graphical presentation of the conductance data, empirical polynomial fits were made for the equivalent conductance as a function of the square root of molality. This fitting was done using a double precision computer least square program utilizing matrix inversion techniques. The power series used to fit the equivalent conductance data were of the form

$$\Lambda = \sum_{j=0}^p B_j m^{j/2} \quad (5.1)$$

where p is the order of the fit.

The variance of a fit S^2 (the square of the standard deviation), which is an estimation of the variance of the data, is given by

$$S^2 = \frac{\frac{1}{\nu} \sum_i \left\{ \frac{1}{\sigma_i^2} [y_i - y(x_i)]^2 \right\}}{\frac{1}{N} \sum_i \frac{1}{\sigma_i^2}} \quad (5.2)$$

where N is the number of data points, $\nu = N-p-1$, σ_i is the standard deviation of the i^{th} data point, y_i is a measured value of the property being fitted as a function of x , and $y(x_i)$ is the calculated value of y_i for the fit being considered. The standard deviation of the data, is given by

$$\sigma_y = \sqrt{\frac{1}{N-1} \sum_i (y_i - \bar{y})^2} \quad (5.3)$$

where the bar indicates an average value. Another quantity of interest is the reduced chi-squared

$$\chi_\nu^2 = \frac{1}{\nu} \sum_i \frac{1}{\sigma_i^2} [y_i - y(x_i)]^2 \quad (5.4)$$

This reduced chi-squared has the property of being a measure of the "goodness of the fit" (69, chap. 10). If the fitting function can represent the data to within the experimental error, then $\chi_\nu^2 \approx 1$. A χ_ν^2 much greater than one indicates that the function tested cannot adequately represent the

experimental data, while a χ_v^2 much less than one indicates that the σ_1 's were overestimated. This latter case is possible if the "standard deviations" used are only approximated values.

The least square criteria can be applied to χ_v^2 or S^2 so

$$\frac{\partial}{\partial B_j} (S^2) = \frac{\partial}{\partial B_j} (\chi_v^2) = 0 \quad (5.5)$$

for all the B_j 's simultaneously. The error in each coefficient can be calculated, since

$$\sigma_{B_j} = \sum_i \sigma_i^2 \left(\frac{\partial B_j}{\partial y_i} \right)^2 \quad (5.6)$$

All the conductance data from one tenth molal to saturation was fit to power series in $m^{1/2}$. On the dilute concentration side, one point below one tenth molal was used in each case to better tie down this end of the curves. The more dilute data was not included in this fitting process since the conductance changes rapidly with concentration for dilute solutions. A simple polynomial was not found which would fit both concentration regions. Including the very dilute data would have made the fits less accurate at higher concentrations. Since the dilute data was not included, no significance should be given to

conductances below one tenth molal calculated from these power series.

The $\delta\Lambda$ values calculated in section III were used as approximations to the standard deviations in Λ . These $\delta\Lambda$'s are really probable errors and not standard deviations. In terms of these quantities, equation 5.3 becomes

$$\chi_v^2 = \frac{1}{v} \sum_i \left\{ \frac{1}{\delta\Lambda_i} [\Lambda_i - \Lambda(m_i)] \right\}^2 \quad (5.7)$$

where m is the molality, Λ_i is the experimental average conductance of the i th solution, and $\Lambda(m)$ is the calculated conductance of this solution.

It was found that a 7th order fit was suitable in all cases, with a considerable reduction in χ_v^2 usually occurring between the 6th and 7th order fits. The number of data points used for individual salts ranged from 25 to 32 and was greater than three times the number of constants used to represent the data. A rule of thumb frequently used is that the number of data points should be at least three times the number of constants used in representing them. For this order of fit, χ_v^2 was less than 2 for 22 of the salts and 1 or less for 16 of the salts. The remaining 2 salts had a χ_v^2 less than 2.75. The two largest values were for $\text{Tb}(\text{NO}_3)_3$ and $\text{Lu}(\text{NO}_3)_3$ and were probably due to underestimating the $\delta\Lambda$'s. This can occur

since $\delta\Lambda$ is only an approximation to $\sigma\Lambda$. In terms of the differences between the measured and calculated values, the fits for these two salts were as good as for the other salts. In all cases, the typical difference between calculated and experimental conductance values was .02 units or less, with an occasional deviation as large as .05 units. These larger deviations were usually in dilute solutions where Λ is fairly large.

The original data of Saeger and Spedding (68) was examined and $\delta\Lambda$ values calculated for each solution. To compare their data to the data reported here, the molality of each solution was calculated (they report normalities) and their conductances were converted from international ohms to absolute ohms. Their data was fit to the same form of polynomials used for the data reported here. They report fewer concentrations and consequently an 8 parameter equation over fit their data. For their data, χ_v^2 ranged from 1.40 to 9.85. These larger χ_v^2 values are not due to the quality of their data but are due to using too few data points for this order of fit. The 8 parameter equations were used to maintain consistency with the data reported here and give sufficiently accurate fits to allow a meaningful discussion of their data. The data of Saeger and Spedding will be discussed along with the data in this

thesis and will not be separately identified in the graphs and discussions.

In order that non-significant coefficients would not appear in the series, the uncertainty in each coefficient was calculated using equation 5.5. A test condition was written into the fitting program so that if $\frac{\sigma_{B_j}}{B_j} > 1$, then B_j was set equal to zero and the fitting redone. In no case was it necessary to drop any coefficients for the 7th order fit although it was occasionally necessary for higher or lower order fits. In Tables 27-29, all the polynomial coefficients are listed. The uncertainties in the smaller coefficients are 10% or less and the uncertainties in the dominant coefficients are much less than this. The saturation molalities to be used with the fits of Saeger and Spedding's data are LaCl_3 -3.8959, NdCl_3 -3.9292, SmCl_3 -3.6401, GdCl_3 -3.5906, DyCl_3 -3.6310, ErCl_3 -3.7821, and YbCl_3 -4.0028.

The precision of the data is much greater than can be shown graphically by plotting the original data. In order to graphically present the data such that the small but real differences between the conductances of individual rare earth electrolytes would show up, relative % differences were calculated as functions of molality. These differences are relative to the Lu salt and are given by

$$\% \Delta \Lambda = \frac{\Lambda_{\text{ReX}_3} - \Lambda_{\text{LuX}_3}}{\Lambda_{\text{LuX}_3}} \cdot 100 \quad (5.8)$$

Table 27. Conductance polynomial coefficients for chlorides

Salt	$\frac{B_0}{B_4}$	$\frac{B_1}{B_5}$	$\frac{B_2}{B_6}$	$\frac{B_3}{B_7}$
LaCl ₃	123.437546 495.423030	-191.286752 -256.398930	387.335371 73.213099	-571.029774 -8.77352118
PrCl ₃	114.929248 87.5885244	-118.846661 -30.7011658	145.388177 7.00565173	-152.4686419 -0.778194961
NdCl ₃	121.326562 389.422071	-171.956615 -197.355301	323.839653 55.7282392	-462.298230 -6.63804017
SmCl ₃	125.908335 678.381643	-215.748555 -363.558304	478.534918 106.160321	-745.282120 -12.9231724
EuCl ₃	120.765284 443.145239	-175.545348 -229.200510	342.816492 65.2725779	-508.717326 -7.79560067
GdCl ₃	121.943758 445.793583	-184.227716 -226.311144	358.890498 63.5875468	-522.151848 -7.54463307
TbCl ₃	121.643402 516.183423	-189.945605 -269.487390	386.819627 77.3477510	-584.164751 -9.33743725
DyCl ₃	122.232251 516.756641	-194.706015 -265.515096	396.260651 74.9096355	-592.513956 -8.88701583
HoCl ₃	120.175836 507.597885	-183.460975 -270.265888	369.125686 79.1767184	-564.523862 -9.75243209
ErCl ₃	120.363538 489.834751	-183.747701 -257.640366	365.678931 74.7466424	-552.193787 -9.13398163
TmCl ₃	118.671733 426.398065	-171.839718 -221.325262	328.098680 63.6147989	-488.173521 -7.71753621
YbCl ₃	119.589566 406.612279	-175.643258 -205.139404	330.681918 57.5057613	-479.115211 -6.83142137
LuCl ₃	118.080032 348.921780	-164.060811 -173.354589	294.336909 48.1673447	-418.869239 -5.69718599

Table 28. Conductance polynomial coefficients for perchlorates

Salt	$\frac{B_0}{B_4}$	$\frac{B_1}{B_5}$	$\frac{B_2}{B_6}$	$\frac{B_3}{B_7}$
La(ClO ₄) ₃	113.755644 300.887992	-133.865051 -150.716050	250.664759 42.4226658	-362.979281 -5.03245629
Pr(ClO ₄) ₃	112.709943 258.876234	-125.819473 -127.191732	225.023065 35.4473810	-319.880772 -4.18715132
Nd(ClO ₄) ₃	112.384826 223.493003	-120.223678 -109.039229	203.032449 30.5627797	-281.684257 -3.64653777
Sm(ClO ₄) ₃	113.722978 324.737789	-137.885487 -159.774179	265.889823 43.5348830	-390.941918 -4.97352759
Gd(ClO ₄) ₃	112.999666 335.126600	-138.635838 -166.361377	267.818563 45.5448518	-398.119408 -5.22309077
Dy(ClO ₄) ₃	111.619667 260.679872	-130.573806 -120.672584	233.247016 31.1075186	-330.125866 -3.40584028
Ho(ClO ₄) ₃	110.683936 247.840798	-126.733062 -115.303952	221.014053 29.9547094	-312.945925 -3.31212709
Er(ClO ₄) ₃	111.544708 301.044753	-136.164521 -142.937823	254.363940 37.5419784	-370.218577 -4.17157148
Lu(ClO ₄) ₃	111.057621 275.235942	-132.944367 -128.149488	240.917770 33.1975841	-345.260014 -3.66087542

Table 29. Conductance polynomial coefficients for nitrates

Salt	$\frac{B_0}{B_4}$	$\frac{B_1}{B_5}$	$\frac{B_2}{B_6}$	$\frac{B_3}{B_7}$
La(NO ₃) ₃	115.952716 314.552366	-175.225859 -139.465816	279.429544 32.3516152	-390.538087 -3.09424485
Pr(NO ₃) ₃	113.840235 234.099819	-170.310674 -94.4325869	251.818908 19.8816906	-319.065783 -1.72486870
Nd(NO ₃) ₃	113.626725 232.686311	-177.045110 -91.3287088	266.598683 18.7648090	-327.541711 -1.59022150
Sm(NO ₃) ₃	112.585469 238.721067	-180.137332 -98.0212982	273.924249 21.8637691	-332.450421 -2.08358289
Gd(NO ₃) ₃	113.154322 256.769865	-173.936802 -109.871081	268.594652 25.4419662	-342.006532 -2.50193664
Tb(NO ₃) ₃	113.040173 247.421721	-163.627147 -103.055855	252.776985 22.7969831	-330.24896 -2.11472803
Ho(NO ₃) ₃	113.768854 237.125233	-159.363170 -90.3121540	255.234721 17.6349871	-333.206061 -1.39602299
Er(NO ₃) ₃	113.920368 224.113480	-157.910509 -81.1431465	254.067972 14.7733427	-326.107978 -1.06139279
Lu(NO ₃) ₃	113.029556 180.229400	-148.800824 -60.8685888	226.898044 10.2220201	-277.832674 -0.669968973

where $\chi = \text{Cl}^-$ or ClO_4^- or NO_3^- . These plots are on a % basis in order to compensate somewhat for the net drop in conductance occurring with increasing concentration. The Lu^{+3} salts were chosen as the references since they occur at the end of the cation series, and the differences in conductances for the various anions are smaller for the Lu^{+3} salts than for any of the other cations. In addition, for the chlorides and nitrates, Lu^{+3} forms the most soluble salt, so a single reference can be used to represent the other salts to saturation. For the rare earth perchlorates, the Lu^{+3} salt is slightly less soluble than the light rare earth perchlorates but the difference is not very large. A number of plots representing the conductance data for all 31 salts are given in Figures 3-16.

In Figures 17-22, plots are given for the product of the equivalent conductance and the relative viscosity ($\eta_R = \eta_{\text{solution}}/\eta_{\text{H}_2\text{O}}$) as a function of molality for several rare earth electrolytes. The viscosity data is that of Spedding and Pikal (92) and Spedding and co-workers¹.

C. Specific Conductivities

In Figure 3 the specific conductivity curves are given for the three gadolinium electrolytes. These curves are

¹F. H. Spedding, L. E. Shiers and D. Witte, Iowa State University, Ames, Iowa. Private communication. 1972.

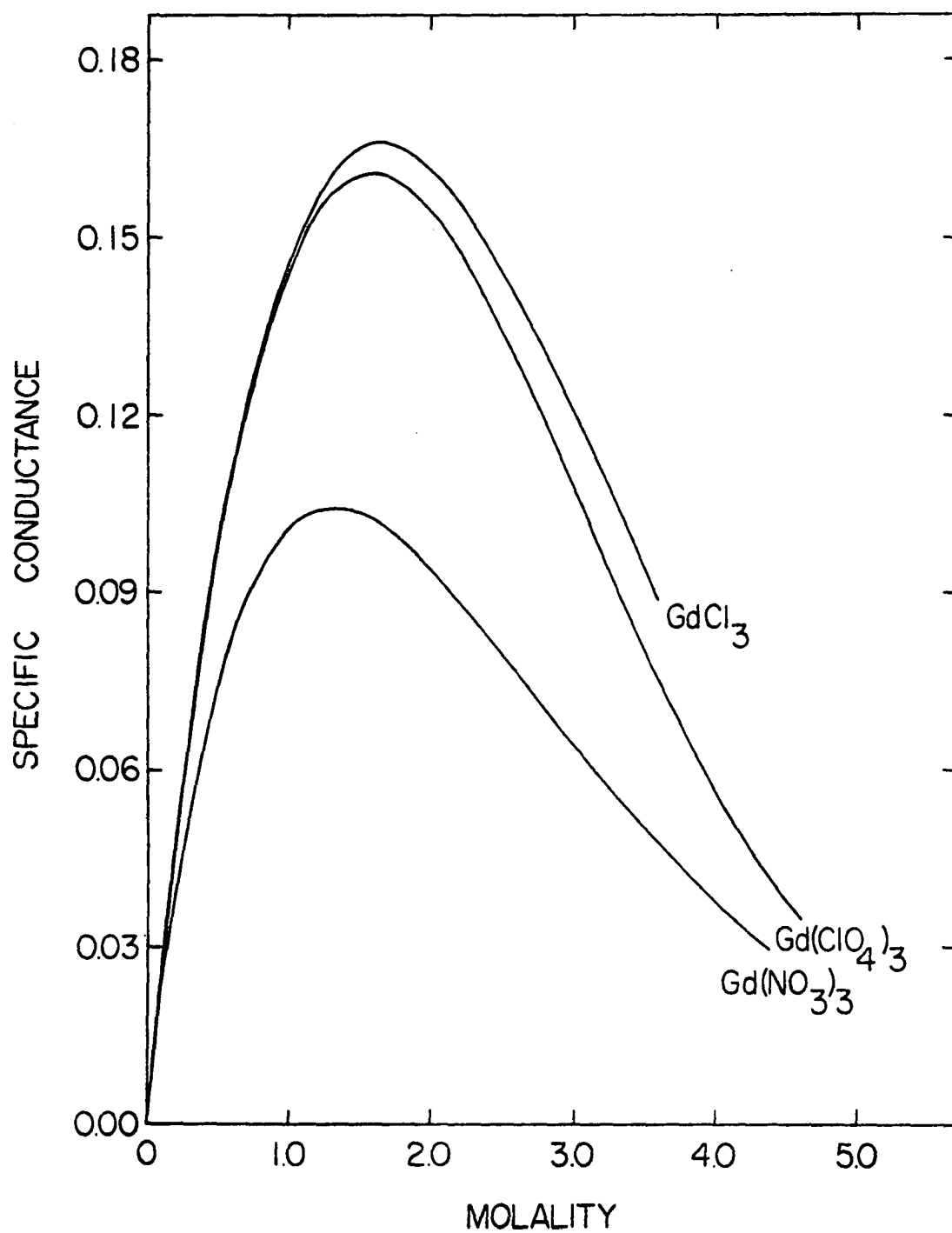


Figure 3. Specific conductances of gadolinium electrolytes

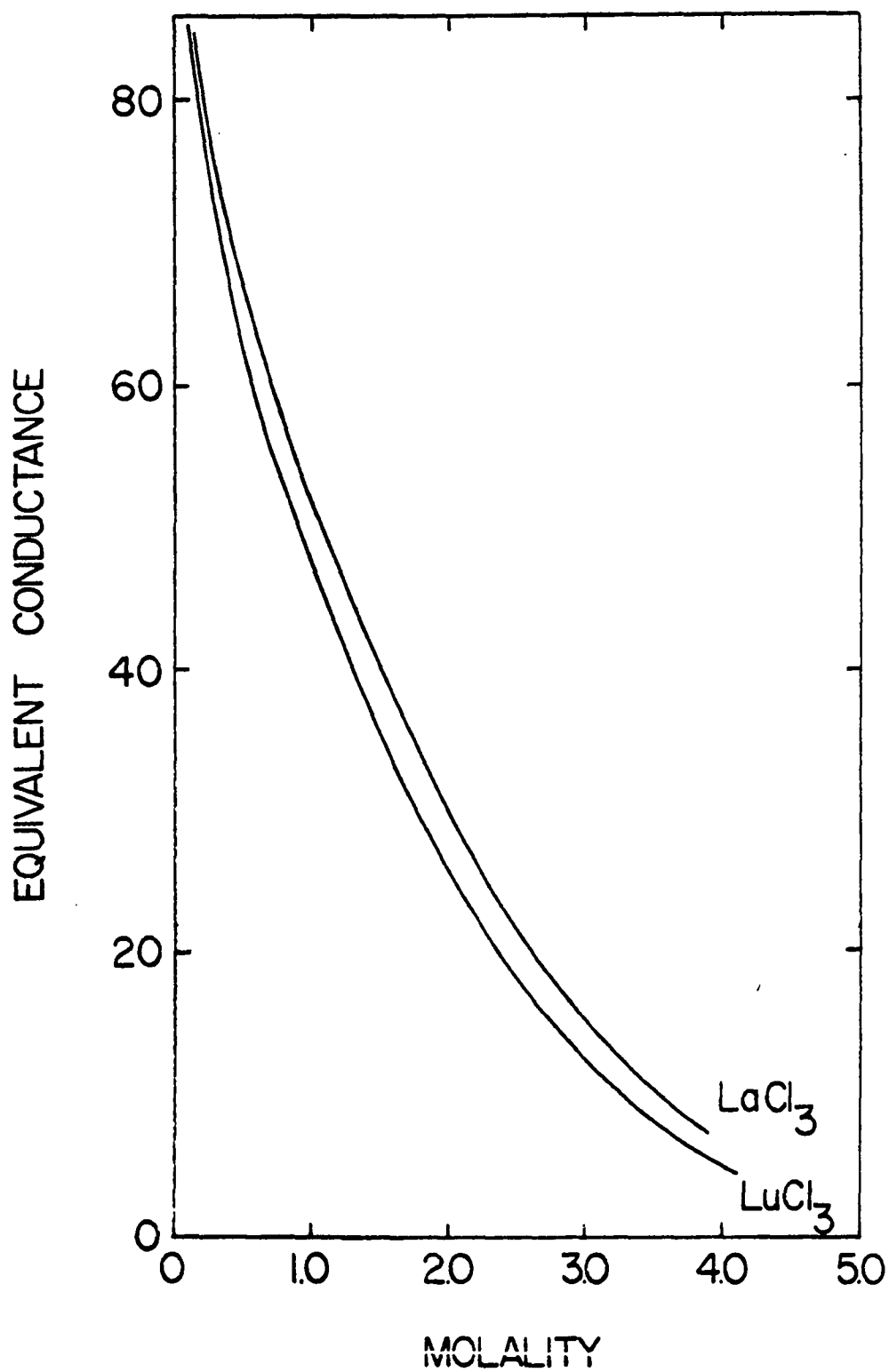


Figure 4. Equivalent conductances of two rare earth chlorides

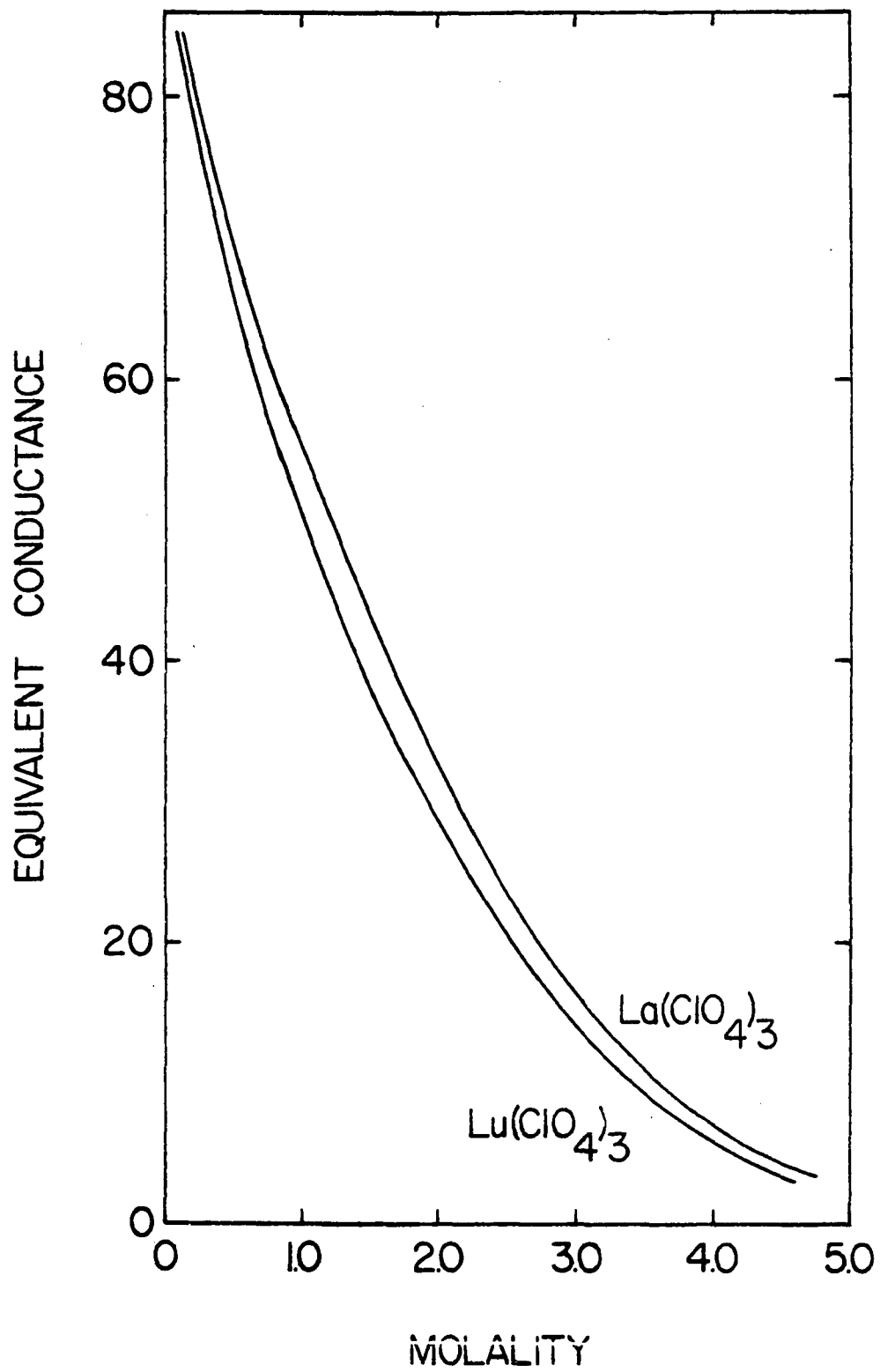


Figure 5. Equivalent conductances of two rare earth perchlorates

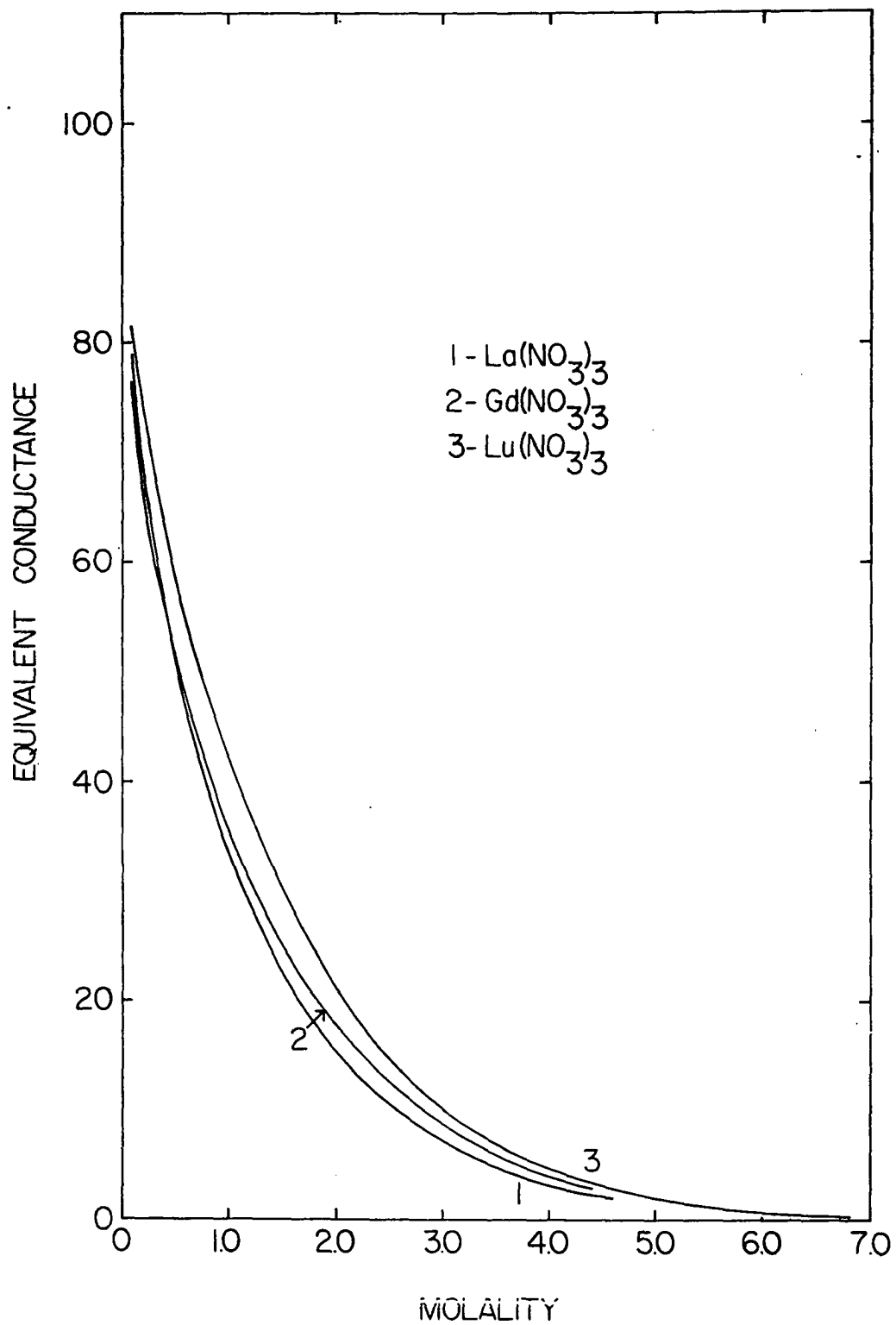


Figure 6. Equivalent conductances of three rare earth nitrates

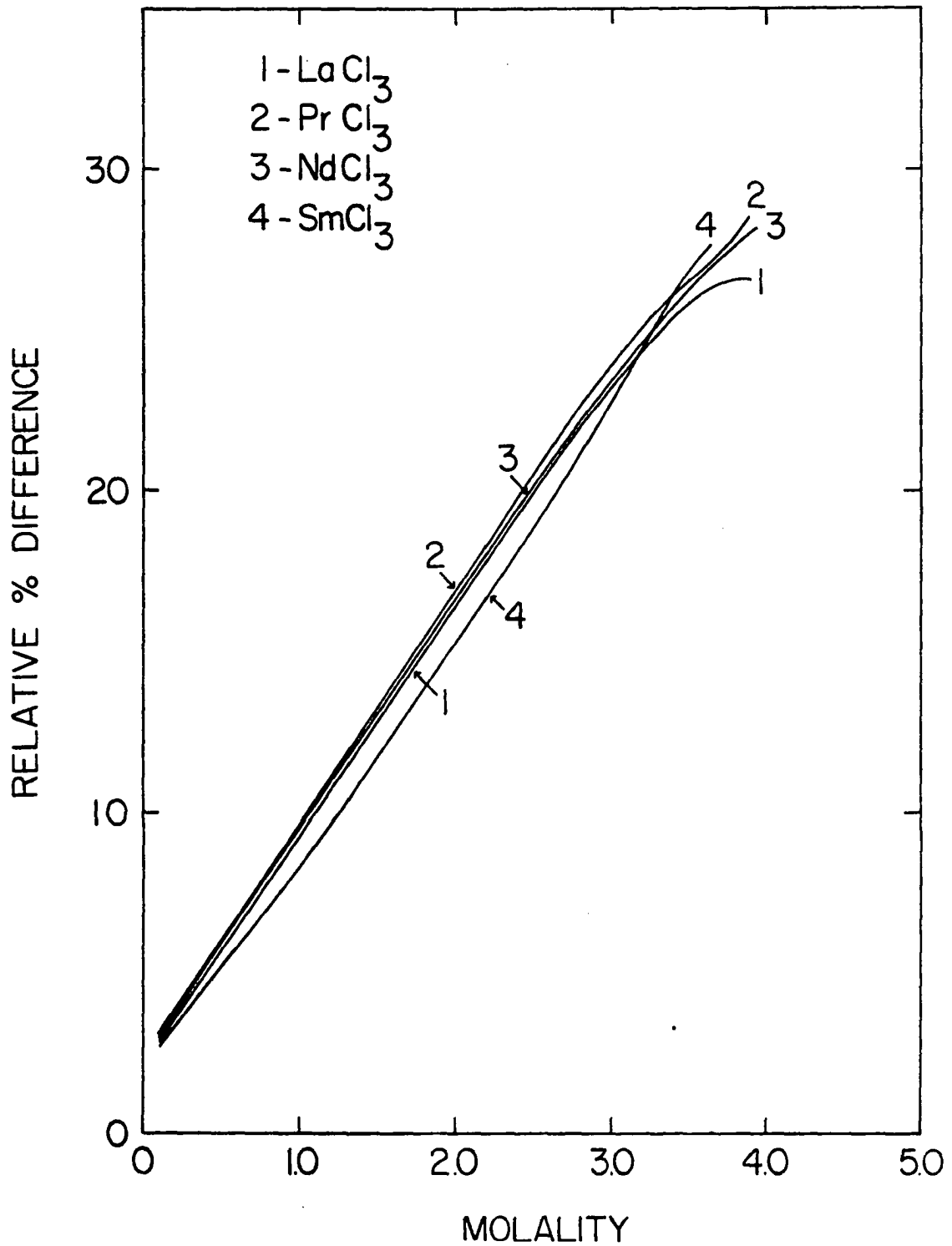


Figure 7. Percent differences in equivalent conductances relative to LuCl_3 , for some light rare earth chlorides

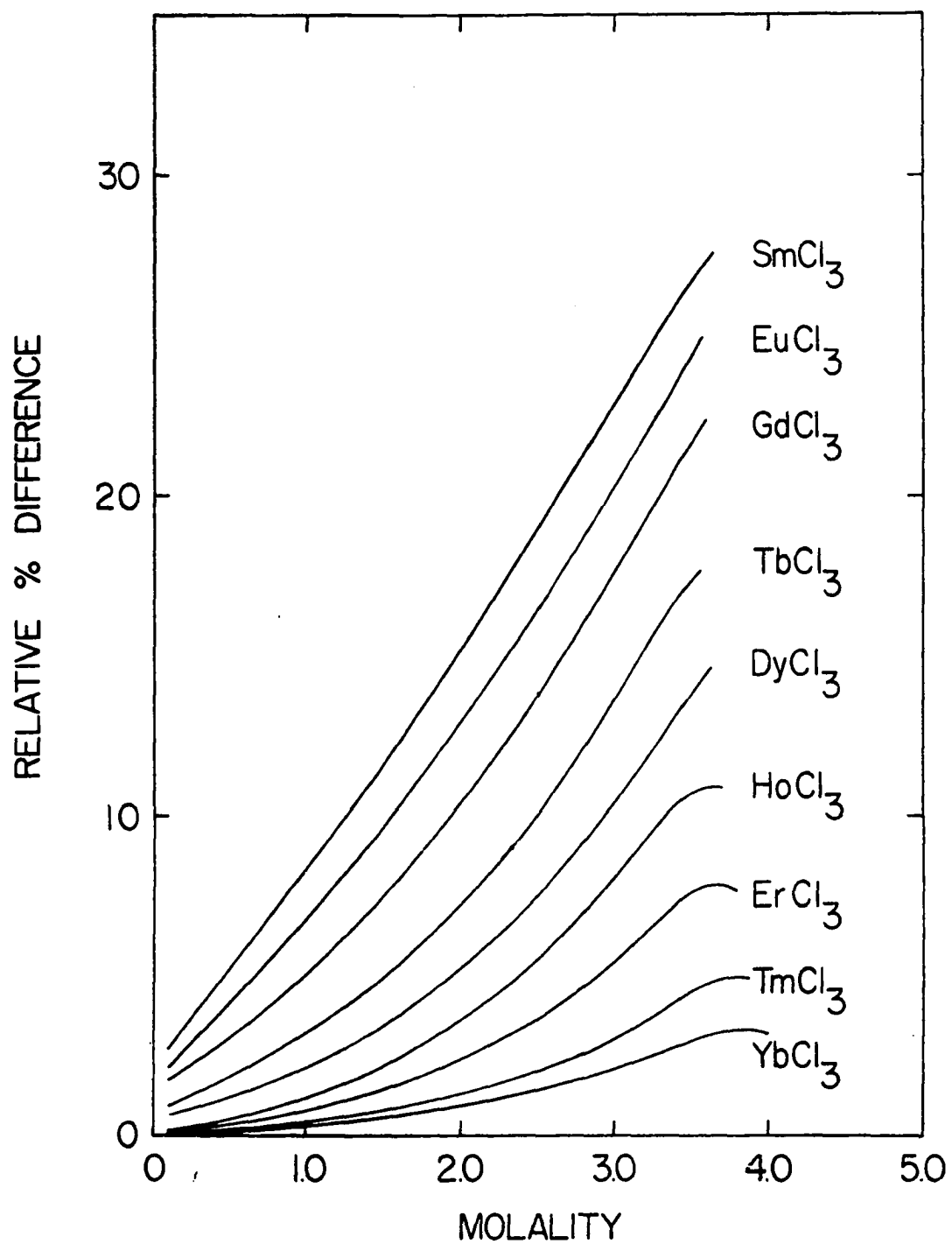


Figure 8. Percent differences in equivalent conductances relative to LuCl_3 for some middle and heavy rare earth chlorides.

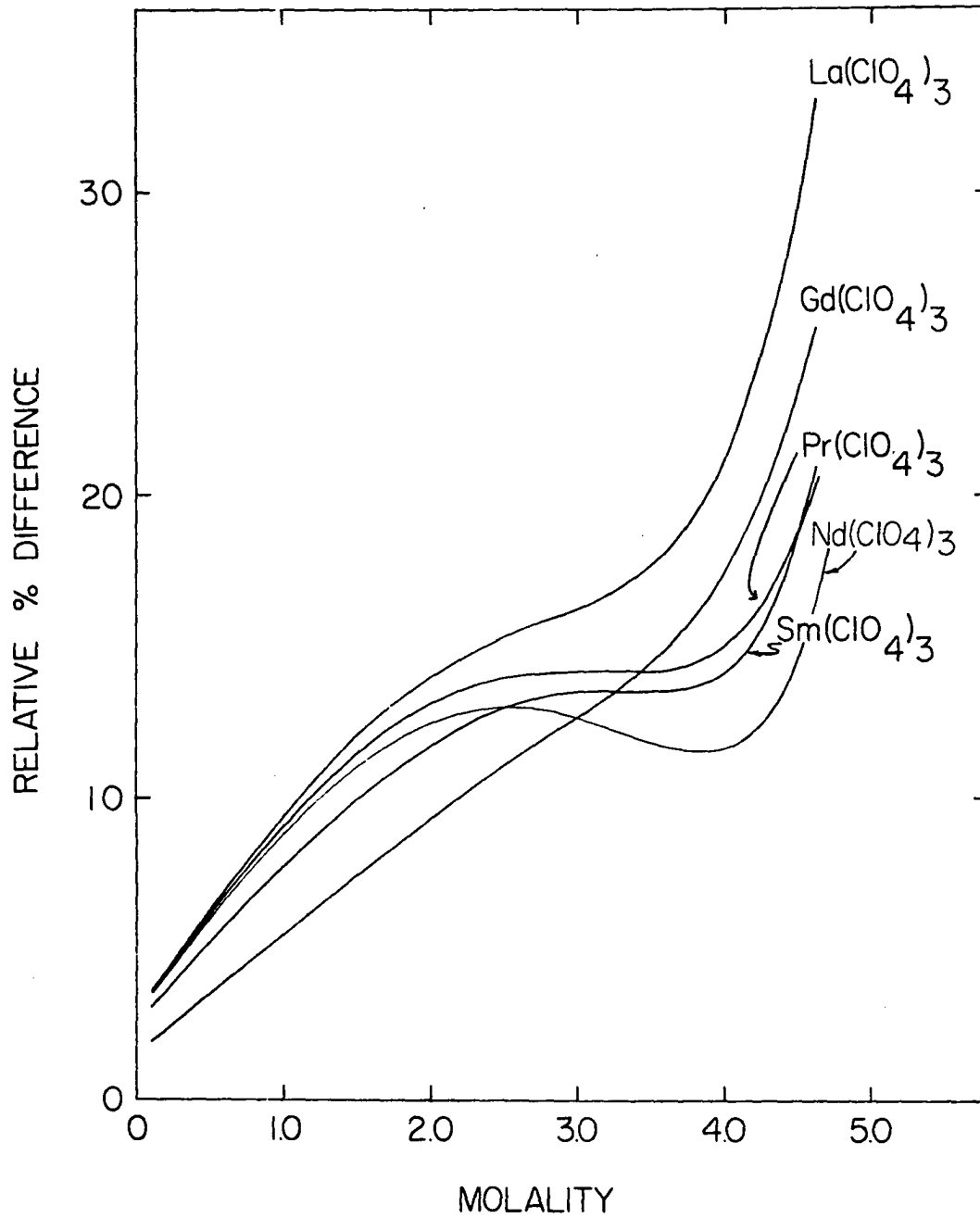


Figure 9. Percent differences in equivalent conductances relative to $\text{Lu}(\text{ClO}_4)_3$ for some light and middle rare earth perchlorates

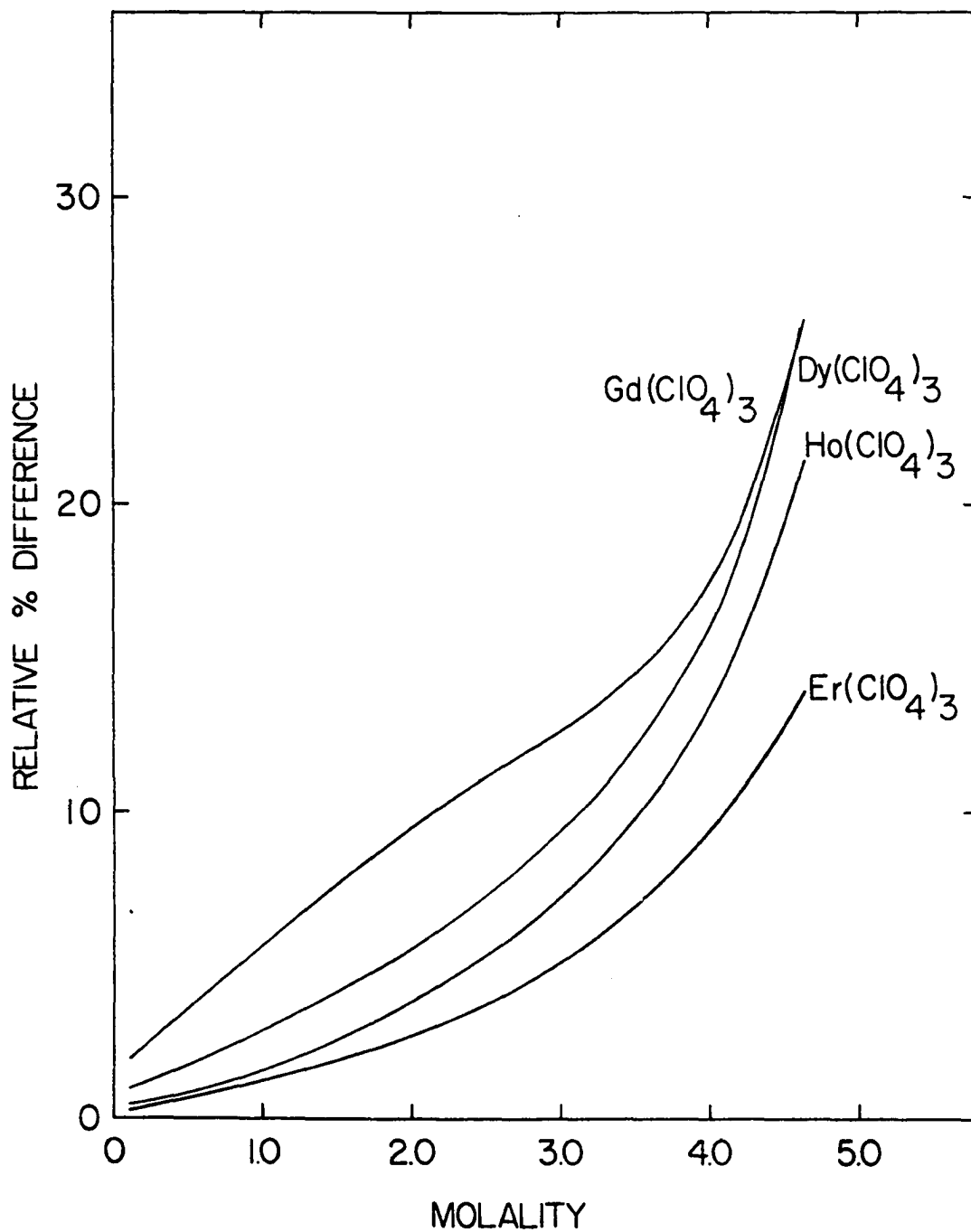


Figure 10. Percent differences in equivalent conductances relative to $\text{Lu}(\text{ClO}_4)_3$ for some middle and heavy rare earth perchlorates

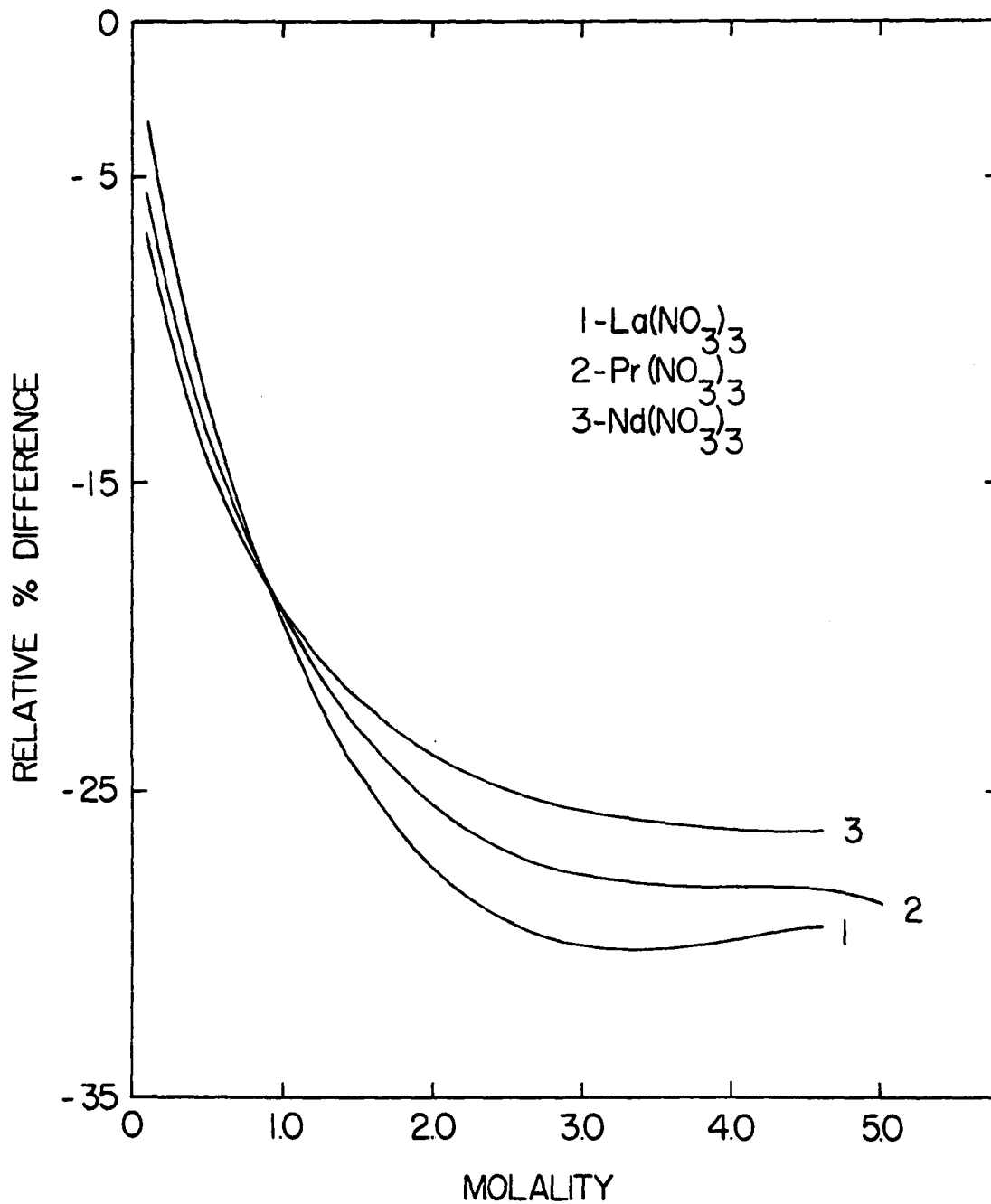


Figure 11. Percent differences in equivalent conductances relative to $\text{Lu}(\text{NO}_3)_3$ for some light rare earth nitrates

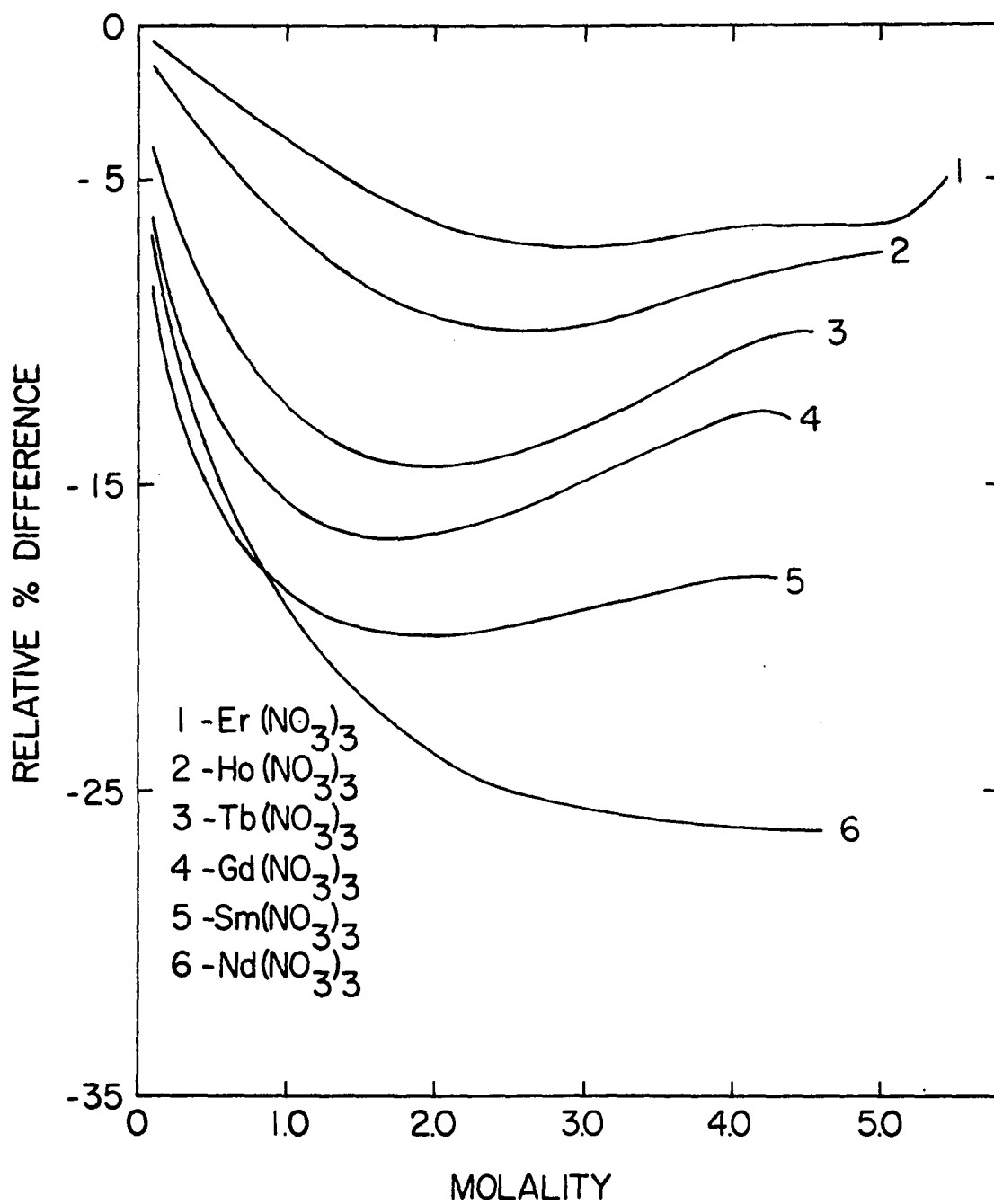


Figure 12. Percent differences in equivalent conductances relative to $\text{Lu}(\text{NO}_3)_3$ for some middle and heavy rare earth nitrates

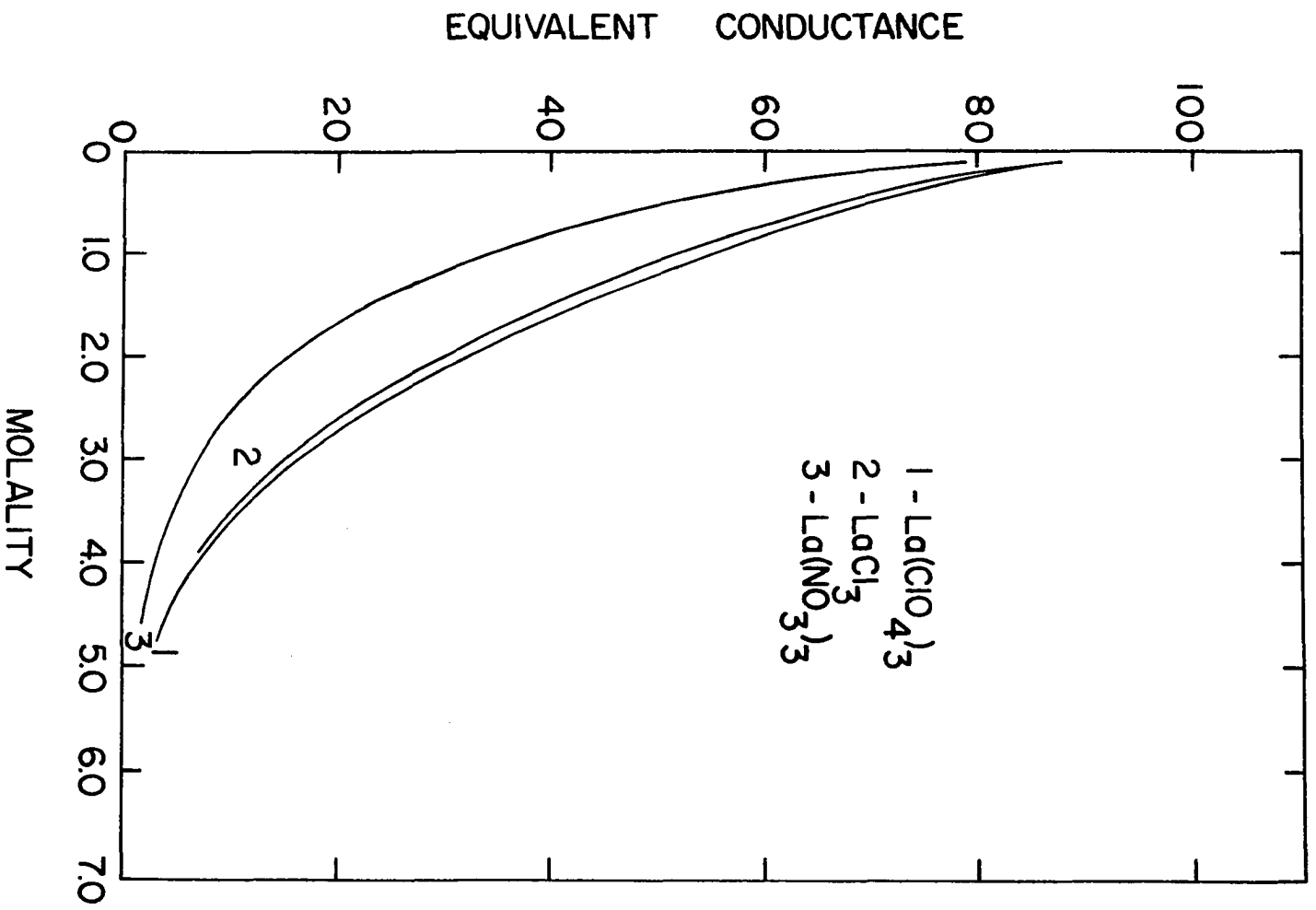


Figure 13. Equivalent conductances of lanthanum electrolytes

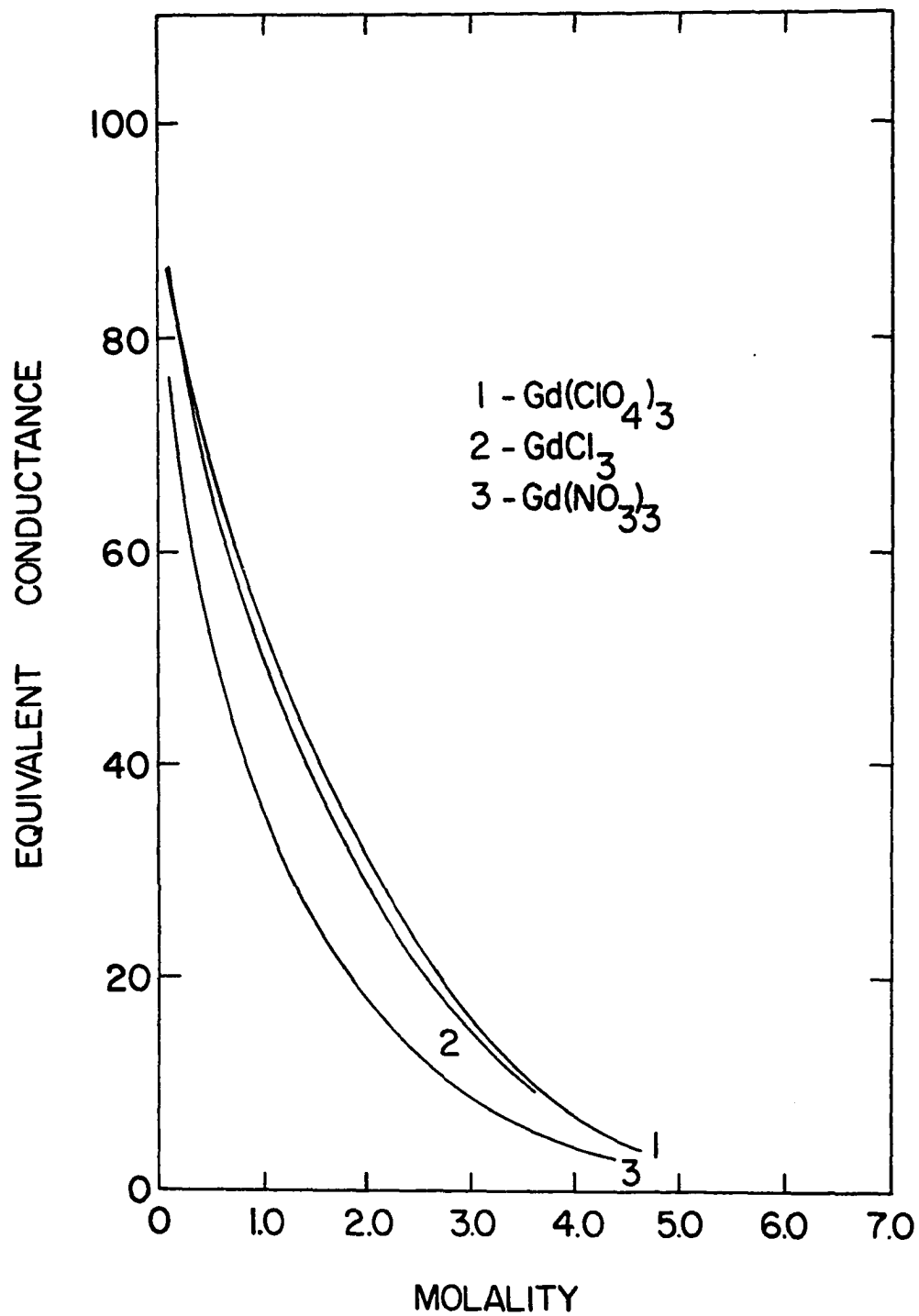


Figure 14. Equivalent conductances of gadolinium electrolytes

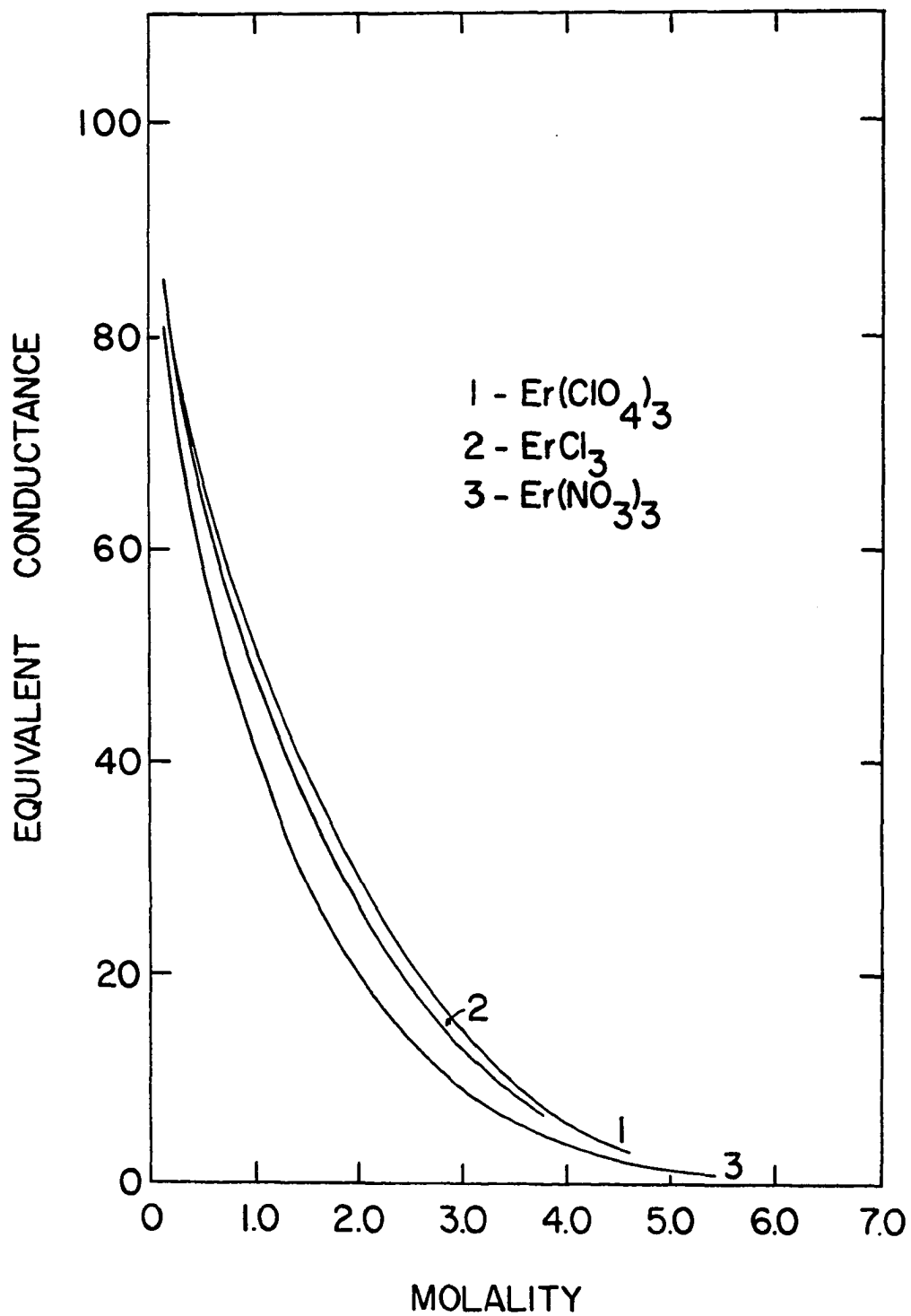


Figure 15. Equivalent conductances of erbium electrolytes

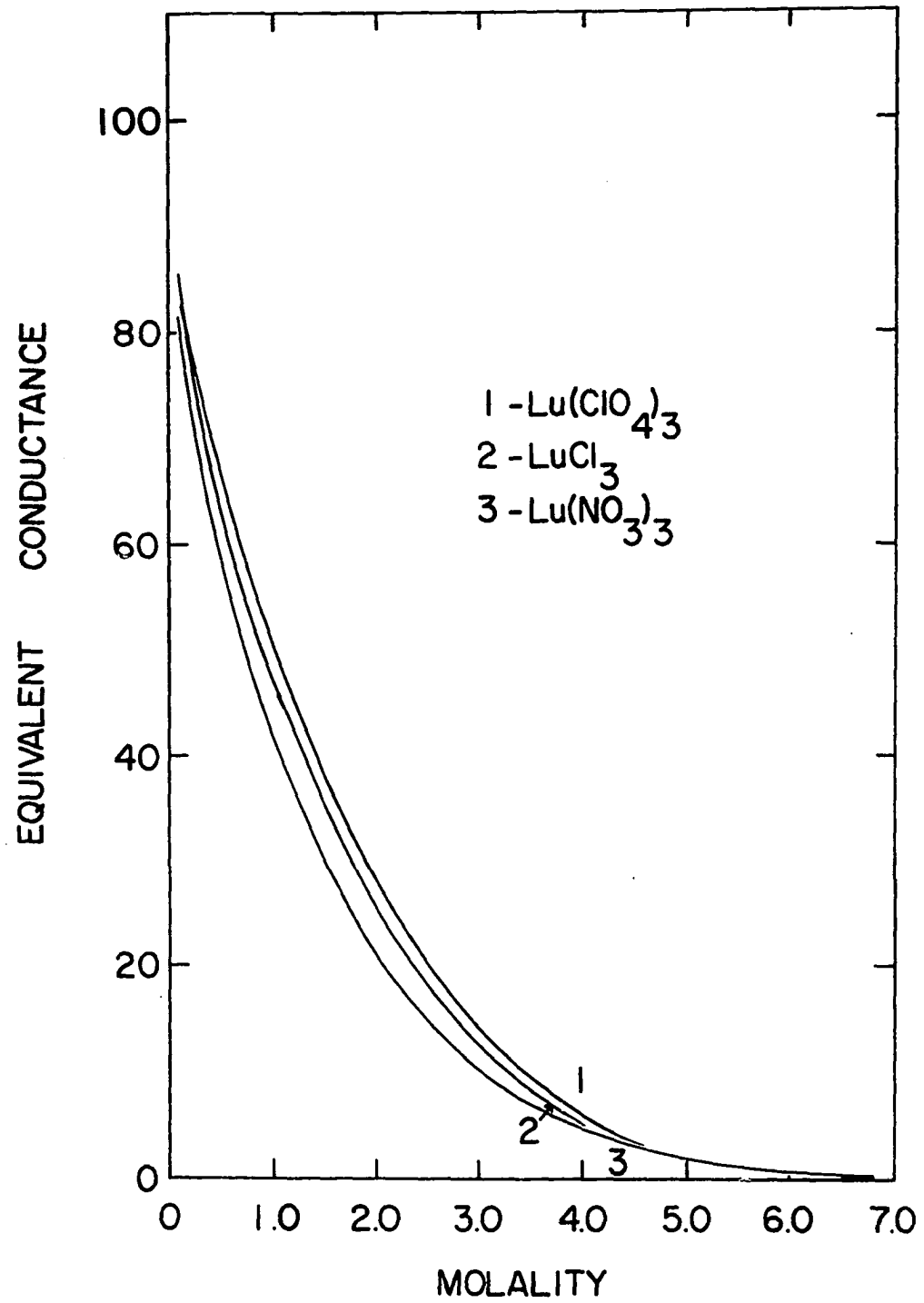


Figure 16. Equivalent conductances of lutetium electrolytes

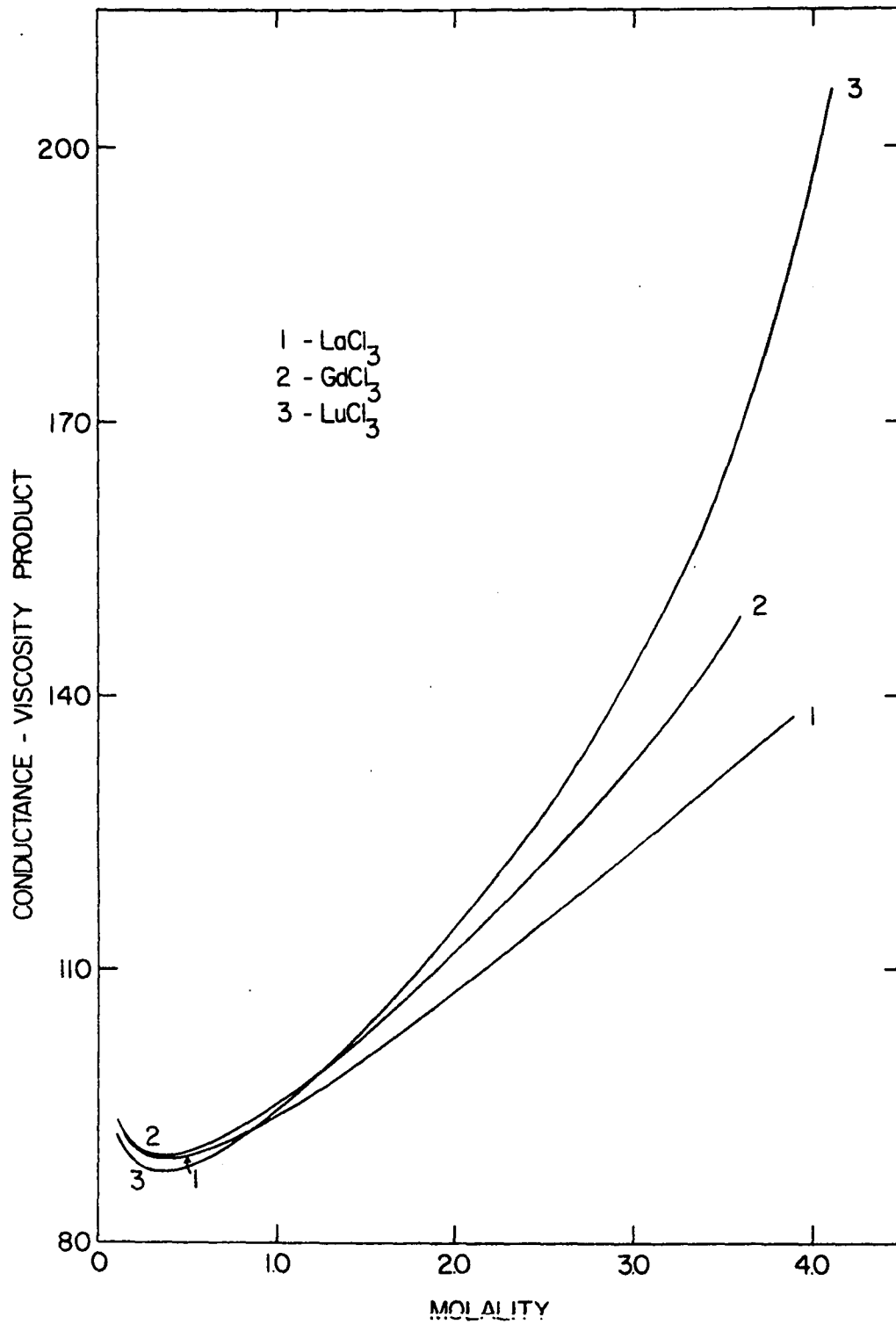


Figure 17. Product of the equivalent conductance and the relative viscosity for three rare earth chlorides

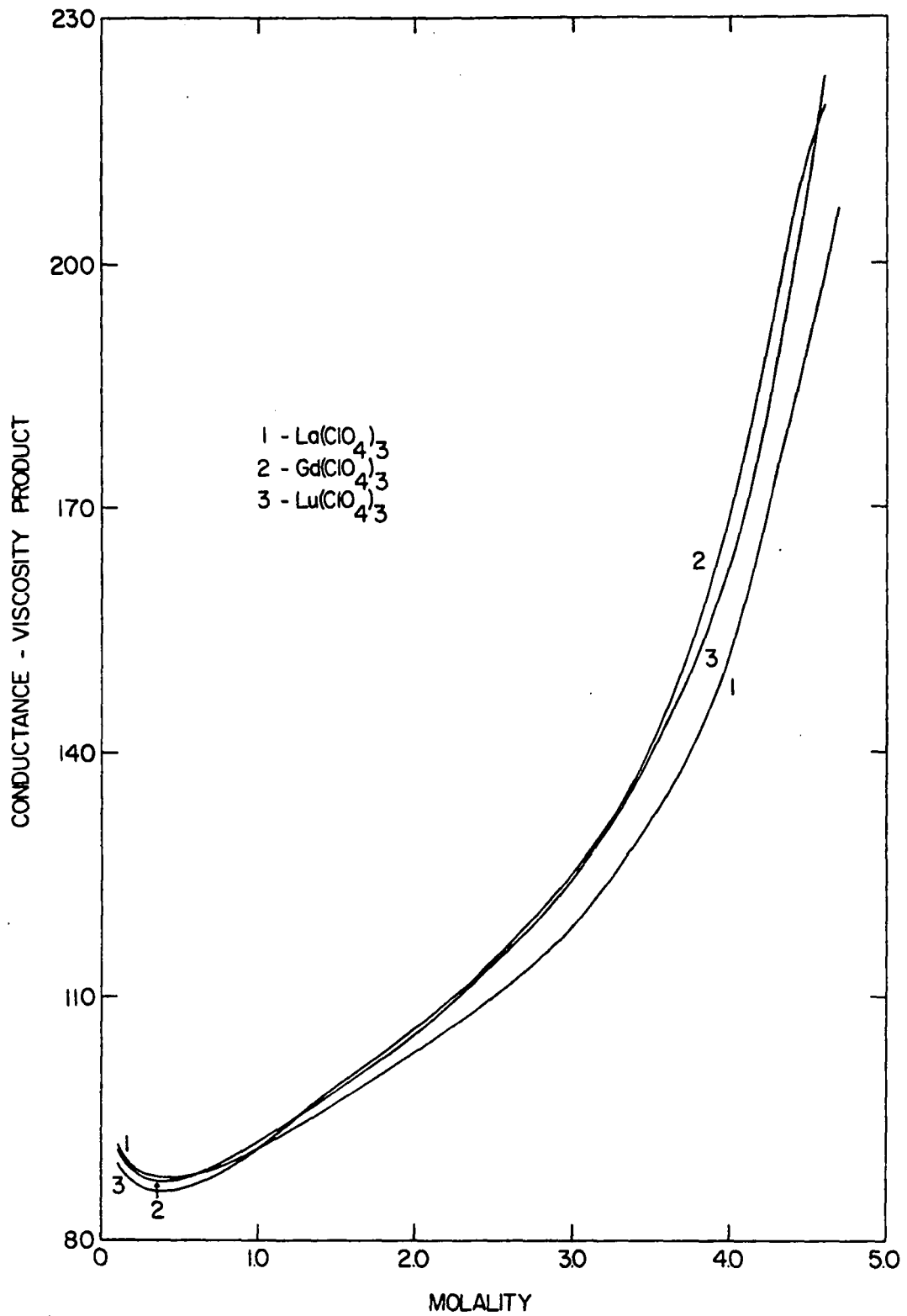


Figure 18. Product of the equivalent conductance and the relative viscosity for three rare earth perchlorates

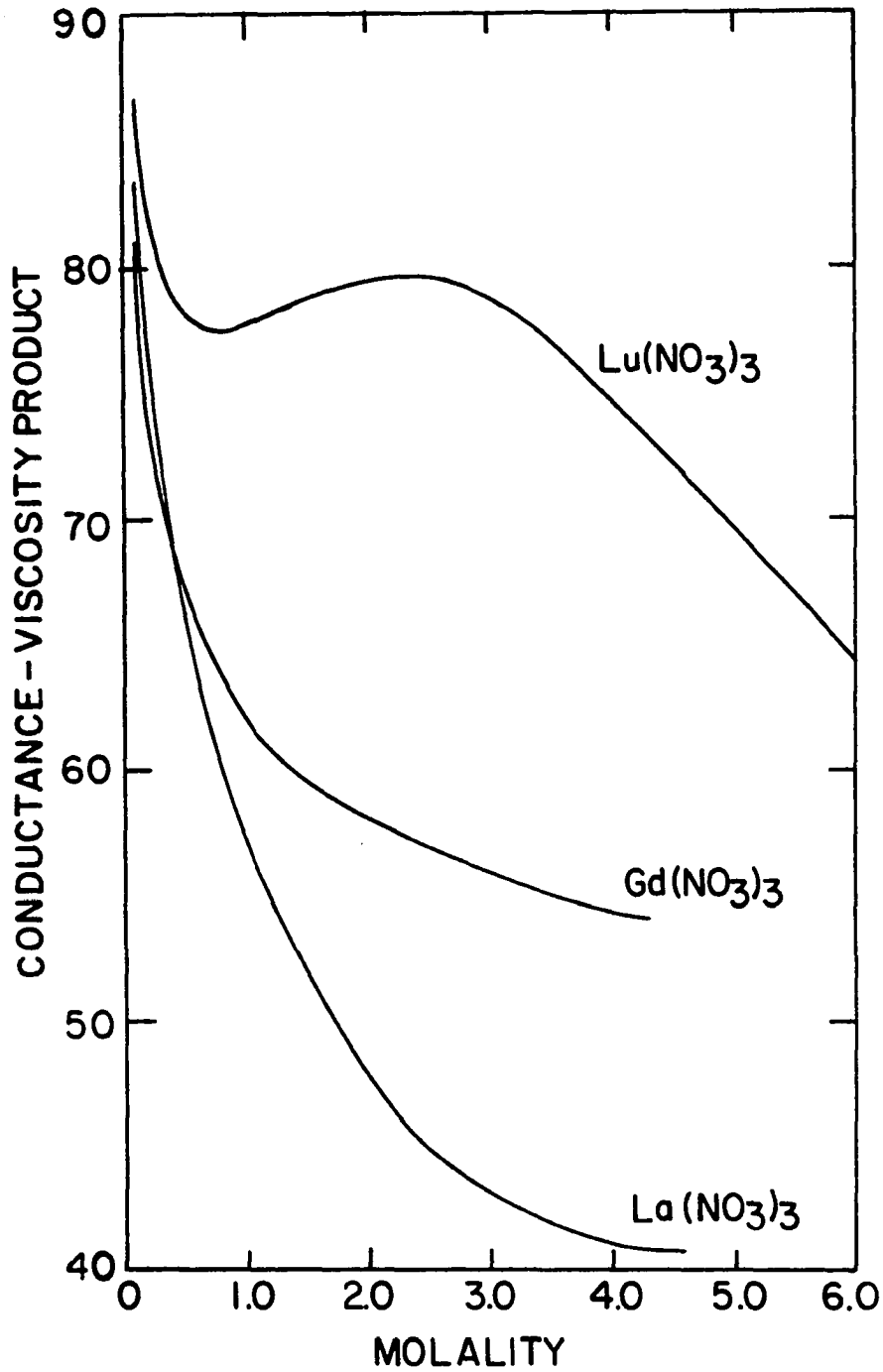


Figure 19. Product of the equivalent conductance and the relative viscosity for three rare earth nitrates

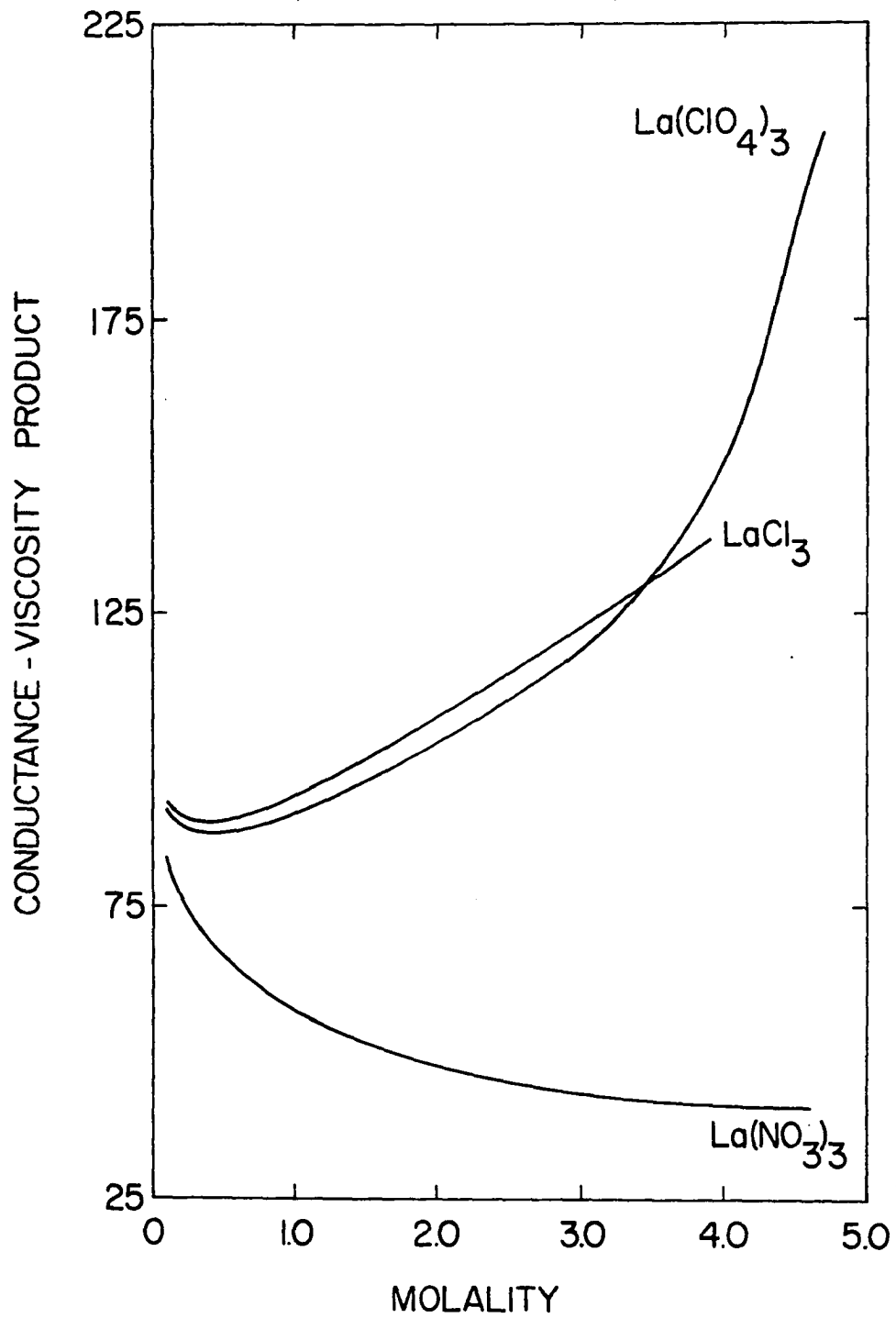


Figure 20. Product of the equivalent conductance and the relative viscosity for lanthanum electrolytes

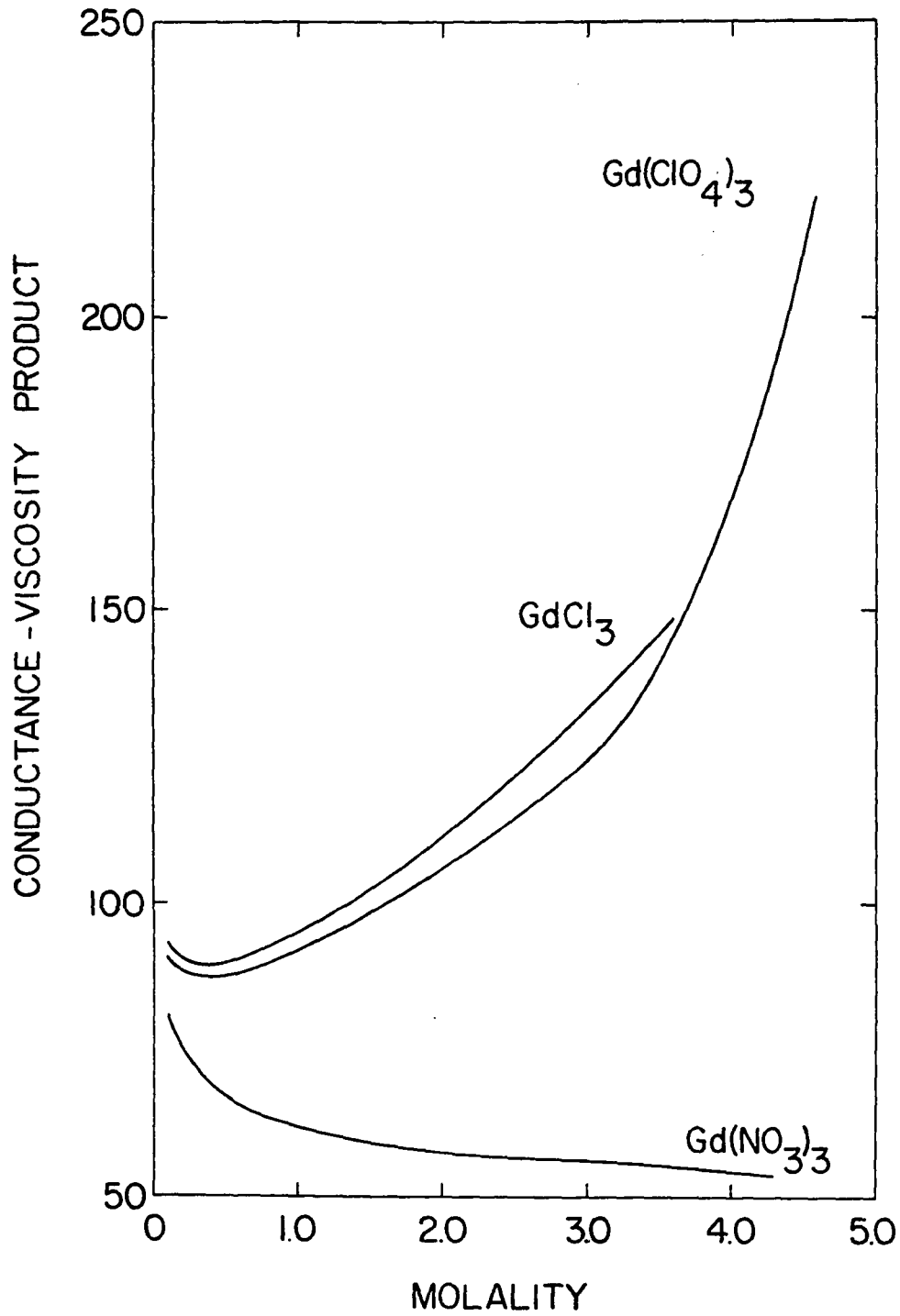


Figure 21. Product of the equivalent conductance and the relative viscosity for gadolinium electrolytes

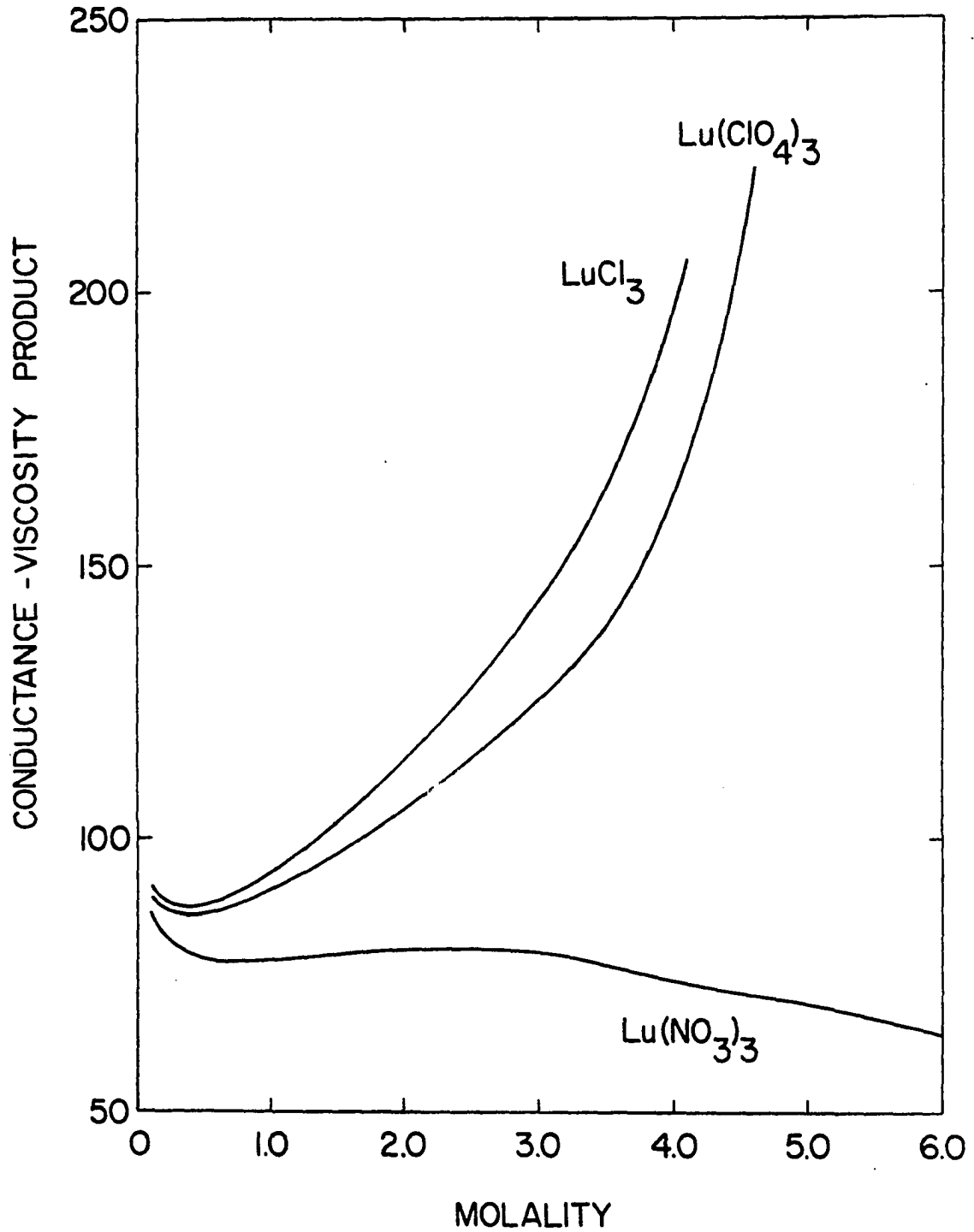


Figure 22. Product of the equivalent conductance and the relative viscosity for lutetium electrolytes

typical for the rare earth electrolytes. For a constant anion, the specific conductivity curves follow the same relative order as the equivalent conductance curves. The chloride solutions of each rare earth have higher specific conductivities above 0.15 molal than the corresponding perchlorates, while for the equivalent conductances above 0.15 molal the opposite is true. This different behavior for the specific conductivities is due mainly to the fact that 1 cm³ of solution has a different ratio of salt to water for the perchlorate and chloride solutions at constant molality. Since the equivalent conductances are on the basis of 1/3 of a mole, they are more readily interpreted than the specific conductivities, so the latter will be discussed only briefly.

There have been attempts to correlate the maximum in the specific conductivity curves with a structural transition occurring in solution (93). Others have tried to relate the concentration position of this maximum to the eutectic composition for those salts which form crystal hydrates (94, pp. 147-9). The interpretation of the conductance maximum in terms of a structural transition is not generally accepted. The absence of extrema in the corresponding equivalent conductance implies that if a structural transition is occurring in solution, then it must be of a continuous type and not readily studied by conductivity measurements.

D. Results for Equivalent Conductance

1. The rare earth perchlorates

a. Literature survey Water, at room temperature, is believed to be a highly structured liquid, due to hydrogen bonding. Eisenberg and Kautzmann (95, Chap. 4) have extensively discussed experimental evidence and theories concerning the nature of this structure. The bulky perchlorate ion is believed to promote a breakdown of this structure.

Evidence for the structure breaking nature of the perchlorate ion comes from the semi-theoretical Jones-Dole viscosity equation (96). This equation contains a "B-coefficient" in a term linear in the concentration of the electrolyte in solution. The perchlorate ion and several other large singly charged ions possess negative B-coefficients. According to Stokes and Mills (97) this negative value is "...probably related to the disturbance of the structure which is present in such liquids [especially water]."

Walrafen (98) studied the vibrational spectra of $\text{H}_2\text{O}-\text{D}_2\text{O}$ mixtures and analyzed his results in terms of a model in which hydrogen bonds are either present or absent between adjacent water molecules. He observed that the addition of perchlorate salts to water behaved like an increase in temperature on water, and interpreted this as an enhancement of the non-hydrogen bonded -OH and -OD peaks at the expense

of the hydrogen bonded peaks. While the bulky halides are also believed to be structure breakers, Walrafen concluded that the halide ions form a directed hydrogen bond with water while the perchlorate ions do not.

Brink and Falk (99) studied the IR spectra of HDO and concluded that the -OH to perchlorate interaction was equivalent to a weak hydrogen bond. They felt that bulky monovalent anions such as the halides, and especially the perchlorates, have too low a surface charge density to rigidly orient water molecules. Consequently, water molecules could then weakly interact simultaneously with other waters and with a perchlorate ion. This model predicts a lesser degree of structure breaking by the perchlorate ion than the model of Walrafen. Brink and Falk also obtained evidence for the existence of solvent separated ion-pairs in saturated solutions of several monovalent and divalent perchlorate salts.

A large amount of data available in the literature indicates the absence of strong complexation between the lanthanide and perchlorate ions in aqueous solutions. Klanberg, et al. (100) studied the NMR line broadening for perchlorate solutions containing $^{35}\text{ClO}_4^-$ and saw no line broadening in the presence of Ce^{+3} . This suggests the absence of strong complexation. Abrahamer and Marcus (101) found that the H_2O^{17} NMR shift in aqueous Er^{+3} solutions was independent of perchlorate ion concentration. This indicates

that no tightly bound water was being displaced by perchlorate ions. Reuben and Fiat (102) found that the H_2O^{17} NMR shift for Gd^{+3} , Dy^{+3} , Er^{+3} and Yb^{+3} perchlorate solutions was linear with molality to concentrations greater to 2.3 molal. This linear shift is a cation effect and gives no evidence for complexation between the rare earth and perchlorate ions at these concentrations. Nakamura and Kawamura (103) observed that the $^{139}\text{La}^{+3}$ NMR line width varied slightly with perchlorate concentration but they did not speculate about complexation.

Garnsey and Ebdon (104) studied the ultrasonic absorption of several dilute rare earth perchlorates and saw no evidence to indicate complexation. Choppin, et al. (105) have measured the visible spectra of Nd^{+3} in the presence of excess perchlorate ions and observed no change in the 7900-8000 Å band shape for perchlorate concentrations below 6.0 molar. Some perchlorate concentration dependence was observed at higher perchlorate concentrations, but too little data is presented from which to draw conclusions about complexation. Hester and Plane (106) studied the Raman spectra of La^{+3} and Ce^{+3} perchlorate concentrated solutions and concluded that the T_d symmetry of the perchlorate ion was preserved. Outer sphere complexation cannot be eliminated since it would probably not affect the

perchlorate ion symmetry appreciably. Similar conclusions have been reached in this laboratory¹.

On the other hand, a small amount of data exists suggesting the formation of weak complexes, at moderate concentrations, between the lanthanide and perchlorate ions. Heidt and Berestecki (107) inferred the existence of weak, solvent separated, ion-pairs between Ce^{+3} and ClO_4^- from UV spectra. Sutcliffe and Weber (108) have postulated a similar species to explain the kinetics of the reduction of Co^{+3} by Ce^{+3} . Outer sphere ion-pairs have also been suggested for ClO_4^- with Cr^{+3} (109) and Fe^{+3} (110,111).

The activity coefficients of several rare earth perchlorates are currently being measured by Spedding and co-workers². Their preliminary data indicates rather low water activities for concentrated rare earth perchlorate solutions. Other concentrated perchlorates also show this behavior (112). The water activities are approximately 30% higher for the rare earth chlorides³ (68) than for the corresponding perchlorates at 3.2 molal. Low water activities are usually

¹F. H. Spedding, B. Mundy, L. Gutierrez and M. A. Brown, Iowa State University, Ames, Iowa. Private communication. 1972.

²F. H. Spedding, H. O. Weber and L. E. Shiers, Iowa State University, Ames, Iowa. Private communication. 1972.

³F. H. Spedding and H. O. Weber, Iowa State University, Ames, Iowa. Private communication. 1972.

attributed to strong ionic hydration (35, p. 226). Since the rare earth chlorides do not show the low water activity, it may be concluded that some type of perchlorate ion hydration occurs. If this is the case, the reduction in the free water could result in some water sharing between ions beginning at 2 to 3 molal since insufficient water is available to separately satisfy the hydration needs of all the ions. This condition would force ion-pairing to occur. Preliminary crystal structure data¹ indicates that the perchlorate ions are outer sphere in the hydrated perchlorate salts. This type of outer sphere ion-pairing is probably the strongest complex that occurs in concentrated solutions of the perchlorates.

A large amount of data exists which suggests a decrease in the inner sphere hydration number for the rare earth ions across the series. Spedding et al. (87) have suggested that an inner sphere coordination number of 9 for La^{+3} to Nd^{+3} and a value of 8 for Tb^{+3} to Lu^{+3} was consistent with dilute apparent molal volume data for the rare earth chlorides and nitrates. The rare earths between Nd^{+3} and Tb^{+3} were assumed to exist as equilibrium mixtures of the two hydrated species. Subsequent apparent and partial

¹F. H. Spedding and L. Martin, Iowa State University, Ames, Iowa. Private communication. 1972.

molal volume determinations by Saeger and Spedding (68) and Spedding and co-workers¹ at higher concentrations indicate that this effect persists almost to saturation for aqueous rare earth chloride and perchlorate solutions with the two series effect becoming less distinct at very high concentrations. A number of thermodynamic properties for the perchlorates show this same effect, to varying degrees, including heat of dilution data² (113) and heat capacity data (90,91).

Lewis et al. (114) measured the H_2O^{17} NMR shift of most of the rare earth cations in aqueous solutions approximately one molar in Re^{+3} . These solutions contained perchloric acid and were enriched in D_2O . They obtained a sharp two series effect but tried to explain it in terms of co-valent bond formation between the rare earth ion and water. A hydration number decrease seems to be a more plausible explanation. Reuben and Fiat (102) studied the H_2O^{17} NMR shift for perchlorate solutions of Gd^{+3} , Dy^{+3} , Er^{+3} and Yb^{+3} . These rare earths are all near the end of the coordination shift and beyond, so no two series effect was observed.

¹ F. H. Spedding and co-workers, Iowa State University, Ames, Iowa. Private communication. 1972.

² F. H. Spedding and J. L. Derer, Iowa State University, Ames, Iowa. Private communication. 1972.

Morgan (115) suggested an inner sphere coordination number of 8 or 9 for Gd^{+3} , in perchlorate solution, from NMR data. He agreed with a coordination number decrease but suggested that it may be from 9 to 6. Nakamura and Kawamura (103) studied the $^{139}La^{+3}$ NMR spectra and concluded that both 8 and 9 hydrated La^{+3} may exist. Graffeo and Bear (116) studied the effect of a sudden change in pressure on the rare earth ion-oxalate system using A.C. conductivity methods. They proposed a rate determining step involving the loss of inner sphere water and attributed their two series effect to a decrease in primary coordination water.

Karraker (117) studied the visible spectra hypersensitive transitions of Nd^{+3} , Ho^{+3} and Er^{+3} in solutions containing concentrated HCl, LiCl and $HClO_4$. By comparing his spectra to crystal spectra with known symmetry, he concluded that, in dilute solutions, Nd^{+3} was 9 coordinated and the other two rare earths were 8 coordinated. In the concentrated electrolyte solutions he found that Nd^{+3} shifted to 8 coordinated. He suggested that the presence of large amounts of the monovalent electrolytes could have forced this change by tying up the free water. It would be expected that for stoichiometric rare earth perchlorate solutions that the dehydration would be nowhere near as complete.

Although a fair amount of data exists for the aqueous rare earth perchlorate solutions, very few definite quantitative conclusions can be drawn. The consensus of opinion is that the perchlorate ion is a structure breaker and possibly hydrated, and that the rare earth perchlorates are uncomplexed except for some outer sphere ion-pairing in concentrated solutions. In addition, an inner sphere hydration decrease is occurring for the rare earth cation across the rare earth series, and may possibly be from 9 to 8 waters.

b. The conductance data In Figure 5 the equivalent conductance curves are given for $\text{La}(\text{ClO}_4)_3$ and $\text{Lu}(\text{ClO}_4)_3$ as a function of molality. The full accuracy of the data cannot be presented on such a small graph. The conductance of each salt decreases regularly with increasing concentration. This type of behavior is generally observed for aqueous electrolyte solutions. Water adjacent to rare earth ions is strongly bound and probably close to a condition of dielectric saturation. As a result, the dielectric constant of the solution is reduced as the concentration of the electrolyte increases. Increasing the concentration causes the oppositely charged ions, on the average, to approach each other more closely. Both of these effects lead to ion-pairing in concentrated solutions and results in a lowering of the conductance. Hydration of the ions results

in a tying up of the solvent, leaving less free solvent for flow in more concentrated solutions. These hydrated ions also behave as obstructions to flow and produce a viscous drag which increases with the concentration of these obstructions. In dilute solutions, the drag of the ionic-atmosphere by the ions through the free solvent with its characteristic time of relaxation is a major factor influencing conductance. In addition, electrophoresis, or the movement of the solvent relative to the ions, plays an important role. In very concentrated solutions, the interpenetration of the hydration spheres becomes the major factor affecting conductance.

In Figures 9 and 10 the relative % difference in conductance are given for the rare earth perchlorates. These differences are relative to $\text{Lu}(\text{ClO}_4)_3$, which forms the x-axis in both graphs. These curves allow one to graphically study the small but real differences between the various rare earth perchlorate salts. Due to the accuracy of the polynomial fits, the curves at saturation are uncertain to about $\pm 1\%$ while in more dilute solutions the % differences are more reliable.

Below 2.4 molal, the rare earth perchlorate conductances are cleanly separated with the isomolal conductance decreasing as the rare earth atomic number increases. The decrease for the light rare earths is smaller than for the

middle and heavy rare earths. In Figure 24 the relative % differences in conductance and the relative viscosities (viscosity data of Spedding and Shiers) are shown at 2.5 molal for the various rare earth perchlorates. The decrease in conductance across the rare earth series at this concentration, and lower concentrations, is to be expected from the following elementary considerations. The radius of each rare earth ion is decreasing as the atomic number increases and the radius of the inner hydration sphere should do likewise. As a consequence of the higher surface charge density present for the smaller ions, the second hydration sphere will be bound more strongly with increasing atomic number and the total size of the hydration sphere will increase with the rare earth atomic number. A similar conclusion has been reached by Spedding and Weber¹ from rare earth chloride activity coefficient data. The total hydration sphere is involved in conductance so the cation mobility decreases with increasing atomic number. The anion contribution to conductance will be very similar for all the rare earth perchlorates so the order of the cation mobilities is given by the order of the conductance curves.

¹F. H. Spedding and H. C. Weber, Iowa State University, Ames, Iowa. Private communication. 1972.

Although an inner sphere hydration decrease is occurring in the middle of the series, the liberation of one mole of water to a system with a large amount of free solvent is not sufficient to overcome the effects which reduce the conductance as the atomic number increases. At low concentrations, only a very slight two series effect appears to be present.

In Figures 23 and 24, plots of the relative % differences in conductances and the relative viscosities for the various rare earth perchlorates are given at several isomolal concentrations. Beginning at 2.4 molal, the relative % differences in conductance at isomolal concentrations begin to form two series and this effect becomes very sharp by 3 molal. For the aqueous perchlorates at high concentrations, the isomolal conductances decrease from La^{+3} to Nd^{+3} , then rise to Gd^{+3} (and probably Tb^{+3}), and then decrease regularly to Lu^{+3} . The viscosity reflects these anomalies beginning at approximately the same concentration, for the same rare earths, and persisting to saturation. The same rare earth perchlorates that show the isomolal conductance rise and the isomolal viscosity decrease with increasing atomic number are those for which an equilibrium is believed to exist between the two hydrated forms of the cation.

Since both the conductance and the viscosity involve ionic mobilities, it might be expected that, as a very crude approximation, an inverse proportionality should exist

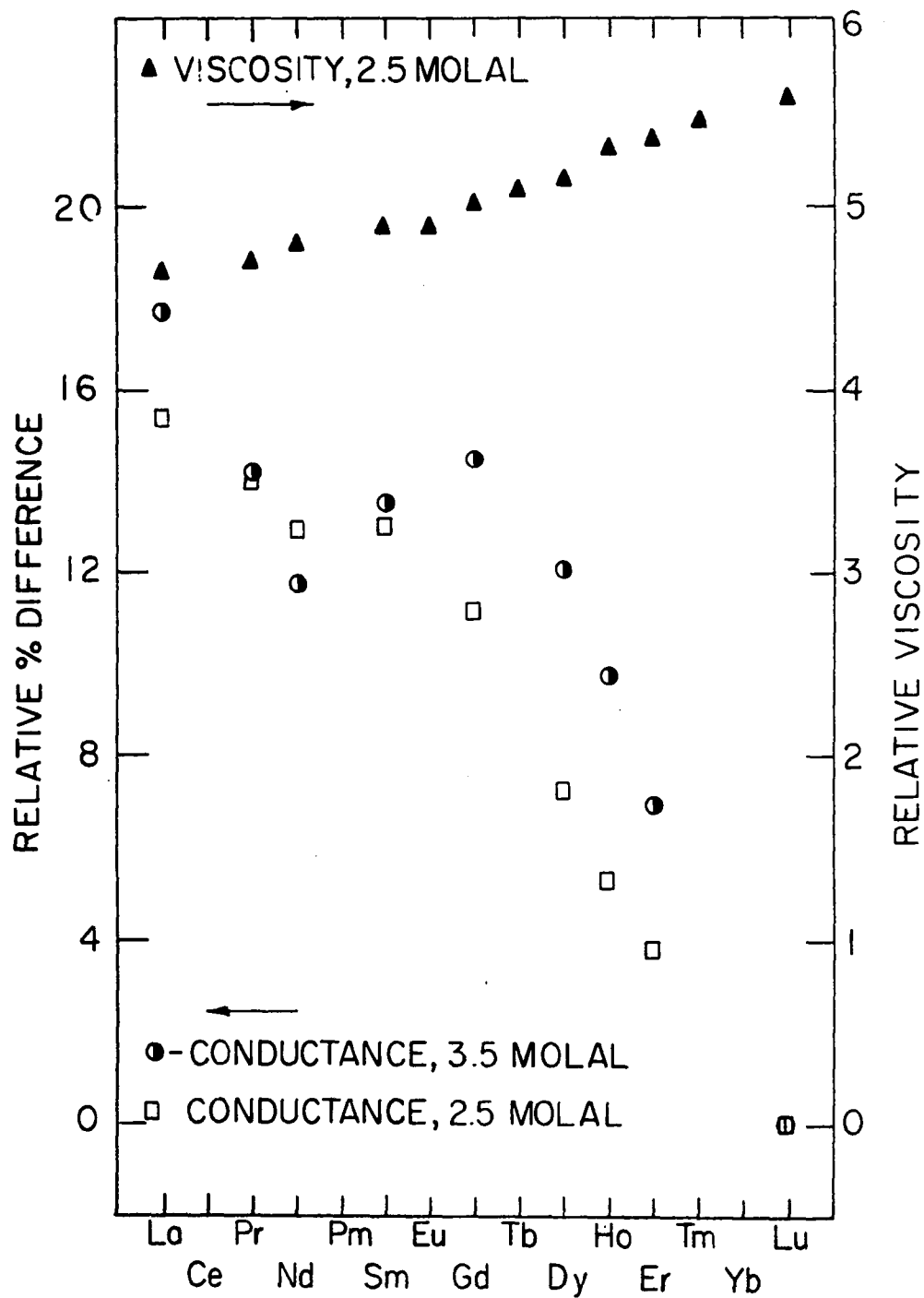


Figure 23. Relative percent differences in equivalent conductances and relative viscosities at constant molality for the rare earth perchlorates

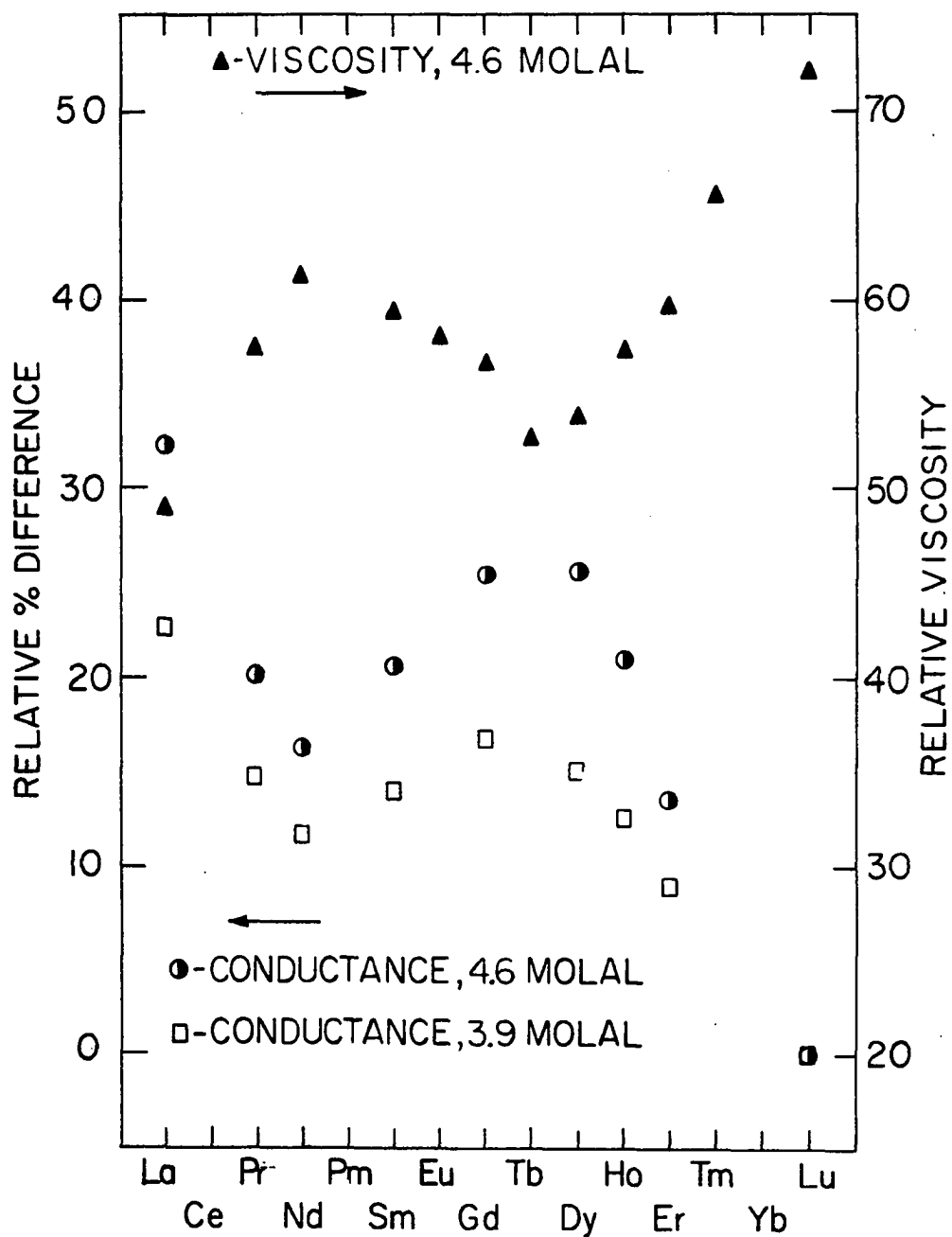


Figure 24. Relative percent differences in equivalent conductances and relative viscosities at constant molality for the rare earth perchlorates

between them. Between 0.1 molal and saturation the conductance-viscosity product varies by less than a factor of three for the perchlorates as seen from Figure 18. The conductance itself decreases by approximately a factor of 25 over this concentration range. The rise in this product above 0.4 molal indicates that the conductances does not decrease as fast as the viscosity increases. This moderate difference in behavior would be expected since these two transport properties involve somewhat different mechanisms.

By 2.4 molal, the bulk of the water in the rare earth perchlorate solutions is bound in the inner hydration spheres of the anions and cations. Below 2.4 molal, the viscosity increase is mainly due to the decrease in free water and the increase in the number of obstructions to flow. This results in an increasing viscosity, with concentration, and a decreasing conductance. When nearly all the waters are bound to the ions, this mechanism can no longer occur. The viscous flow is now probably dominated by the slippage of these hydrated ions relative to each other.

By 3 molal, too little water remains in the solutions to satisfy the separate inner sphere hydration needs of all the ions. Consequently, by this concentration, some inner sphere water will be shared between anions and cations and outer sphere ion-pairing will result from this. The

conductance will still depend on the slippage of the hydrated ions. In addition, the outer sphere ion-pairs will break and reform as the ions migrate in the electrical field. The ion-pairing may also result in a certain fraction of the perchlorate ions being carried along with the rare earth ion as it migrates in the electrical field.

The rare earth perchlorate solubility data indicates that there are approximately 12 water molecules present per rare earth molecule in saturated solutions. In this case, the bulk of the water surrounding the anions and cations is being shared; this results in extensive outer sphere ion-pair formation. The breaking of these ion-pairs by the electrical field would require considerable energy so the conductance of these solutions is fairly low.

The apparent molal volume data indicates that there is a change in the number of water molecules forming the cation inner hydration sphere across the rare earth series. This change occurs between Nd^{+3} and Tb^{+3} and an equilibrium results between the different hydrate forms of the cation. This equilibrium is shifted in favor of the lower hydrate with increasing atomic number. The water liberated from the inner hydration sphere, when the lower hydrate forms, will be much less firmly bound than when it was in the rare earth inner sphere. In concentrated solutions where nearly all water is inner sphere, the addition of a less firmly bound

water will allow the hydrated ions to slip past each other more easily and result in a viscosity decrease relative to the lighter rare earths. This "extra" water will also reduce the extent of ion-pairing slightly and will contribute to other factors which act to increase the conductance. The net effect will be to increase the conductance for these rare earth ions which have an equilibrium between the two hydrated cation forms, relative to those rare earths with the higher hydration numbers. The end result is the two series effect.

In more dilute solutions, the overall hydration sphere size increases with the atomic number of the rare earth, so the conductance decreases. When all the water is tied up as inner sphere water, then the inner sphere size should be the controlling factor for conductance down the rare earth series. The lanthanide contraction results in a decreasing size for the inner hydration sphere and consequently leads to an increasing surface charge density for the hydrated cation. This causes ion-pairing to increase in strength down the series and gives rise to the isomolal decrease in conductance from La^{+3} to Nd^{+3} and from Tb^{+3} to Lu^{+3} at higher concentrations. The isomolal rise in conductance from Nd^{+3} to Tb^{+3} is, as discussed, due to the inner sphere hydration decrease.

Mohs (113) found that the partial molal entropy of water in three rare earth perchlorate solutions showed unusual behavior beginning around 2.5 to 3.0 molal. This abnormal

behavior is probably due to the onset of the system in which outer sphere water is being shared.

2. The rare earth chlorides

a. Literature survey The chloride ion, like the perchlorate ion, is believed to partially break down the hydrogen bonded structure of water. Evidence for this includes the negative value for the Jones-Dole "B-coefficient" found for the chloride ion (97). The chloride ion would not be expected to produce as large a structure breaking effect as the perchlorate ion due to its smaller size.

Walrafen (98) studied the H_2O - D_2O vibrational spectra in the presence of chloride ions. He concluded that, unlike the perchlorate ion, the halide ion forms linear or nearly linear hydrogen bonds with water. Walrafen's model would predict that the chloride ion is a weaker structure breaker than the perchlorate ion, since the chloride ion participates in hydrogen bonding. Brink and Falk (99) studied chloride solutions of HDO by IR and concluded that the chloride ion, like the perchlorate ion, would not rigidly orient the water molecules. Any structure breaking differences would then be size differences. Samoilov (94, p. 171) concluded from mobility and self-diffusion data that the chloride ion, when it undergoes jumps in solution, generally does so without associated water.

As was mentioned in the perchlorate section, the water activity of the rare earth chlorides is 30% higher than for the rare earth perchlorates at 3.2 molal. This indicates that the halide ion binds less water, and does so less strongly, than the perchlorate ion. The rare earth chlorides should not therefore participate in water sharing to the same extent that the rare earth perchlorates do.

A moderate amount of data available in the literature suggests the presence of weak complexes between the rare earth and chloride ions in aqueous solution. Choppin and Unrein (118) measured the first association constant between the rare earth and chloride ions, at an ionic strength of one, by liquid extraction. They felt that their ΔH and ΔS values were too small to allow a definite assignment of the complex type but they considered an outer sphere complex as most likely. They also found indications of a small amount of two to one complex. Ahrland (119) has discussed the thermodynamic criteria for outer and inner sphere complexes and agreed with Choppin and Unrein's assignment of the rare earth chloride complexes as outer sphere.

Sayre et al. (120) studied the aqueous EuCl_3 fluorescent spectra up to 1.5 molar and saw no evidence for complexation. Choppin et al. (105) studied the visible spectra of Nd^{+3} in the presence of excess chloride ions. They observed no change in the 7900-8000 Å band shape for chloride

concentrations below 5 molar, but did see some effect at higher concentrations. Outer sphere complexes may be too weak to effect spectra which arises from transitions within the 4f shell of the rare earth ion.

Nakamura and Kawamura (103) studied the NMR spectra of aqueous $^{139}\text{La}^{+3}$ and saw no chloride ion concentration dependence of the line width in dilute solution. Ultra-sonic absorption, which is mainly a tool for studying inner sphere complexes, did not detect complexation for rare earth chlorides in moderately dilute solutions (104).

Some methods do detect the presence of weak complexes and there has been a small amount of success in measuring the formation constant of the first outer sphere chloride complex. Peppard et al. (121) and Choppin and Unrein (118) have measured the first formation constant for several different rare earth chloride complexes by liquid extraction, and Bansal et al. (122) did so for Eu^{+3} by ion exchange. Goto and Smutz (123) have measured several values by a potentiometric method. All these measurements were made at an ionic strength of one and indicate that the formation constant for the first chloride complexes of La^{+3} to Eu^{+3} is the same, within experimental error (118,121,123). In addition, the heavy rare earths are probably less complexed than the lights (121). The most complete set of first formation constants was measured by Kozachenko and

Batyaev (124) for 10 rare earths at an ionic strength of 3, using UV spectra. They found that the first formation constant rose from $.82 \pm .02$ for Pr^{+3} to a maximum of $1.10 \pm .02$ at Eu^{+3} , and then decreased to $.78 \pm .02$ for Yb^{+3} . They concluded that in aqueous solution the complexes were outer sphere. There is sufficient variation among the equilibrium constant values reported in the literature that additional measurements should be made before the equilibrium "constants" can be considered as more than qualitatively reliable.

Brady (125) studied the X-ray scattering of aqueous ErCl_3 up to 3 molal. He concluded that two chlorides were associated with the Er^{+3} and that they were separated from the Er^{+3} by a sphere of water. In the hydrated crystals (126-128), two chloride nearest neighbors are present around the rare earth. In nearly saturated solutions, similar coordination for the rare earth ion might be expected.

The same type of data that indicates the inner sphere coordination number decrease for the rare earth perchlorate series also indicates that a two series effect is present for the chlorides. Heats of dilution and partial molal entropies (129,130), heat capacities (89,90) and thermal expansibilities¹ show this effect. Apparent and partial

¹F. H. Spedding and A. Habenschuss, Iowa State University, Ames, Iowa. Private communication. 1972.

molal volume data¹ (68) indicates that this two series effect is present almost to saturation, although it becomes somewhat less distinct at very high concentrations.

From the above data very few quantitative conclusions can be reached. It appears that the chloride ion is structure breaking and hydrated, though to a lesser degree than for the perchlorate ion. The coordination number decrease remains present, in some form or other, for the rare earth chlorides almost to saturation. In addition, the chloride ion forms outer sphere complexes with the rare earth ion by an ionic strength of one and possibly inner sphere complexes in very concentrated solutions.

b. The conductance data In Figures 13-16, the equivalent conductance curves are given for some typical rare earth electrolytes, with a constant cation on each graph. The rare earth chloride and perchlorate conductances are quite similar with the perchlorate salts being more conducting than the chlorides, over most of the concentration range. The limiting conductance, λ_0^- , of the perchlorate ion, due to the ion's large size, is less than that for the chloride ion. At concentrations between 0.11 and 0.15 molal, however, all of the rare earth perchlorate

¹F. H. Spedding and co-workers, Iowa State University, Ames, Iowa. Private communication. 1972.

studied in this research have crossed the curves of the corresponding chlorides.

The rare earth chlorides are believed to form outer sphere complexes in moderately dilute solutions. This would cause the rare earth chloride conductances to be lowered relative to the corresponding perchlorates. The light rare earth perchlorate and chloride conductance curves tend to cross at slightly lower concentrations than do the heavy rare earths. This is to be expected from the dilute equilibrium constant data for the chlorides (121), which indicates that the heavy rare earths are less complexed than the light rare earths. If complexation were the only major factor affecting conductance for the chlorides, then dilute solution equilibrium constant data would predict a more regular concentration dependence of the crossover than is actually observed. Although the rare earth chlorides may be forming inner sphere complexes by saturation, there is no marked evidence for this from the conductance curves.

Another factor affecting the difference in conductance between the rare earth chlorides and perchlorates is the size of the anion. The larger perchlorate ion disrupts the hydrogen bonded structure of water more than the chloride ion does. The breakdown of hydrogen bonding enhances the conductance of the solutions in which it occurs. This effect should be proportional to the anion concentration and

would have little effect on the conductance of dilute solutions. At intermediate concentrations, before water sharing becomes important, this effect would enhance the rare earth perchlorate conductances relative to the corresponding chlorides. The greater amount of outer sphere complexation in the rare earth chlorides, however, is probably the most important effect in lowering the rare earth chloride conductances relative to the corresponding perchlorates.

In Figures 7 and 8 the relative % difference curves are given for the rare earth chloride equivalent conductances. The conductance curves from LaCl_3 to SmCl_3 are close together, while from SmCl_3 to LuCl_3 , the curves are cleanly separated. The PrCl_3 and NdCl_3 curves are very similar and dip below the SmCl_3 curve by saturation. LaCl_3 is less conducting than might be expected. These curves are very similar to the perchlorate curves up to concentrations where water sharing begins in the perchlorates. In Figure 25, the relative % differences in isomolal conductance are given for the rare earth chlorides and perchlorates at 1.0 and 2.0 molal. At 1.0 molal the perchlorate and chloride values are quite similar, but by 2.0 molal the different anions are causing distinctive behavior to occur for the various rare earths.

In Figure 26, the relative % differences and relative viscosities are given for the rare earth chlorides at isomolal concentrations of 2.5 and 3.5 molal. The general

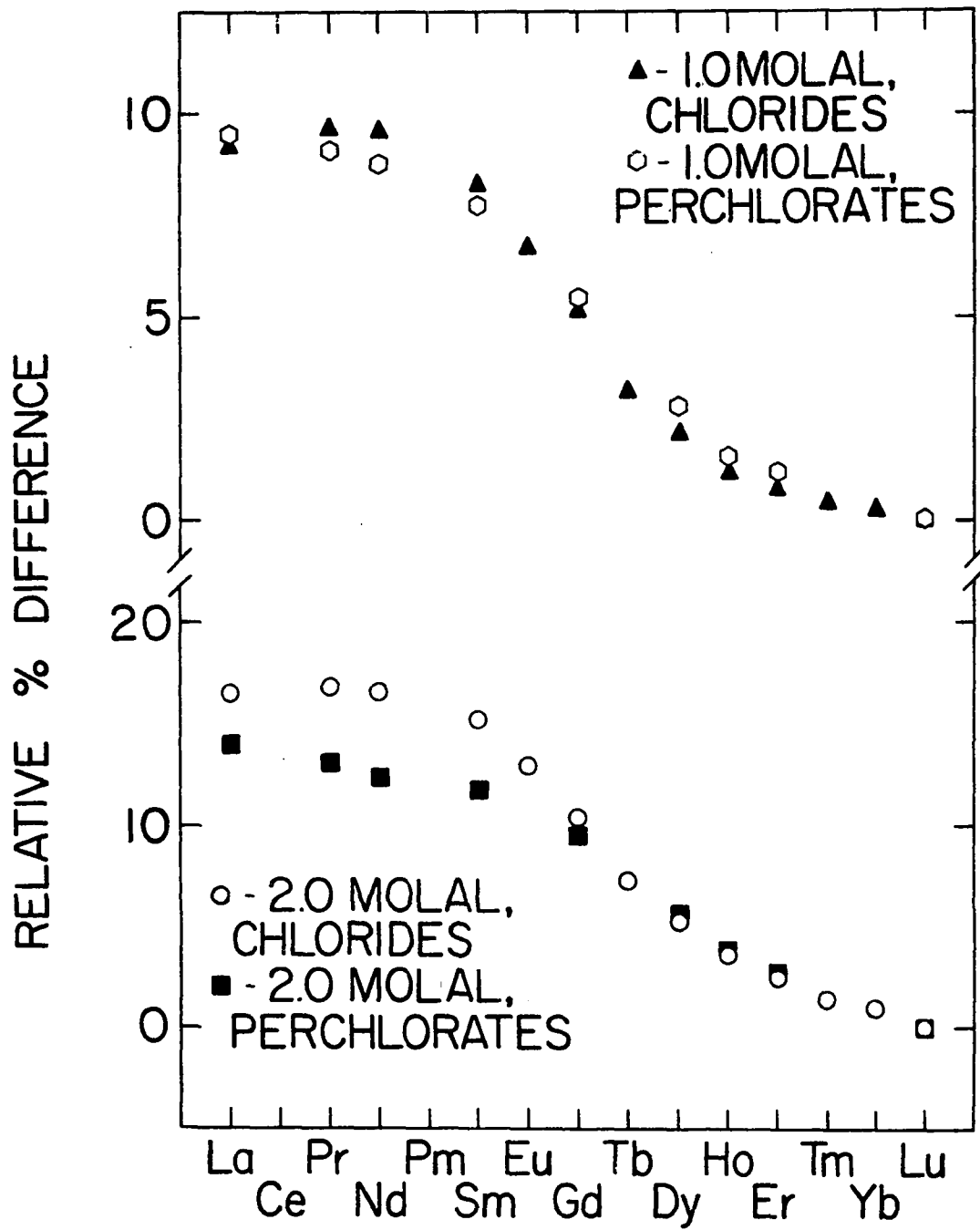


Figure 25. Relative percent differences in equivalent conductances at constant molality for the rare earth chlorides and perchlorates

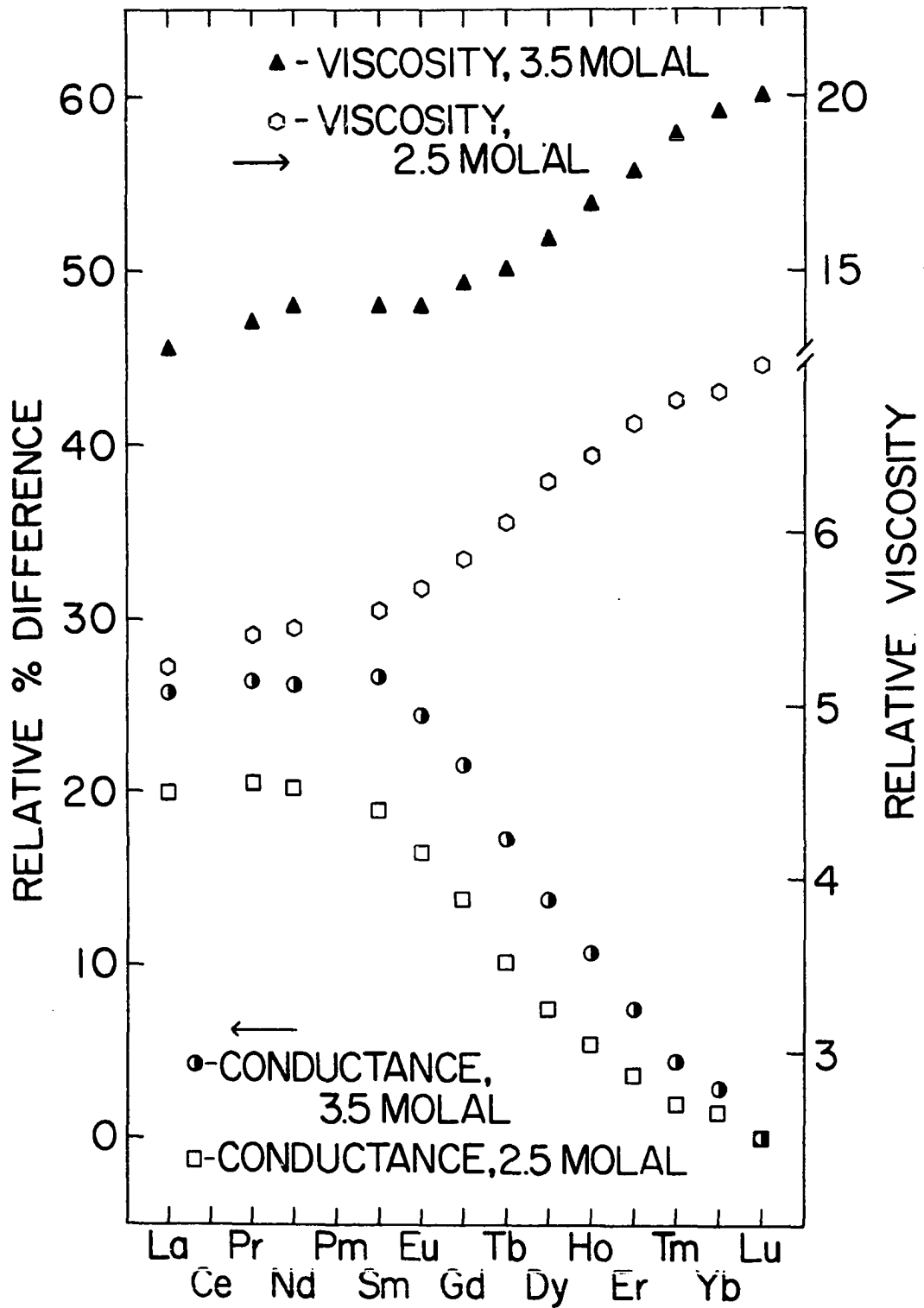


Figure 26. Relative percent differences in equivalent conductances and relative viscosities at constant molality for the rare earth chlorides

shape of the isomolal curves in Figure 26 differs little in shape from the more dilute solution curves in Figure 25. Outside of contributing to the lowering of the rare earth chloride conductances, relative to that of the corresponding perchlorate conductances, complexation does not strongly affect the general shape of the isomolal relative % difference curves.

In Figure 17, the conductance-viscosity products are given for LaCl_3 , GdCl_3 , and LuCl_3 . In Figures 20-22, similar curves are given for the chloride, perchlorate and nitrate salts of these three rare earths. For La^{+3} and Gd^{+3} below 3 molal, the chloride and perchlorate curves are fairly similar. Above this concentration, water sharing causes the perchlorate curves to rise very steeply relative to the corresponding chloride curves. The LuCl_3 and $\text{Lu}(\text{ClO}_4)_3$ conductance-viscosity products are more separated than for La^{+3} and Gd^{+3} , but the shape of the Lu^{+3} curves is quite similar.

3. The rare earth nitrates

a. Literature survey The nitrate ion, like the chloride and perchlorate ion, is believed to be a water structure breaker since it possesses a negative Jones-Dole "B-coefficient" (97). From size considerations, the structure breaking effect of the nitrate ion should be intermediate between that of the chloride and perchlorate ions.

The "B-coefficients" do, in fact, follow this order (131, p. 87).

In dilute rare earth nitrate solutions a mixture of inner and outer sphere complexes probably exists. Choppin et al. (105) found that the shape of the 7900-8000 Å band of Nd^{+3} in the presence of excess nitrate ions showed a strong dependence on the nitrate concentration. They concluded that in dilute solutions a mixture of inner and outer sphere complexes exists with the predominant species being outer sphere. Similar conclusions have been reached from other Nd^{+3} absorption spectra (132). Choppin and Strazik (133) studied the thermodynamics of formation of $\text{Eu}(\text{NO}_3)^{+2}$ in dilute solutions and concluded that outer sphere complexes were formed. Their value for ΔG was more negative than for EuCl^{+2} , indicating a larger amount of outer sphere complexation in the nitrates. Ultrasonic absorption (104,134) indicates that the ratio of the concentrations of outer to inner sphere complexes is on the order of unity for solution concentrations of 0.35 molar and lower.

Nakamura and Kawamura (103) studied the $^{139}\text{La}^{+3}$ NMR spectra in nitrate solutions and found a large line width dependence on nitrate concentration. They concluded that the formation of inner sphere complexes was likely. Abrahamer and Marcus (101) studied the density, the H_2O^{17} NMR shift, and the optical absorbance of $\text{Er}(\text{NO}_3)_3$ up to quite

concentrated solutions. The molar absorptivity of the solutions at 5215 Å was approximately a linear function of both the Er^{+3} and the NO_3^- concentration, which they considered as evidence of inner sphere coordination. They also studied the H_2O^{17} NMR isotopic shift caused by the addition of nitrate ions to $\text{Er}(\text{ClO}_4)_3$ solutions, and concluded that the nitrate ion was forming inner sphere complexes with the rare earth ion. Similar conclusions were reached for the addition of nitrate ions to $\text{Dy}(\text{ClO}_4)_3$ (102). Reuben and Fiat (102) suggested that two waters may be released by the entry of one nitrate into the inner sphere of the rare earth ion.

Hester and Plane (106) studied the $\text{La}(\text{NO}_3)_3$ and $\text{Ce}(\text{NO}_3)_3$ Raman nitrate bands in concentrated solutions. They concluded the "intimate ion-pairing" was occurring with possibly some covalent bond formation. They also felt that the binding was occurring through the oxygens of the nitrate. Using Raman data, Knoeck (135) concluded that bidentate nitrate coordination was occurring in $\text{La}(\text{NO}_3)_3$ solutions. Nelson and Irish (136) studied the Raman spectra of $\text{Gd}(\text{NO}_3)_3$ solutions and concluded, using Job analysis, that hydrated $\text{Gd}(\text{NO}_3)_2^+$ was the predominant species under certain conditions. They felt that one nitrate was bound by two oxygens and the other by a single oxygen.

In solutions containing excess nitrate ions, several complexes have been suggested. Abrahamer and Marcus (137) studied the visible spectra of solutions of 9 different rubidium nitrate-rare earth nitrate double salts. They felt that their data indicates the formation of hydrated $\text{Re}(\text{NO}_3)_2^+$ in concentrated aqueous solutions. In solutions containing a 7 to 1 excess of NO_3^- to La^{+3} , Knoeck (135) obtained polarographic evidence for the formation of a 3 to 1 complex. Electrotransport measurements in the presence of huge excesses of nitrate indicates that negatively charged species may also form (138).

Several measurements have been made for the first formation constants of the rare earth nitrate complexes. Bansal et al. (122) studied the $\text{Eu}(\text{NO}_3)^{+2}$ system by liquid extraction. Choppin and Strazik (133) studied Ce^{+3} , Pm^{+3} , Eu^{+3} , Tb^{+3} and Tm^{+3} nitrate complexes at an ionic strength of one by liquid extraction, and found a maximum in complexation in the vicinity of Pm^{+3} , with the heavy rare earths less complexed than the lights. Peppard et al. (121) studied La^{+3} , Ce^{+3} , Pr^{+3} , Eu^{+3} , Tm^{+3} , Yb^{+3} and Lu^{+3} using similar methods, and found a maximum in complexation in the vicinity of Eu^{+3} with the heavies also less complexed than the lights. The equilibrium constants for 4 rare earth nitrates have been measured at an ionic strength of 4 using visible spectra (139,140). The various equilibrium constant

determinations are not in complete agreement, and additional measurements need to be made.

Several rare earth series with other anions have a stability complex maxima around Eu^{+3} (141). Manning (142) interpreted this behavior for the monoacetate complexes as a shift from bidentate to monodentate coordination across the rare earth series. Such an effect could possibly be occurring in the nitrates but such behavior would not necessarily persist after higher order complexes begin to form.

Crystal structure measurements have been made on some light rare earth nitrate hydrated crystals (143). The $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ crystal was found to possess three doubly coordinated nitrates and 4 waters in the inner sphere. Walters and Spedding (90) and Baker and Spedding (91), using partial molal heat capacity data, have suggested the possibility of hydrated neutral $\text{Re}(\text{NO}_3)_3$ formation in highly concentrated $\text{Tm}(\text{NO}_3)_3$, $\text{Yb}(\text{NO}_3)_3$ and $\text{Lu}(\text{NO}_3)_3$ solutions.

Higher complexes and non-equivalent nitrates have been suggested in several non-aqueous solutions. In tri-n-butylphosphate, Karraker (144) suggested that two bidentate and one monodentate nitrates were present in the Nd^{+3} complex, while the three nitrates were monodentate for the Er^{+3} complex. In dimethyl formamide, La^{+3} - Sm^{+3} were felt to have two bidentate and one monodentate nitrates (145).

In hexamethylphosphoramide, La^{+3} and Nd^{+3} were found to have all coordinated nitrate, while Sm^{+3} to Yb^{+3} had ionic and coordinated nitrate (146). In each of these cases the light rare earths were found to be more strongly complexed than the heavier rare earths.

From the above data it can be concluded that in dilute solutions of the rare earth nitrates, a mixture of inner and outer sphere complexes exists. In more concentrated solutions, predominately inner sphere complexation is occurring. In highly concentrated solutions, hydrated $\text{Re}(\text{NO}_3)_2^+$ may be forming. The nitrate to rare earth coordination may be monodentate or bidentate or an equilibrium of the two forms across the rare earth series. From the available literature data it is not possible to conclude the exact type of coordination and extent of higher complex formation with any certainty, since different species have been postulated from different experimental data.

b. The conductance data In Figures 13-16, plots are given for the equivalent conductances of the rare earth perchlorate, chloride and nitrate salts of 4 different rare earth cations. In each case the nitrate is the least conducting salt. This is to be expected if complexation with the nitrate ion is reducing the numbers of free ions and the charge on the rare earth ions. The chloride and perchlorate conductances decrease across the rare earth series, except

for some crossing among the concentrated light and middle rare earths. The rare earth nitrate curves above 0.8 molal are increasing in conductance from La^{+3} to Lu^{+3} .

In Figures 11 and 12, the relative % differences in conductances are given for the various rare earth nitrates. Above 0.8 molal all the salts fall in the reverse of the order found for the chlorides and perchlorates. Below 0.8 molal, La^{+3} to Nd^{+3} show the regular order. From the dilute rare earth nitrate conductance data of Spedding and Jaffe (147) and Heiser (148), it appears that the reversal in the Sm^{+3} to Lu^{+3} order occurs at concentrations on the order of a few millomolal. This dilute conductance data has been reviewed by Spedding and Atkinson (70).

In Figure 27, the relative % differences in conductance are given for the various rare earth nitrates at isomolal concentrations of 0.5 and 1.0. At 0.5 molal, the conductance data indicates that the conductance minima should occur at Eu^{+3} . The data of Peppard et al. (121) indicates that the maximum in complexation may occur at Eu^{+3} , with the heavy rare earths complexed less than the lights. This causes the conductance of the rare earth nitrates to decrease from La^{+3} to (presumably) Eu^{+3} , and then to increase to Lu^{+3} as the association constant decreases. This conductance is precisely what one would expect from the limited equilibrium constant data available. By one molal the minima in the

isomolal conductance curve has vanished. In Figure 28 the equivalent conductance isomolal curves are given at 2.0 and 4.0 molal, and the relative viscosities at 4.0 molal. At these higher concentrations, the isomolal conductance is increasing regularly from La^{+3} to Lu^{+3} .

The conductance of a salt in solution depends on the mobility, charge and concentration of each species. The mobility of a free nitrate ion, at a constant concentration, should be fairly similar for all the rare earth nitrates. The mobility of the hydrated Re^{+3} ion, and of any series of complexes of the same stoichiometry, should decrease from La^{+3} to Lu^{+3} . The increase in the isomolal conductance in going from La^{+3} to Lu^{+3} can therefore only be due to a decrease in the amount of complexation across the series. Above 1 molal, consequently, the overall formation constant will decrease from La^{+3} to Lu^{+3} , and this trend in stability will persist to saturation for the various rare earth nitrates studied in this research.

Apparent molal volume data for the rare earth chloride and perchlorates indicates that an inner sphere hydration change occurs across the rare earth series. No evidence for this two series effect above 0.5 molal appears in the apparent molal volume data for the nitrates¹. The

¹F. H. Spedding and co-workers, Iowa State University, Ames, Iowa. Private communication. 1972.

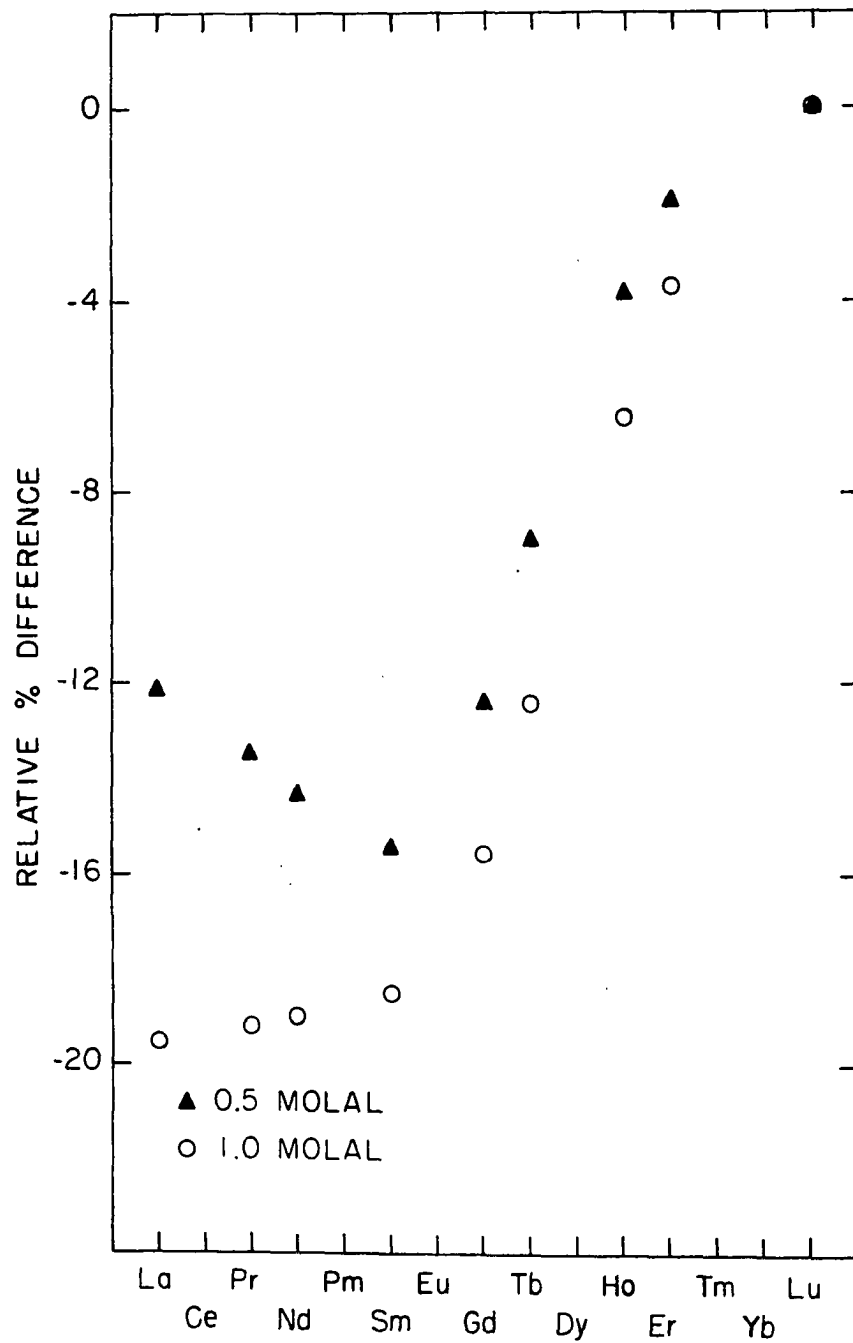


Figure 27. Relative percent differences in equivalent conductances at constant molality for the rare earth nitrates

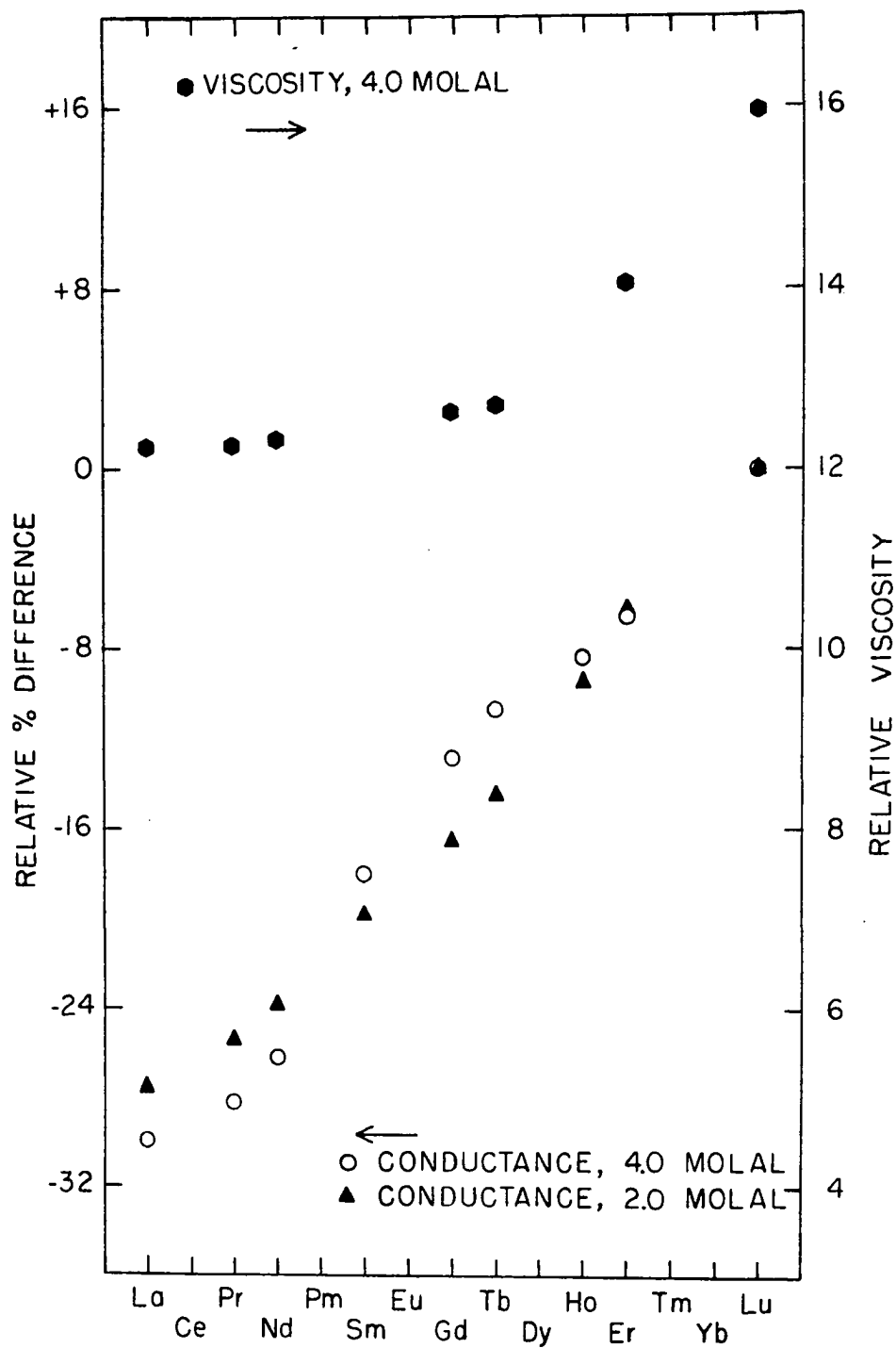


Figure 28. Relative percent differences in equivalent conductances and relative viscosities at constant molality for the rare earth nitrates

displacement of inner sphere water by nitrate ions could cause this double series hydration effect to vanish when the amount of inner sphere complexation becomes large.

The lanthanide contraction, with its reduction in the surface area for the rare earth cation, causes the water coordination number decrease to occur for the chlorides and perchlorates. This same surface area decrease will occur in the nitrates, but if fewer inner sphere waters remain after complexation occurs, its effect may be exerted on the inner sphere nitrate "ions". This could cause a shift in nitrate coordination from bidentate to monodentate across the series and would result in a decreasing equilibrium constant.

Another possibility is that a nitrate could be shifting from inner to outer sphere across the rare earth series. In view of the data discussed in the literature survey section, no choice can presently be made between these alternatives.

The conductance-viscosity product curves are given in Figures 17-22. This product decreases with concentration for the nitrates while it increases for the perchlorates and chlorides. This decrease indicates that the displacement of inner sphere water does not enhance the viscosity sufficiently to compensate for the reduction in conductance resulting from complexation.

VI. SUMMARY

The electrical conductances of aqueous solutions of 6 rare earth chlorides, 9 rare earth perchlorates and 9 rare earth nitrates were accurately measured from 0.05 molal to saturation at 25°C. This data was compared to the conductance data of Saeger and Spedding (68) for 7 other rare earth chlorides.

Increasing the electrolyte concentration in solution causes the ions to approach each other more closely, on the average, and also leads to a reduction in the bulk dielectric constant. These effects enhance ion-pairing which causes a reduction in the number of free ions and a reduction in the average cation charge. The viscosity of these solutions increase with concentration, as ionic hydration ties up the solvent and produces obstructions to flow. This viscosity increase gives rise to decreasing ionic mobilities. These above effects result in a marked decrease in conductance with increasing concentration. At very high concentrations, the slippage of the hydrated ions past each other becomes an important factor in the conductance mechanism.

The lanthanide contraction results in a decreasing ionic size with increasing atomic number. The smaller ions have a larger surface charge density than the larger ions, so the smaller ions bind an overall larger number of waters. The

larger hydrated cations are less mobile, so the isomolal rare earth electrolyte equivalent conductances should decrease down the rare earth series. This is observed for the rare earth perchlorates below 2.4 molal and the rare earth chlorides up to saturation. The rare earth and chloride ions tend to form ion-pairs at lower concentrations than do the rare earth and perchlorate ions. Consequently, by 0.15 molal the rare earth chloride equivalent conductances have become lower than for the corresponding perchlorates.

Above 2.4 molal, the rare earth perchlorate isomolal equivalent conductances decrease from La^{+3} to Nd^{+3} , rise from Nd^{+3} to (probably) Tb^{+3} , and then decrease to Lu^{+3} . Viscosity data also reflects this two series effect. It has previously been postulated that the light and heavy rare earth ions have different inner sphere hydration numbers, with the heavy rare earths having the lower value. From Nd^{+3} to Tb^{+3} an equilibrium of the two different hydrated forms is believed to exist. These are the same rare earths for which the two series effect is observed in the conductance.

The rare earth and perchlorate ions are strongly hydrated. Between 2 and 3 molal these ions begin to share waters and this effect increases up to saturation. This water sharing results in outer sphere ion-pairing. When the inner sphere hydration decrease occurs between Nd^{+3} and Tb^{+3} ,

water is liberated from its tightly bound position in the rare earth inner sphere. The addition of this "extra" water to the water sharing system allows the slippage of the hydrated ions to occur more readily. This gives rise to the observed two series effect.

Rare earth nitrate solutions are believed to involve inner sphere complexation between the rare earth and nitrate ions by moderate concentrations. Between several millimolal and 0.8 molal in concentration, the rare earth nitrate isomolal conductances decrease from La^{+3} to (probably) Eu^{+3} and then rise to Lu^{+3} . This trend is consistent with published equilibrium constant data. Above 0.8 molal, the isomolal equivalent conductances increase from La^{+3} to Lu^{+3} , for the rare earth nitrates studied in this research. This implies that the overall formation constants for the rare earth nitrate complexes decrease from La^{+3} to Lu^{+3} at these higher concentrations.

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