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Some physical properties of rare-earth chlorides in aqueous solution

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SOME PHYSICAL PROPERTIES OF RARE-EARTH

CHLORIDES IN AQUEOUS SOLUTION

by

Victor William Saeger

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I. INTRODUCTION

One of the great challenges in the field of physical chemistry at the present time is the development of an adequate theoretical basis for the interpretation of electrolytic solution behavior at concentrations beyond the range of applicability of the Debye-Hückel theory.

Since its introduction in 1923, the Debye-Hückel theory (1) through its treatment of long-range interionic forces has achieved considerable success in explaining the deviations of measured properties of dilute electrolytic solutions from ideality. The limitation of the theory to dilute solutions of strong electrolytes arises from the simplifying assumptions in both the physical model and mathematical treatment. Many attempts have been made to extend the validity of the theory to higher concentrations by taking into account such factors as the change of dielectric constant with concentration, ion-pair formation, solvation, and deviations from the Boltzmann distribution of ions. However, these attempts have resulted mainly in equations containing additional parameters by which better agreement with experimental data can be obtained, but which have little theoretical significance. It is now acknowledged that the development of an adequate theory of concentrated solutions will require a detailed knowledge of short range ion-ion and ion-solvent interactions and

the microscopic structure of solutions.

In studying electrolytic solutions experimentally, one generally is limited to measurements on the solution as a whole. From the results of such macroscopic measurements, one tries to infer a microscopic description of the solution. This interpretation is complicated by the large number of factors upon which solution behavior depends. Among the factors are solute concentration, ionic charge, ionic size, dielectric constant of the solvent, temperature, and pressure.

The valence type of the electrolyte plays an important role in determining solution properties. Its importance is shown by the presence of ionic charge as a square term in the Debye-Hückel activity coefficient expression. Polyvalent electrolytes not only show greater deviations from ideality, but show deviations from theoretical predictions at lower concentrations than uni-univalent electrolytes. These greater deviations are partly due to the stronger interactions with the solvent, i.e., higher degree of solvation, of polyvalent ions. Experimental studies of polyvalent electrolytes thus provide a rigorous test for any theory and should indicate directions for theoretical modifications.

While a vast number of studies have been carried out on uni-univalent electrolytes, studies of polyvalent electrolytes have been limited, for the most part, to di-univalent and uni-divalent electrolytes. The main deterrent to

studies of polyvalent electrolytes has been undesirable properties exhibited by most electrolytes of this type. Most polyvalent cations are weakly acidic, so that there are considerable hydrolysis and association even in dilute aqueous solutions. This leads to greater difficulty in the interpretation of results.

Of all trivalent cations, the natural choices for experimental studies are those of the rare-earth elements. These cations in combination with anions of the strong acids form several series of very soluble salts. Relative to other cations of Groups III and IV and transition-group elements, those of the rare earths present a simpler picture in their aqueous chemistry due to their greater basicity. Their hydrolysis and association properties are of a minor nature in dilute solutions and should be less complex in more concentrated solutions than those of other trivalent and tetravalent cations.

In addition, the rare-earth salts offer the best system available for studying the effect of change in ionic size on solution properties. This arises from the unique electronic structure of the rare earths. As the atomic number increases in the rare-earth series from lanthanum to lutetium, the additional electrons go into the inner 4f shell. Since the 4f shell is well shielded by the closed shells that surround it, the chemical properties of the rare

earths are relatively unaffected by these inner electron changes, and are determined predominantly by the three valence electrons common to all of the rare earths. The rare earths therefore possess very similar chemical properties. However, the increasing nuclear charge with increasing atomic number exerts a greater attraction for the electron shells causing a gradual contraction in atomic radius from one rare earth to the next. This gradual decrease in atomic radius is known as the "Lanthanide Contraction".

Due to their similarity in chemical properties, the individual rare earths were not, until the past ten years, available in the quantities and purity necessary for extensive experimental investigations. With the development of ion-exchange separation techniques (2, 3, 4, 5) at the Ames Laboratory of the Atomic Energy Commission, the rare earths became available in kilogram quantities and spectroscopic purity. An extensive program therefore was initiated at this laboratory for the investigation of electrolytic solution properties of rare-earth salts. Since that time, a large amount of data on a number of properties of rare-earth salts in dilute aqueous solutions has been collected. These properties include conductances, transference numbers, activity coefficients, solubilities, heats of dilutions, heats of solution, partial molal volumes, and partial molal compressibilities (6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17,

18, 19, 20, 21, 22). This work up to 1957 has been reviewed
by Spedding and Atkinson (23). Irregularities have been ob-
served in many of the properties measured, showing the com-
plexity of solution phenomena. The simple effect of decreas-
ing ionic radius with increasing atomic number is complicated
by solvation and coordination effects.

In the light of these irregularities in the dilute
concentration range, it seemed advisable to extend the
measurements of some of these properties to more concentrated
solutions. This thesis is concerned with measurements of
conductances, partial molal volumes, and activity coefficients
of some rare-earths chlorides in the concentration range 0.1
normal to saturation. Since larger differences in solution
properties between individual rare earths are to be expected
in more concentrated solutions, it is hoped that the accumu-
lation of such data will aid in the interpretation of these
irregularities.

II. GENERAL THEORY

A. Thermodynamic Concepts and Definitions

The methods of thermodynamics provide the chemist with a powerful tool in his investigation of physicochemical systems in equilibrium. Some of the basic concepts and definitions having an important relevance in this research will be reviewed in this section.

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

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

in which

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

T is the absolute temperature of the system,

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

P is the pressure of the system,

V is the volume of the system, and

$\mu_i = (\partial E / \partial n_i)_{S,V,n_j}$ is the chemical potential of component i, present in an amount, n_j moles, in a system containing a total of k components.

The above differential equation expresses any variation in the

internal energy of a one-phase system provided all other variables, such as electrical charge, the force of gravity, and external fields, are kept constant.

The internal energy, entropy, temperature, pressure, and volume are thermodynamic state functions, that is, dependent only on the state of the system and not on the path by which the state is reached or the previous history of the system. In the application of thermodynamics to many problems, it is convenient to use other thermodynamic state functions defined as follows:

$$\text{Enthalpy} = H = E + PV \quad , \qquad (2)$$

$$\text{Work function} = A = E - TS \quad , \qquad (3)$$

$$\text{Free energy} = F = H - TS = E - TS + PV \quad . \qquad (4)$$

If a function is a state function, then its differential is an exact differential. The variations in enthalpy, work function, and free energy may therefore be expressed as total differentials, similar to Equation 1 for the internal energy. Differentiation of Equations 2, 3, and 4 and substitution with Equation 1 yield the differentials of the enthalpy, work function, and free energy in the following forms:

$$dH = TdS + VdP + \sum_{i=1}^{k} \mu_i \, dn_i \quad , \qquad (5)$$

$$dA = -SdT - PdV + \sum_{i=1}^{k} \mu_i \, dn_i \quad , \qquad (6)$$

$$dF = -SdT + VdP + \sum_{i=1}^{k} \mu_i \, dn_i \quad . \tag{7}$$

From Equations 1, 5, 6, and 7, it follows that

$$\mu_i = (\partial E/\partial n_i)_{S,V,n_j} = (\partial H/\partial n_i)_{S,P,n_j}$$
$$= (\partial A/\partial n_i)_{T,V,n_j} = (\partial F/\partial n_i)_{T,P,n_j} \quad . \tag{8}$$

In working with solutions, it is desirable to have quantities which express the dependence of the thermodynamic state functions on the concentrations of the various components of the system under the usual constant temperature and pressure conditions of measurement. Extensive functions, such as free energy and volume, are dependent on the number of moles of each component in the system; while intensive functions, such as temperature and pressure, are independent of the amounts of components. For any extensive thermodynamic function G, a corresponding intensive function may be defined as

$$\bar{G}_i = (\partial G/\partial n_i)_{T,P,n_j} \quad . \tag{9}$$

The partial molal quantity $\bar{G}_i$ is the variation in G with variation in the number of moles n_i of component i, the temperature, pressure, and the number of moles of all other components in the system being kept constant.

Any extensive thermodynamic function is a homogeneous

function of the first degree, satisfying the necessary condition that multiplication of each independent variable by a constant b merely multiplies the function by b, i.e.,

$$G(bn_1, bn_2,...,bn_k) = bG(n_1,n_2,..,n_k) \quad . \tag{10}$$

The mathematical transformation known as Euler's theorem can therefore be applied to the function to give

$$G = \sum_{i=1}^{k} n_i(\partial G/ \partial n_i)_{T,P,n_j} \quad . \tag{11}$$

But by definition

$$(\partial G/ \partial n_i)_{T,P,n_j} = \bar{G}_i \quad . \tag{12}$$

As a result

$$G = \sum_{i=1}^{k} n_i\bar{G}_i \quad . \tag{13}$$

Differentiation of Equation 13 gives

$$dG = \sum_{i=1}^{k} n_i d\bar{G}_i + \sum_{i=1}^{k} \bar{G}_i dn_i \quad . \tag{14}$$

Since G is a thermodynamic state function, its differential may be written as a total differential. At constant temperature and pressure

$$dG = \sum_{i=1}^{k} (\partial G / \partial n_i)_{T,P,n_j} \, dn_i$$

$$= \sum_{i=1}^{k} \bar{G}_i \, dn_i \quad . \tag{15}$$

Combination of Equations 14 and 15 gives

$$\sum_{i=1}^{k} n_i d\bar{G}_i = 0 \quad , \tag{16}$$

which is a form of the Gibbs-Duhem equation.

For the two-component systems considered in this thesis, Equations 13 and 16 reduce to

$$G = n_1 \bar{G}_1 + n_2 \bar{G}_2 \tag{17}$$

and

$$n_1 d\bar{G}_1 + n_2 d\bar{G}_2 = 0 \quad . \tag{18}$$

It is thus necessary to determine the partial molal quantity for only one component of a two-component system, since the value for the second component can be obtained from Equation 18 by integration.

Just as the theory of pure substances is based on ordinary thermodynamic functions, the thermodynamic theory of solutions is expressed in terms of partial molal quantities and their derivatives. Partial molal quantities of particular interest in this thesis are the partial molal volume

and the partial molal free energy.

From Equation 8 and the definition of the partial molal quantity, it is seen that the partial molal free energy and chemical potential are identities, i.e.,

$$\mu_i = \overline{F}_i = (\partial F / \partial n_i)_{T,P,n_j} \quad . \qquad (19)$$

The chemical potential is an important quantity in chemical thermodynamics. The chemical potential, μ_i, of the ith component of a system is a measure of the "escaping tendency" or reactive potential of that component. At constant temperature and pressure in a multi-phase system, the chemical potential of any given component is the same in all phases in equilibrium.

In the application of thermodynamics to solutions, it is convenient to use a more restricted function than the chemical potential. The activity function was introduced in 1907 by G. N. Lewis (24). The activity, a_i, of component i of a solution may be given general definition by the equation:

$$\mu_i = \mu_i^o + RT \ln a_i \quad , \qquad (20)$$

where μ_i^o is the chemical potential of component i in some arbitrary standard state.

The value of the activity is dependent on the choice of standard state. Its choice, however, is not dictated by

physical principles but by convenience. In a system consist-
ing of solvent and solute components, the component desig-
nated as the solvent tends to obey Raoult's Law as the
solution is pregressively diluted, that is, the activity of
the solvent approaches its mole fraction concentration as
the composition of the solution approaches pure solvent.
A convenient choice for the standard state of the solvent
is, therefore, the "pure solvent". At high dilutions, how-
ever, the solute always tends to follow Henry's Law, that
is, the activity of the solute approaches proportionality
to its mole fraction concentration. The standard state for
the solute is chosen so that the activity becomes equal to
the mole fraction in very dilute solutions. A hypothetical
"ideal solution" is defined as a solution for which the
activity of the solute equals the mole fraction at all con-
centrations. To measure the departure of the solute be-
havior from this concept of ideality, the rational activity
coefficient, f_N, is defined as

$$f_N = a_N/N \quad ; \quad f_N \longrightarrow 1 \text{ as } N \longrightarrow 0 \quad , \tag{21}$$

where N is the mole fraction of solute and a_N is the
activity of the solute on a mole fraction basis. The chemi-
cal potential can therefore be expressed as

$$\mu = \mu_N^o + RT \ln (f_N N)$$

$$= \mu_N^o + RT \ln f_N + RT \ln N \quad . \tag{22}$$

Thus, as a limiting law for any solute in an infinitely dilute solution,

$$\mu = \mu_N^o + RT \ln N \quad . \tag{23}$$

In dealing with electrolytic solutions, it would be most convenient to consider the solute components of the solution as the different ionic species present. A component is an independently variable constituent; but the individual ionic species cannot be independently varied due to the requirement of overall electro-neutrality. Therefore in an aqueous electrolytic solution, the electrolyte must be considered the component rather than the ions into which it dissociates. While they are thermodynamically impossible to evaluate, it is advantageous to define ionic functions and to express thermodynamic developments in terms of these hypothetical quantities.

If an electrolyte $C_{\nu_+} A_{\nu_-}$ dissociates in solution in the following manner:

$$C_{\nu_+} A_{\nu_-} \longrightarrow \nu_+ C + \nu_- A \quad , \tag{24}$$
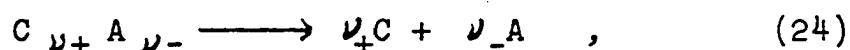
where ν_+ is the number of cations C formed on dissociation and ν_- is the number of anions A formed on dissociation, then the activity of the electrolyte may be expressed as

$$a_i = (a_+^{\nu_+}) \cdot (a_-^{\nu_-}) = a_{\pm}^{\nu} \quad ; \quad \nu = \nu_+ + \nu_- \quad , \tag{25}$$

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

The chemical potential can then be expressed as

$$\mu = \mu^0 + RT \ln (a_+^{\nu_+} \cdot a_-^{\nu_-}) = \mu^0 + \nu RT \ln a_\pm \quad . \quad (26)$$

To express the mean ionic activity on a mole fraction basis, the mean ionic mole fraction, $N_\pm$, and the mean ionic rational activity coefficient, $f_\pm$, are defined as

$$f_\pm = \frac{a_{N_\pm}}{N_\pm} \quad ; \quad N_\pm = (N_+^{\nu_+} N_-^{\nu_-})^{1/\nu} \quad . \quad (27)$$

In dealing with electrolytic solutions, it is more usual to express concentrations in terms of the molality, m, or molarity, c. The mean ionic activity coefficients and mean ionic concentrations on these bases are defined as

$$\gamma_\pm = \frac{a_{m_\pm}}{m_\pm} \quad ; \quad m_\pm = (m_+^{\nu_+} m_-^{\nu_-})^{1/\nu} = m(\nu_+^{\nu_+} \nu_-^{\nu_-})^{1/\nu} \quad , \quad (28)$$

$$y_\pm = \frac{a_{c_\pm}}{c_\pm} \quad ; \quad c_\pm = (c_+^{\nu_+} c_-^{\nu_-})^{1/\nu} = c(\nu_+^{\nu_+} \nu_-^{\nu_-})^{1/\nu} \quad , \quad (29)$$

where

$\gamma_\pm$ is the stoichiometric mean ionic molal or practical activity coefficient,

$y_\pm$ is the stoichiometric mean ionic molar activity coefficient,

$m_{\pm}$ is the mean ionic molality, and

$c_{\pm}$ is the mean ionic molarity.

The activities expressed on these different concentration bases are different, being defined by different standard states. The standard states are chosen so that

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

$$\gamma_{\pm} \longrightarrow 1 \quad \text{as} \quad m_{\pm} \longrightarrow 0 \quad , \qquad (30)$$

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

Since the value of the chemical potential is independent of any standard state, the following relation must hold:

$$
\begin{aligned}
\mu &= \bar{\mu}^0_N + \nu RT \ln (f_{\pm} N_{\pm}) \\
&= \bar{\mu}^0_m + \nu RT \ln (\gamma_{\pm} m_{\pm}) \\
&= \bar{\mu}^0_c + \nu RT \ln (y_{\pm} c_{\pm}) \quad .
\end{aligned}
\qquad (31)
$$

The mole fraction, molality, and molarity are related at all concentrations by

$$N_{\pm} = \frac{m_{\pm}}{\nu m + 1000/M_1} = \frac{c_{\pm} M_1}{\nu c M_1 + 1000\, d - c M_2} \quad , \qquad (32)$$

where

M_1 is the molecular weight of the solvent,

M_2 is the molecular weight of the solute, and

d is the density of the solution.

At infinite dilution, it follows that

$$N_{\pm} = \frac{m_{\pm} M_1}{1000} = \frac{c_{\pm} M_1}{1000\ d_0}$$

(33)

and

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

(34)

where d_0 is the density of the solvent. Utilizing Equations 31, 33 and 34, one obtains the relation:

$$\mu_N^0 = \mu_m^0 + \nu RT \ln (1000/M_1) = \mu_c^0$$
$$+ \nu RT \ln [1000\ (d_0/M_1)] \quad . $$

(35)

Combination of Equations 31, 32 and 35 then gives the general relationships between the various activity coefficients:

$$\ln (f_{\pm}) = \ln (\gamma_{\pm}) + \ln(1 + \nu m M_1/1000)$$

$$\ln (f_{\pm}) = \ln (y_{\pm}) + \ln \left[\frac{d}{d_0} + c\ \frac{\nu M_1 - M_2}{1000\ d_0} \right]$$

(36)

$$\ln (\gamma_{\pm}) = \ln (y_{\pm}) + \ln \left[\frac{d}{d_0} - c\ \frac{M_2}{1000\ d_0} \right] \quad . $$

B. Electrolytic Solution Theory

Although many of the fundamental principles of electrochemistry had been discovered previously, it was not until 1887 that an organized theoretical and experimental

investigation of electrolytic solutions was begun. In that year Arrhenius (25) proposed his classical theory of electrolytic dissociation. He postulated that when an electrolyte is dissolved in water, dissociation of the electrolyte into ions occurs, resulting in an equilibrium between undissociated solute molecules and ions. Arrhenius considered the dossiciation into ions to be complete only at extreme dilutions. He further proposed that the degree of dissociation could be found by taking the ratio of the equivalent conductance of the solution in question to the equivalent conductance at infinite dilution. These concepts of Arrhenius found support in the contemporary work of van't Hoff (26) on the colligative properties of electrolytic solutions.

The Arrhenius theory achieved remarkable success with weak electrolytes, but for strong electrolytes the theory was unsatisfactory on a number of points. Neither the Ostwald dilution law or mass-action law was obeyed by strong electrolytes. In addition, for all electrolytes, the hypothesis of Arrhenius with regard to conductance, which assumed the mobilities of ions to be independent of concentration, was not in agreement with the observed dependence of transference numbers upon concentration. Two potent arguments for the complete dissociation of strong electrolytes were provided by the ionic structure of crystalline salts and studies of the absorption spectra of solutions of

strong electrolytes which failed to reveal any evidence for undissociated molecules. Notwithstanding the shortcomings of the Arrhenius theory, the assumption that solutions of electrolytes contain ions in exact electrical balance is the basis for the modern theory of electrolytic solution behavior.

As early as 1894, the correct path for future theoretical developments was pointed out by van Laar (27), who showed that the electrostatic forces between ions in solution must produce a measurable effect on solution properties. This viewpoint was adopted by Sutherland (28) and Bjerrum (29) who suggested that strong electrolytes are completely dissociated in dilute aqueous solutions and that the deviations of such solutions from ideality are due to the ionic interactions. Sutherland (30) in 1907 made the first attempt to calculate the magnitude of the effects of the electrostatic forces between ions, but obtained only an exceedingly approximate solution. Hertz (31) and Ghosh (32, 33, 34) attempted to give mathematical expression to the effects, but the basis of their treatments was inadequate.

In 1912, however, Milner (35) successfully analyzed the problem of ionic interactions and developed a mathematical theory which was essentially correct. Unfortunately, his treatment was too involved to be of any practical use. He was able to show that at low concentrations, the deviations

from ideality of electrolytic solutions should be proportional to the square root of the concentration.

The first successful theoretical treatment of strong electrolytes in solution was presented in 1923 by Debye and Hückel (1). By introducing the concept of the "ionic atmosphere" and through use of Poisson's equation of electrostatics, they effected a mathematical simplification of the interionic attraction problem leading to exact relations for the equilibrium properties of strong electrolytes in dilute solutions. The basic assumptions inherent in their theory may be summarized as follows:

1. Strong electrolytes are completely dissociated into ions in solution.

2. All deviations from ideality are due entirely to the electrostatic interactions between the ions.

3. The solvent can be treated as a continuous medium of uniform dielectric constant.

4. The ions are rigid spheres of finite size, having a mean distance of closest approach.

5. A given ion in solution will be surrounded by an atmosphere which contains on the average more ions of opposite charge and less ions of like charge than the bulk of the solution; this excess of ions of opposite charge around the ion constitutes an "ionic atmosphere", which in the absence of external forces possesses spherical symmetry.

6. The time-average distribution of ions in the ionic atmosphere of a given ion is expressed by the Boltzmann distribution law.

7. The electrostatic potential at a point in the solution can be calculated from Poisson's equation utilizing the Boltzmann distribution law and the principle of linear superposition of fields.

8. The electrostatic potential energy of the ions is small compared to their thermal energy; the Poisson-Boltzmann equation therefore may be solved by an exponential expansion with the dropping of terms higher than the second.

Using these assumptions, Debye and Hückel were able to calculate the average electrostatic potential due to an ion and its ionic atmosphere. From the contribution of the ionic atmosphere to the potential, it was then possible to calculate the electrical contribution to the chemical potential of the ion. Since all deviations from ideality were assumed to arise from electrostatic interactions, a theoretical expression for the activity coefficient could be obtained. The Debye-Hückel expression for the mean ionic rational activity coefficient is given by

$$
\log(f_{\pm}) = - \frac{\dfrac{1}{2.303} \left[\dfrac{1}{\nu} \sum_{1} \nu_i z_i^2 \right] \sqrt{\dfrac{2\pi N \epsilon^6}{1000(DkT)^3}} \; \sqrt{S}}{1 + a^o \sqrt{\dfrac{8\pi N \epsilon^2}{1000 \; DkT}} \; \sqrt{S}} \tag{37}
$$

$$= - \frac{\left[\frac{1}{\nu} \sum_i \nu_i z_i^2\right] A \sqrt{S}}{1 + a^O B \sqrt{S}} \quad ,$$

where $S = 1/2 \sum_i c_i z_i^2$ is the ionic strength; ν, the number of moles of ions produced by the dissociation of one mole of electrolyte; ν_i, the number of moles of ions of the ith kind produced in the dissociation; z_i, the valence of ions of the ith kind; c_i, the concentration of ions of the ith kind in moles per liter; N, Avogadro's number; ϵ, the electronic charge; D, the dielectric constant of the solvent; k, Boltzmann's constant; T, the absolute temperature; and a^O, the mean distance of closest approach.

In the limit of infinite dilution, Equation 37 reduces to the Debye-Hückel limiting law:

$$\log(f_\pm) = - \frac{1}{\nu} \sum_i \nu_i z_i^2 A \sqrt{S} \quad . \tag{38}$$

The limiting law was arrived at in the Debye-Hückel treatment by neglecting the finite size of the ions, i.e., considering the ions as point charges.

For a complete treatment of the Debye-Hückel theory, the treatise of Harned and Owen (36) may be consulted. The success of the theory has prompted critical examination of its assumptions from the viewpoint of statistical mechanics. The contributions of Kramers (37), Fowler (38), Onsager (39), Kirkwood (40), Fowler and Guggenheim (41), and Kirkwood and

Poirier (42) have clarified the basis of the theory and have served to prove the exact validity of the limiting law.

The development of the Debye-Hückel expression for activity coefficients gave a theoretical basis to the concept of ionic strength, which had been derived empirically by G. N. Lewis (43). Utilizing a^o as an adjustable parameter, the calculated values of the activity coefficient are in excellent agreement with the experimental values up to concentrations of about 0.1 normal, although the assumptions of the theory do not necessarily hold this far. In theory, the quantity a^o is the mean distance of closest approach of the ions, i.e., mean ionic diameter, in solution. However, for many salts, normally regarded as strong electrolytes, the value of a^o necessary to fit the experimental data is impossibly small. Therefore, it must be concluded that a^o is not an actual ionic diameter, but a parameter correcting for a number of imperfections in the theory. Nevertheless for low concentrations of electrolyte, small ionic charges, and large ionic diameters, the assumptions postulated in the theory are very nearly fulfilled.

Since the Debye-Hückel theory successfully predicts the behavior of very dilute electrolytic solutions, much effort has been directed toward extending the theory to higher concentrations by taking into account effects which were neglected by Debye and Hückel. A brief summary of some of the

extensions is given here.

The first essential modification of the Debye-Hückel treatment involved the use of more accurate solutions of the Poisson-Boltzmann equation. The procedure for the accurate numerical solution of the equation was described by Müller (44) in 1927. Müller carried out a few such integrations but only for symmetrical electrolytes. Gronwall, La Mer, and Sandved (45) solved the equation for symmetrical electrolytes in terms of a power series expansion, while La Mer, Gronwall, and Greiff (46) by the same method obtained solutions for unsymmetrical electrolytes. Although the use of these potential functions leads to more reasonable values for a^o, the potential functions themselves are not self-consistent. Fowler and Guggenheim (41) have pointed out that different values for the electrical contribution to the chemical potential are obtained from the Debye and the Güntelberg (47) charging processes using these potential functions; while for the approximate Debye-Hückel potential, the same value is obtained. Onsager (39) has concluded that the discrepancy is due to the limitation of the Poisson-Boltzmann equation at higher concentrations where the potentials of the ionic atmospheres are no longer additive, i.e., the principle of linear superposition of fields no longer holds. In order to obtain a detailed picture of the ionic distribution according to the Poisson-Boltzmann equation and the extent of its

divergence from the distribution according to the Debye-Hückel approximation, Guggenheim (48) recently solved the Poisson-Boltzmann equation numerically using an electronic computer for four charge types over a range of ionic strength. He has reserved discussion of the implications of his results for a future paper.

An entirely different approach was proposed by Bjerrum (49) in his theory of ionic association or ion-pair formation. In his treatment the ions are assumed to be rigid unpolarizable spheres in a medium of fixed macroscopic dielectric constant. All ion-solvent interactions as well as non-polar quantum bonds are excluded. By assuming a Maxwell-Boltzmann distribution with a Coulombic potential energy function for the ions, Bjerrum shows that for a distance $r = q = \epsilon^2 |z_i z_j|/2DkT$, the probability that an i-ion is at a distance r from a j-ion possesses a minimum if the ions are of opposite charge. It is assumed that two ions at a distance of r less than q are associated. Bjerrum further assumes that the electrostatic interaction of an associated pair with the remaining ions is negligible, while the unassociated ions obey the Debye-Hückel predictions. Bjerrum's theory has been invaluable in interpreting experimental results as a function of dielectric constant and temperature. Fuoss and Kraus (50) have extended the theory to include triple and quadropole ions. Somewhat different

treatments of ion-pair formation have been carried out by Gilkerson (51) and Denison and Ramsey (52).

A number of different approaches to ion-solvent interactions have been employed. Hückel (53), and later Scatchard (54), treated the ion-solvent interactions in terms of an electrostatic salting-out effect arising from the fact that the electrolyte lowers the dielectric constant. Hückel proposed that a term, linear in concentration, be added to the Debye-Hückel activity coefficient expression to take into account the variation of the dielectric constant with concentration. Although this added term leads to better agreement with experimental activity coefficient values, its theoretical foundation has been criticized.

Stokes and Robinson (55) (56, p. 238) have adopted a different approach. They suggest that the activity coefficient predicted by the Debye-Hückel theory is actually the mean rational activity coefficient of the solvated ions. In their treatment they assume that in a system containing S moles of solvent and one mole of solute, h moles of solvent are associated with the ν moles of ions, leaving (S - h) moles of free solvent. They obtain an expression for the activity coefficient which contains two parameters, a° and h. While their equation is capable of accurately predicting values of the activity coefficient to much higher concentrations than the Debye-Hückel equation, the value of h, the

hydration number of the solute, obtained in curve fitting is frequently at variance with reasonable expectation and other experimental evidence. Glueckauf (57) has modified this treatment by substituting volume-fraction statistics for the conventional mole-fraction statistics.

Two modifications of the Debye-Hückel treatment in   - cent years have involved substitution of other distribui on functions for the Boltzmann distribution function. Eigen and Wicke (58, 59, 60, 61) have modified the Boltzmann distribution function in such a way as to include hydration and volume effects. They adopt a pseudo-lattice picture of the solution, deriving their statistics by considering the distribution of ions and possible ion sites around a central ion. The available ion sites are computed on the basis of the volume requirements of the hydrated ions. This picture restricts the number of possibilities for arrangement of the ions. In addition to this restriction, an ion can penetrate the hydration shell of an oppositely charged ion causing incomplete dissociation. The treatment of Dutta and Bagchi (62, 63, 64) is very similar. They obtain essentially a Fermi-Dirac distribution function. The possible equivalence of these treatments has been argued by the authors. Although the activity coefficient expressions obtained from these treatments sometimes give better theoretical predictions in the higher concentration range than the Debye-Hückel

expression, the additional arbitrary parameters present cast doubt on their validity.

An entirely new theoretical approach to electrolytic solutions was put forth by Mayer (65) in 1950. By adapting his statistical mechanical cluster theory of imperfect gases to electrolytic solutions, he derived equations for the computation of the osmotic pressure and activity coefficient. However, it was not until 1953 that his results were put into usable form by Poirier (66). Using Mayer's complex expression for the activity coefficient, Poirier derived equations for the stoichiometric mean ionic molar activity coefficient, apparent and partial molal volumes, and relative apparent and partial molal heat contents. He also calculated the activity coefficients of four salts of different charge types, using a° as the only adjustable parameter. The predicted and experimental values were in good agreement up to about the same concentration for which the Debye-Hückel equation holds.

While this summary does not exhaust the different theoretical approaches to electrolytic solutions, it does serve to emphasize the difficulties of extending the Debye-Huckel theory to higher concentrations. Each of the treatments mentioned has some merit but all of them can be criticized on fundamental grounds or because of failure to include all of the factors.

III.   PREPARATION OF RARE-EARTH CHLORIDE SOLUTIONS

The rare earths employed in this research were obtained as oxides from the rare earth separation group of the Ames Laboratory of the Atomic Energy Commission. The degree of purity of each oxide was determined by emission spectrography. A summary of the spectrographic analyses is given in Table 1. About three kilograms of each rare-earth oxide were utilized in this research.

The rare-earth chloride solutions were prepared by reacting the oxides with hydrochloric acid. Such a method of preparation, however, is complicated by the hydrolysis of the trivalent rare-earth cation. The primary hydrolysis equilibrium is considered to be:

$$R^{+++} + H_2O \rightleftharpoons R(OH)^{++} + H^+ \quad .$$
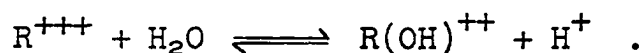
Thus the dissolution of a pure sample of anhydrous or hydrated rare-earth chloride in water will result in an acidic solution. With increasing salt concentration and increasing atomic number of the rare-earth, the extent of the hydrolysis also increases. A rare-earth chloride solution of a particular concentration will, therefore, have a characteristic or "stoichiometric" pH value. The general problem in the indirect preparation of a rare-earth chloride solution is the determination of and adjustment of the

Table 1. Spectrographic analyses of rare-earth oxides

Oxide	Analysis (per cent)	
La_2O_3	Nd:	less than 0.02
	Pr:	less than 0.03
	Ce:	less than 0.03
	Ca:	approximately 0.05
	Fe:	less than 0.01
Nd_2O_3	Pr:	less than 0.08
	Sm:	less than 0.06
	Ca:	approximately 0.05
	Fe:	less than 0.01
Sm_2O_3	Nd:	less than 0.02
	Eu:	less than 0.01
	Gd:	less than 0.02
	Ca:	less than 0.05
Gd_2O_3	Y:	less than 0.05
	Sm:	less than 0.05
	Eu:	less than 0.01
	Tb:	less than 0.02
	Ca:	less than 0.05
	Fe:	less than 0.01
Dy_2O_3	Y:	less than 0.007
	Tb:	less than 0.01
	Ho:	less than 0.05
	Er:	less than 0.01
	Yb:	less than 0.005
	Ca:	less than 0.05
Er_2O_3	Y:	less than 0.005
	Dy:	less than 0.005
	Ho:	less than 0.01
	Tm:	less than 0.005
	Yb:	less than 0.016
	Ca:	approximately 0.05
	Fe:	less than 0.01
Yb_2O_3	Y:	less than 0.005
	Sc:	less than 0.005
	Er:	less than 0.005
	Tm:	less than 0.005
	Lu:	less than 0.005
	Ca:	less than 0.03
	Fe:	less than 0.01

solution to this stoichiometric pH value. At this pH value the ratio of rare earth to chlorine in the solution will be identical to that in the solid rare-earth chloride.

In the preparation of a particular rare-earth chloride solution, the appropriate oxide was added with heating to a less than stoichiometric amount of C. P. hydrochloric acid. After dissolution had ceased, the excess oxide was filtered off. The resulting solution had a pH value of about 3. Due to the hydrogen ion resulting from the hydrolysis of the rare-earth ion, slightly more than a stoichiometric amount of the oxide was dissolved. A moderate amount of the colloidal oxide was also present. To dissolve the colloidal oxide, the solution was adjusted to a pH value of about 2 with hydrochloric acid and heated to near the boiling point for several hours. The resulting solution was then evaporated until saturation at room temperature was assured.

To determine the stoichiometric pH value, an aliquot of the solution was titrated with 0.1 N hydrochloric acid. The course of the titration was followed with a Beckman Model G pH meter. A plot of pH vs. milliliters of acid added gave a strong acid-weak base titration curve. From a differential plot of (ΔpH/Δ milliliter) vs. average milliliters of acid added, the stoichiometric pH value was then determined. After adjustment to the determined pH value, the bulk solution was heated for several hours to dissolve any colloidal

oxide still present. The titration of an aliquot and pH adjustment and heating of the bulk solution were then repeated until no change in the pH value of the bulk solution occurred upon heating. In general, the stoichiometric pH value was reproducible within 0.1 pH unit. Solutions prepared in this manner exhibited no Tyndall cone and were stable indefinitely. For the saturated solution, the stoichiometric pH value varied from 2.1 for lanthanum chloride to 0.8 for ytterbium chloride.

One liter of each solution thus prepared was reserved for measurements on the saturated solution. The remaining solution after dilution to a concentration of 3 to 3.5 molal was used as the primary stock solution for the preparation of solutions of lower concentrations. Several secondary stock solutions were also prepared from the primary stock solution by weight dilution.

To determine the concentration of the stock solution, triplicate analyses for the rare-earth ion were made by precipitation as the oxalate and subsequent ignition to the oxide. Samples of the stock solution were weighed directly into porcelain crucibles which had been previously brought to constant weight. A slight excess of oxalic acid solution was slowly added with stirring to each sample of rare-earth chloride solution, both solutions having been heated prior to the precipitation. After evaporation to dryness under

infra-red lamps, the rare-earth oxalate samples were ignited at 900° C. in a muffle furnace for a period of 12 to 18 hours. The resultant oxide samples were then cooled over anhydrous calcium chloride in a desiccator and weighed rapidly to avoid absorption of moisture. If the first ignition was carried out over the specified length of time, no significant change in weight of the samples was noted after a second ignition. From the weight of oxide and weight of solution, the molality of the solution was then calculated. A precision of better than 0.1 per cent was easily obtainable by this method.

A series of solutions of each rare-earth chloride with a lower concentration limit of 0.02 molal was prepared from the primary and secondary stock solutions by weight dilution with conductivity water. The conductivity water, prepared by the distillation of ordinary distilled water from an alkaline potassium permanganate solution in a Barnstead conductivity still, had a specific conductance of less than 1.0×10^{-6} mho per centimeter and a pH in the range 5.8 to 6.1.

For each rare-earth chloride, a secondary stock solution of about one molal concentration was analyzed for rare-earth ion by the method previously described and for chloride ion by the standard gravimetric procedure. The chloride analyses were consistently lower than the oxide analyses by

about 0.1 per cent. Since the probable error in such chloride analyses is about 0.1 per cent, this was considered satisfactory evidence that the method of preparation yielded stoichiometric solutions.

IV. SOLUBILITIES

For the measurement at 25° C. of some physical prop-
erties of the saturated rare-earth chloride solutions, the
determination of solubilities was a necessary prequisite.

The saturated solutions of lanthanum, neodymium,
samarium, gadolinium, dysprosium, erbium, and ytterbium
chlorides were prepared by the method described in the pre-
vious section. Completion of the preparation required thermal
equilibration of the solution and solid hydrate phases at the
desired temperature of measurement. For all of these rare-
earth chlorides except lanthanum chloride, the hexahydrate is
the stable hydrate form at room temperature; the heptahydrate
is the stable form for lanthanum chloride.

The thermal equilibration of the saturated solutions was
carried out in the same constant-temperature bath employed
in the osmotic and activity coefficient measurements, the
bath temperature being maintained at 25.00 ± 0.01° C. Prior
to the start of the equilibration, each solution, contained
in a one-liter volumetric flask, was heated until the solid
phase had completely dissolved. After cooling to the
temperature of the bath, each solution was seeded with a
crystal of the appropriate hydrate. The flasks were then
placed on a platform in the bath for a period of two weeks.
Due to the large volume of solution and high solution density,

mechanical shaking of the solutions was not possible. Periodic shaking by hand was therefore employed. At the end of the two-week equilibration period, an aliquot of each solution was withdrawn and transferred to a weight burette. Triplicate analyses for rare-earth ion were carried out by the method described in the previous section. The solutions were then allowed to equilibrate for an additional week, whereupon second aliquots were withdrawn and analyzed. Since the first and second analyses agreed in all cases within 0.1 per cent, the thermal equilibration was considered complete. Each saturated solution was then separated from its solid phase by filtration in preparation for measurements of the density and electrolytic conductance.

The analyses of these solutions thus yielded the solubilities of the rare-earth chlorides at 25° C. The solubilities in terms of molality, moles per 1000 grams of water, are given in Table 2.

The solubilities of lanthanum, neodymium, samarium, gadolinium, and dysprosium chlorides at 25° C. were also determined by a second method. This method involved the simultaneous determination of solubility and osmotic coefficient of the saturated solution, and will be described in a later section. The solubilities obtained by this isopiestic method are also given in Table 2.

A considerable amount of solubility data for the rare-

Table 2. Solubilities of some rare-earth chlorides in water at 25° C.

Rare-earth chloride	Molal solubility	
	Direct method	Isopiestic method
$LaCl_3$	3.8959	3.8944
$NdCl_3$	3.9292	3.9307
$SmCl_3$	3.6401	3.6416
$GdCl_3$	3.5906	3.5898
$DyCl_3$	3.6310	3.6302
$ErCl_3$	3.7821	.
$YbCl_3$	4.0028	

earth chlorides is contained in the chemical literature.
Williams, Fogg, and James (67) measured the solubilities at
10°, 20°, 30°, 40°, and 50° C. of the hexahydrates of
samarium and neodymium chlorides in water and an aqueous
hydrochloric acid solution, and that of ytterbium chloride
hexahydrate in the latter solvent. Friend and Hale (68)
measured the solubilities of the heptahydrates of lanthanum
and praseodymium chlorides and the hexahydrate of neodymium
chloride at a variety of temperatures in water, and that of
lanthanum chloride is some aqueous hydrochloric acid solu-
tions at 25° and 50° C. In a recent study, Powell and
Burkholder (69) determined the solubilities of lanthanum
chloride heptahydrate in the temperature range 0° to 95° C.

and the hexahydrate in the range 40° to 72.5° C. The solubilities of the hexahydrated chlorides of the rare earths, neodymium through lutetium, were also measured by Powell (70) at 0°, 25°, and 60° C. A general summary of the aqueous solubility data for the rare-earth chlorides at 25° C. is given in Table 3. The solubilities are expressed in grams of rare-earth chloride per 100 grams of water.

In Figure 1, the solubility at 25° C. in grams of rare-earth chloride per 100 grams of water is plotted as a function of the atomic number of the rare earth. The solubilities determined in this research and those by Powell (70) are plotted. The results indicate that the solubility rises to a maximum for cerium or praseodymium chloride, reaches a minimum at europium chloride, and continues to increase for the heavier rare-earth chlorides. A similar trend in the solubilities of the rare-earth sulfates has been observed by Jackson and Rienacker (71) and Spedding and Jaffe (11).

Table 3. Comparison of solubilities at 25° C.

Rare-earth chloride	Solubility in grams of rare-earth chloride (RCl_3)/100 grams of H_2O				
	This research[a]	Powell and Burkholder (69)	Powell (70)	Friend and Hale (68)	Williams, Fogg, and James (67)
$LaCl_3$	95.55	95.57		97.12	
$CeCl_3$					
$PrCl_3$				98.3[b]	
$NdCl_3$	98.50		98.9	98.2[b]	98.8[b]
$SmCl_3$	93.47		94.7		94.0[b]
$EuCl_3$			93.5		
$GdCl_3$	94.65		94.9		
$TbCl_3$			95.0		
$DyCl_3$	97.62		97.8		
$HoCl_3$			101.4		
$ErCl_3$	103.49		103.7		
$TmCl_3$			107.0		
$YbCl_3$	111.84		112.0		
$LuCl_3$			117.2		

[a]Average of direct and isopiestic determinations except for erbium and ytterbium chlorides.

[b]Obtained by interpolation of solubility-temperature data.

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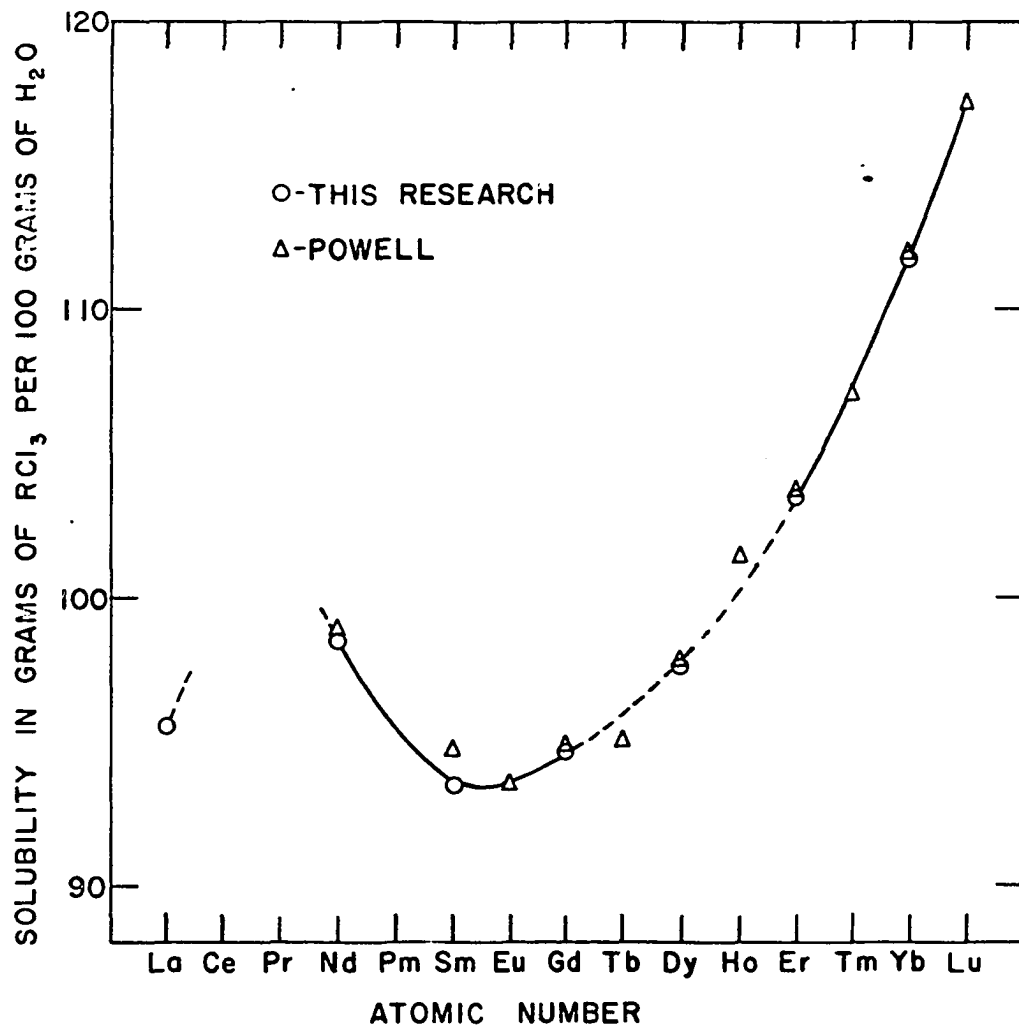
Figure 1. Solubilities of rare-earth chlorides in water at 25° C.

V. APPARENT AND PARTIAL MOLAL VOLUMES

A. Introduction and Theory

The interpretation of volume changes occurring in the solvent upon dissolution of electrolytes is unquestionably a problem of considerable complexity. These volume changes involve not only the actual volume of the ions, but changes in the orientation and packing of the solvent molecules. The determination of the partial molal volume as a function of concentration may thus serve as a powerful tool for examining the structure of solutions.

For a two-component system consisting of solvent, 1, and solute, 2, the partial molal volume of the solute is defined as

$$\bar{V}_2 = (\partial V/\partial n_2)_{T,P,n_1} \quad . \tag{39}$$

A convenient function from the experimental point of view is the apparent molal volume, $\emptyset_V$, which is defined by

$$\emptyset_V = \frac{V - n_1\bar{V}_1^0}{n_2} \quad . \tag{40}$$

Substituting $V = (n_1M_1 + n_2M_2)/d$, $\bar{V}_1 = M_1/d_0$, and $n_2 = n_1M_1m/1000$ into Equation 40, one obtains the following expression for the apparent molal volume:

$$\emptyset_V = \frac{1000}{mdd_0}(d_0 - d) + \frac{M_2}{d} \quad , \tag{41}$$

where m is the molal concentration of solute; d, the density of the solution; d_o, the density of the solvent; and M_2, the molecular weight of the solute. Since the molal concentration, m, and the molar concentration, c, are related by

$$\frac{1}{c} = \frac{1}{md} + \frac{M_2}{1000\ d} \quad , \tag{42}$$

the apparent molal volume can also be expressed as

$$\phi_V = \frac{1000}{cd_o}(d_o - d) + \frac{M_2}{d_o} \quad . \tag{43}$$

The determination of apparent molal volumes is thus resolved into the accurate measurement of densities of solutions.

The apparent molal volume is a convenient function for calculating partial molal volumes. Through partial differentiation of Equation 40, the relationship between apparent and partial molal volumes is obtained:

$$\overline{V}_2 = \frac{\partial (n_2 \phi_V)}{\partial n_2} = \phi_V + n_2 (\partial \phi_V / \partial n_2)_{T,P,n_1} \tag{44}$$

$$= \phi_V + m(\partial \phi_V / \partial m)_{T,P,n_1} \quad .$$

If the apparent molal volume is known as a function of concentration through an equation of the form

$$\phi_V = A + Bm^{1/2} + Cm + \ldots + Lm^k \quad , \tag{45}$$

where A, B, C, ..., and L are constants, then by means of Equation 44, a corresponding equation for the partial molal volume can be obtained:

$$\bar{V}_2 = A + (3/2)Bm^{1/2} + 2Cm + \ldots + (k + 1)Lm^k \quad . \quad (46)$$

From this equation, the value of the partial molal volume at any given concentration can then be calculated.

The partial molal volume can be given theoretical expression through its thermodynamic relationship to the activity coefficient. It follows from Equation 7 that

$$V = \left(\frac{\partial F}{\partial P}\right)_{T,n_i} \quad \text{or} \quad V - V^O = \left(\frac{\partial (F - F^O)}{\partial P}\right)_{T,n_i} \quad . \quad (47)$$

Differentiation of Equation 47 with respect to n_2 gives

$$\bar{V}_2 - \bar{V}_2^O = \left(\frac{\partial (\bar{F}_2 - \bar{F}_2^O)}{\partial P}\right)_{T,n_i} \quad , \quad (48)$$

where $\bar{V}_2^O$ and $\bar{F}_2^O$ are the partial molal volume and the partial molal free energy, respectively, of the solute in the standard state of infinute dilution. Utilizing Equations 19, 26, and 27, the relation between the partial molal volume and the mean ionic rational activity coefficient is obtained:

$$\bar{V}_2 - \bar{V}_2^O = \nu RT \left(\frac{\partial \ln f_\pm}{\partial P}\right)_{T,n_i} \quad . \quad (49)$$

Through this equation the partial molal volume can be related to the Debye-Hückel equation for the activity coefficient.

For the purposes at hand, the Debye-Hückel equation for the activity coefficient, Equation 37, is best expressed in the form

$$\ln(f_\pm) = \frac{-2.303\ \mathscr{S}_f\ \sqrt{\Gamma}}{1 + A\ \sqrt{\Gamma}} \quad , \quad (50)$$

where

$$\Gamma = \sum_i c_i z_i^2 = \text{ional concentration} \quad ;$$

$$\mathscr{S}_f = \frac{1}{\nu}\sum_i \frac{\nu_i z_i^2}{2.303}\left[\frac{\pi N\ \epsilon^6}{1000\ (DkT)^3}\right]^{1/2} \quad ;$$

$$A = \left[\frac{4\pi N\ \epsilon^2}{1000\ DkT}\right]^{1/2} a^0 \quad .$$

Differentiation of Equation 50 with respect to P at constant T and n_i followed by substitution into Equation 49 gives

$$\bar{V}_2 - \bar{V}_2^0 = \frac{\mathscr{S}_v}{1 + A\sqrt{\Gamma}}\ \frac{W_v}{(1 + A\sqrt{\Gamma})^2} \quad , \quad (51)$$

where

$$\mathscr{S}_v = 2.303\ \nu RT\ \mathscr{S}_f\ \frac{1}{2}\left(\frac{3\ \partial \ln D}{\partial P} - \beta\right) \quad ;$$

$$W_v = -2.303 \ \nu RT \ \phi_f \ A \ \frac{1}{2} \left(\frac{\partial \ln D}{\partial P} - \frac{2 \ \partial \ln a^o}{\partial P} - \beta \right) ;$$

$$\beta = (\partial \ln \Gamma / \partial P) = \text{coefficient of compressibility of the solution.}$$

The theoretical evaluation of the partial molal volume by means of Equation 51 thus requires knowledge of certain partial differential coefficients. Although values of the coefficient of compressibility, β , and ($\partial \ln D/ \partial P$) are known for water at room temperatures, nothing whatever is known about the coefficient ($\partial \ln a^o/ \partial P$). One is therefore generally confined to the use of the limiting law

$$\bar{V}_2 - \bar{V}_2^o = \phi_v \sqrt{\Gamma} = S_v \sqrt{c} \qquad , \qquad (52)$$

where

$$S_v = \phi_v (\sum_i \nu_i z_i^2)^{1/2} \quad .$$

A theoretical expression can also be derived for the apparent molal volume. From Equation 44, it follows that

$$\phi_v = \frac{1}{n_2} \int_0^{n_2} \bar{V}_2 \ dn_2 \quad . \qquad (53)$$

Substitution for $\bar{V}_2$ from Equation 52 gives

$$\phi_v = \frac{1}{n_2} \int_0^{n_2} (\bar{V}_2^o + S_v \sqrt{c} \ ) \ dn_2 = \frac{1}{m} \int_0^{m} (\bar{V}_2^o + S_v \sqrt{c} \ ) \ dm. \quad (54)$$

At extreme dilutions, $c \simeq m$, so that

$$\phi_V = \frac{1}{c} \int_0^c (\overline{V}_2^0 + S_V \sqrt{c}\,)\,dc \quad . \tag{55}$$

Integration of this equation then gives

$$\phi_V = \overline{V}_2^0 + (2/3)S_V \sqrt{c} = \phi_V^0 + S_\phi \sqrt{c} \quad , \tag{56}$$

where $\phi_V^0 = \overline{V}_2^0$ and $S_\phi = (2/3)S_V$, as the limiting law for the apparent molal volume. According to theory, the coefficient S_ϕ or limiting slope should be common to all strong electrolytes of the same valence type in a given solvent at a given temperature and pressure. This limiting equation for the apparent molal volume was derived first by Redlich and Rosenfeld (72) in 1931.

Two years previous to 1931, Masson (73) derived an empirical equation of the same form as the limiting law. He found that the apparent molal volumes of a number of strong electrolytes could be represented to quite high concentrations by such an equation. However, the constants of the equation, analogous to ϕ_V^0 and S_ϕ, were characteristics of each electrolyte. Scott (74) in 1931 applied the Masson equation to the data of Baxter and Wallace (75) for 15 alkali halides and found good agreement. He also found that the difference between ϕ_V^0 and between S_ϕ for any pair of these salts with a common ion was practically independent of

the nature of the common ion. The average deviation from additivity for ϕ_V^0 was about 0.07 cubic centimeter. Geffcken (76), combining the data of Baxter and Wallace with his own and some from other sources (77, 78, 79, 80), obtained essentially the same results. Except for the lithium halides, the Masson equation represents the apparent molal volume data extremely well over the concentration range measured and for temperatures from 0° to 70° C. The experimental slope, S_ϕ, is specific for each salt and is also a function of temperature. Although a number of speculations (73, 81) regarding the validity of the Masson equation have been made, no satisfactory explanation has yet been proposed.

Since the slopes obtained in the application of the Masson equation are specific, they do not give experimental verification of the limiting law. In general, apparent molal volume data obtained for moderately concentrated solutions of electrolytes yield slopes which are specific for each electrolyte. With the development of more precise methods for measuring densities of solutions, reliable apparent molal volume data has become available for very dilute solutions. On the whole, the results obtained by magnetic float and dilatometer methods appear to support the limiting law for typical strong electrolytes. However, for salts exhibiting considerable hydrolysis, significant departures from the limiting law are noted at the most dilute solutions

studied. With sufficiently accurate data the apparent molal volume vs. square root of concentration curves of many strong electrolytes show a S-shaped character in the transition from the limiting law, at high dilutions, to the Masson equation, in more concentrated solutions (82, 83, 84, 85).

B. Measurement of Density of Solutions

A large number of methods for the measurement of densities of liquids have been developed over the years. These methods vary from the simplest pycnometric method with an accuracy of $\pm$ 0.001 gm. per ml. to a magnetically controlled float method with an accuracy of $\pm$ 2 x 10^{-8} gm. per ml. The various methods together with their advantages and disadvantages are reviewed by Bauer and Lewin (86).

In order to accurately determine apparent molal volumes in solutions, the accurate measurement of densities of solutions is a necessity. The effect of an uncertainty in density on the apparent molal volume can be shown by differentiation of Equation 43 with respect to density. It is seen from the resulting differential equation

$$\delta \phi_v = - \frac{1000}{c} \frac{\delta d}{d_o} \tag{57}$$

that the uncertainty in the apparent molal volume due to an error in the measurement of density increases with decreasing

concentration. For a concentration of 0.01 molar, an error
of $\pm 1 \times 10^{-5}$ in d results in an uncertainty of ± 1 cubic
centimeter in ϕ_V; for a concentration of one molar, the same
error in d results in an uncertainty in ϕ_V of only ± 0.01
cubic centimeter. Thus for very dilute solutions, the region
where the limiting law may be expected to hold, a very
accurate method of measuring densities must be employed,
while for more concentrated solutions, as are involved in
this research, a less exacting method may be used.

C. Experimental

1. Apparatus and procedure

The method employed in this research for the measurement
of densities of rare-earth chloride solutions was a
pycnometric method utilizing modified Sprengel-Ostwald
pycnometers. Seven pycnometers, each of 40 ml. capacity and
constructed of Pyrex glass, were used; a diagram of the
pycnometers is given in Figure 2.

The barrel of the pycnometers, E, was constructed from
a 10 cm. length of 25 mm. tubing; the J-tube, F, from a 17
cm. length of 7 mm. tubing. Arm A was constructed from the
inner part of a 7/25 capillary standard taper with an
internal diameter of 1 mm.; arm B, from 1 mm. capillary
tubing and the inner part of a 10/30 standard taper. Arms
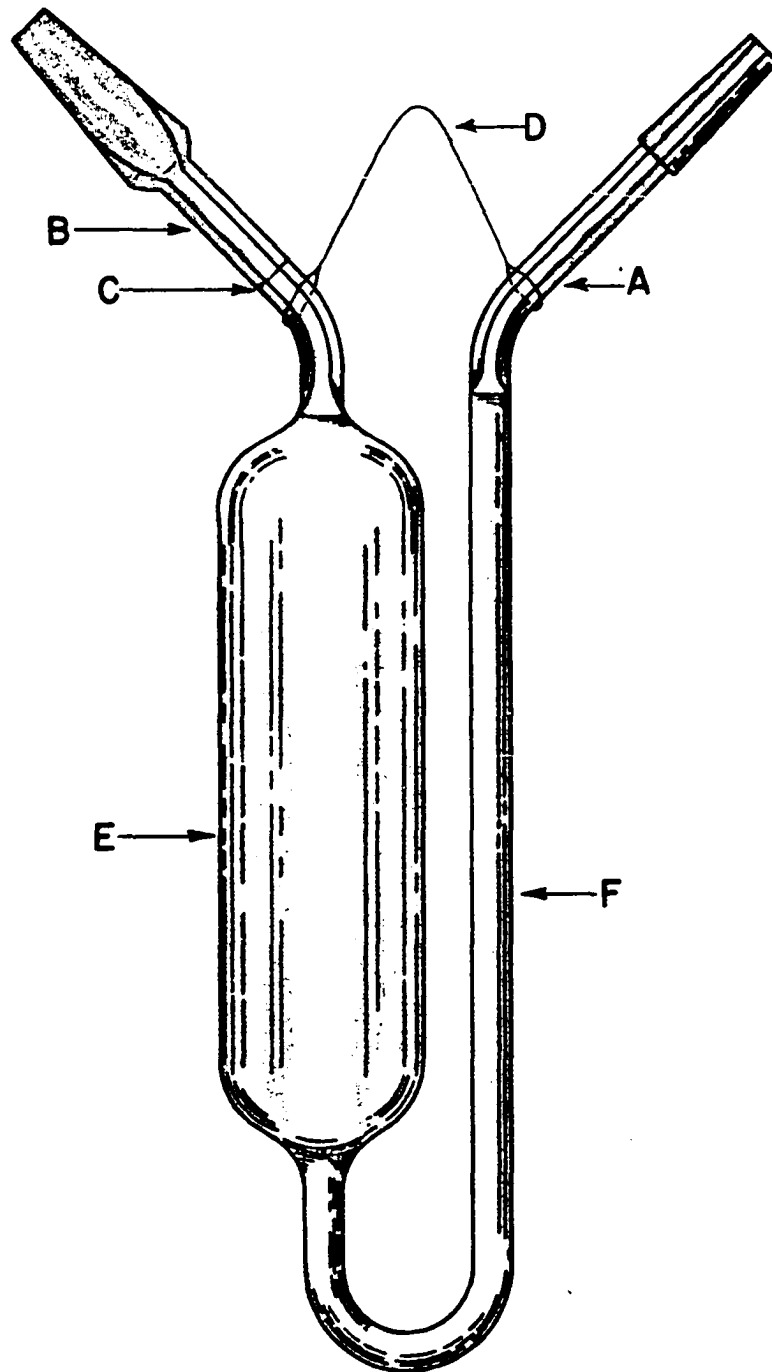
Figure 2. Modified Sprengel-Ostwald pycnometer

A and B were each bent at a 45° angle from the vertical in the same plane. The standard taper part of arm B served as an expansion chamber for the liquid. To ensure proper drainage of the solution in the expansion chamber during the adjustment of the liquid level, the glass surface above the etched calibration mark, C, was coated with Beckman Desicote. A platinum wire, D, was attached to the arms for suspending the pycnometer from the balance during weighings. Caps for the arms were constructed from the outer parts of the appropriate standard tapers.

The constant-temperature bath employed in the thermal equilibration of the solutions was identical to that previously used in density measurements by the magnetically controlled float method (21). The bath temperature was maintained at 25.000 $\pm$ 0.005° C. as read from an Emerson calorimeter thermometer, graduated in units of 0.01° C., which had been checked against a platinum resistance thermometer calibrated by the National Bureau of Standards.

All weighings were made on an Ainsworth type BB analytical balance using a set of Ainsworth Class S certified weights. The individual weights were checked against one another to obtain their relative values. In all pycnometer weighings, a second pycnometer was used as a tare to standardize the effect of the adsorption of moisture and to cancel the buoyancy effect of the air displaced by the

pycnometer. All weights of solution were corrected to weights
in vacuo using the appropriate solution density, density of
weights, and density of air as calculated from the balance-
room temperature, relative humidity, and barometric pressure.

The general procedure for the density determinations was
as follows:

1. Prior to a series of density determinations, each
pycnometer was cleaned with sulfuric acid-potassium di-
chromate cleaning solution. After prolonged rinsing with
distilled water, the pycnometer was allowed to stand in
conductivity water for several hours. After additional rins-
ing with conductivity water, the pycnometer was dried by
passing compressed air, purified by passage through anhydrous
calcium chloride-glass wool traps, through the pycnometer.
Upon completion of the drying process, the expansion chamber
of the pycnometer was coated with Beckman Desicote.

2. Before weighing the empty pycnometer, the pycnometer
and its tare were flushed with air from the balance room,
after which they were wiped with a moist lintless cloth.
The pycnometer and tare were then allowed to stand with caps
removed in the balance case for 15 to 20 minutes before the
weighing.

3. The pycnometer was filled with solution by applying
suction from a water aspirator at the end of arm A through
an air-filled flask. A quantity of solution was allowed to

pass through the pycnometer to eliminate the possibility of error due to evaporation at the surface of the solution during the filling process. After the pycnometer was filled, rubber caps were placed on the ends of the arms.

4. The pycnometer was placed in the constant-temperature bath for thermal equilibration. The time required for the attainment of thermal equilibrium was approximately 30 minutes.

5. At the end of the equilibration period, the caps were removed and the liquid level in the pycnometer was adjusted to the calibration mark by tilting the pycnometer slightly and withdrawing solution from the capillary of arm A by touching a piece of absorbent paper to it. After the adjustment was completed, the ends of the arms were wiped clean and the glass caps placed on them.

6. The pycnometer was removed from the bath and its outer surface carefully rinsed. The pycnometer and tare were then wiped with a moist lintless cloth and allowed to stand in the balance case for 15 to 20 minutes before weighing.

7. From the vacuum-corrected weight of solution and the known volume of the pycnometer, the density of the solution was calculated by the relation $d = W/V$.

The pycnometers were calibrated with conductivity water using the procedure just outlined. From the vacuum-corrected weight of conductivity water and the density of water at

25° C., $d_O = 0.997075$ gm. per ml. (87), the volume of the
pycnometer was calculated by the relation $V = W/d_O$. For each
pycnometer a series of about 10 calibrations was carried out
during the course of the density measurements. The mean
deviation of the volume calibrations for each pycnometer was
in all cases less than $\pm$ 0.0003 milliliter.

For each rare-earth chloride solution, two to four de-
terminations of the density were carried out. For a given
solution a different pycnometer was employed in each deter-
mination as a check on the consistency of the volume cali-
brations. The mean deviation of the density determinations
for any given solution was between $\pm$ 1 x 10^{-5} and $\pm$ 1 x 10^{-6}
gm. per ml.

2. Calculations and results

Densities of aqueous solutions of lanthanum, neodymium,
samarium, gadolinium, dysprosium, erbium, and ytterbium
chlorides was determined by the method previously described.
The concentration range covered for each rare-earth chloride
in these determinations was between 0.02 molal and satura-
tion.

From the densities and known molal concentrations of
the solutions, the apparent molal volume, $\emptyset_V$, for each con-
centration was calculated from Equation 41. The molecular
weight values employed were computed from atomic weight

values reported in 1956 by Wichers (88). For each rare-earth chloride an empirical equation for the apparent molal volume of the form

$$\emptyset_V = A + Bm^{1/2} + Cm^2 + Dm^{3/2} + Em^2 \quad , \tag{58}$$

was determined by the method of least squares using an IBM 650 computer. From this equation, the corresponding equation for the partial molal volume, $\bar{V}_2$, was obtained by application of Equation 44.

The densities, d, apparent molal volumes, $\emptyset_V$, and partial molal volumes, $\bar{V}_2$, for aqueous solutions of the rare-earth chlorides are given in Tables 4 through 10. The least squares equations for the apparent and partial molal volumes are given below the tables. In the tables the concentrations are expressed in moles of solute per 1000 grams of water and the densities in grams per milliliter. The apparent and partial molal volumes are expressed in cubic centimeters per mole. The quantity Δ is the difference between the experimentally determined apparent molal volume for a solution of given molal concentration and the apparent molal volume as calculated from the least squares equation.

The apparent and partial molal volumes for the rare-earth chlorides are shown graphically in Figures 3 through 9. In Figure 10, the apparent molal volumes curves as calculated from the least squares equations are shown.

Table 4. Densities, apparent molal volumes, and partial molal volumes of lanthanum chloride in aqueous solutions at 25° C.

m	$m^{1/2}$	d	ϕ_v	ϕ_v^a L.S.	Δ	$\bar{V}_2^b$
0.020724	0.14396	1.00177	18.0	17.89	+0.11	18.81
0.039982	0.19995	1.00611	18.5	18.59	-0.09	19.84
0.055827	0.23628	1.00966	19.0	19.04	-0.04	20.49
0.11094	0.33308	1.02191	20.30	20.21	+0.09	22.19
0.13259	0.36413	1.02669	20.71	20.58	+0.13	22.72
0.19753	0.44444	1.04096	21.58	21.51	+0.07	24.08
0.29085	0.53931	1.06125	22.60	22.60	0.00	25.69
0.31955	0.56529	1.06746	22.84	22.90	-0.06	26.13
0.37513	0.61248	1.07937	23.41	23.44	-0.03	26.94
0.39047	0.62488	1.08260	23.66	23.58	+0.08	27.15
0.48666	0.69761	1.10305	24.38	24.41	-0.03	28.41
0.58636	0.76574	1.12396	25.14	25.20	-0.06	29.60
0.72096	0.84909	1.15182	26.06	26.16	-0.10	31.08
0.75572	0.86932	1.15890	26.34	26.39	-0.05	31.45
0.90873	0.95327	1.18989	27.30	27.38	-0.08	32.97
0.97118	0.98548	1.20228	27.76	27.75	+0.01	33.56
1.1411	1.0682	1.23570	28.78	28.73	+0.05	35.09
1.2679	1.1260	1.26021	29.48	29.42	+0.06	36.15
1.3594	1.1659	1.27780	29.88	29.90	-0.02	36.89
1.4763	1.2150	1.29975	30.52	30.49	+0.03	37.79
1.6396	1.2805	1.32988	31.37	31.28	+0.09	38.97
1.8548	1.3619	1.36890	32.31	32.26	+0.05	40.41
2.0788	1.4418	1.40837	33.27	33.21	+0.06	41.75
2.2818	1.5106	1.44340	34.03	34.02	+0.01	42.83
2.5285	1.5901	1.48478	34.92	34.93	-0.01	43.98
2.8563	1.6901	1.53786	36.03	36.05	-0.02	45.22
3.0512	1.7668	1.56890	36.54	36.65	-0.11	45.79

$^a \phi_v = 15.953 + 14.086\ m^{1/2} - 5.1844\ m + 4.1906\ m^{3/2} - 1.1195\ m^2$.

$^b \bar{V}_2 = 15.953 + 21.129\ m^{1/2} - 10.369\ m + 10.477\ m^{3/2} - 3.3584\ m^2$.

Table 4 (continued)

m	$m^{1/2}$	d	ϕ_V	$\phi_V{}^a$ L.S.	Δ	$\bar{V}_2{}^b$
3.0819	1.7555	1.57363	36.64	36.74	-0.10	45.87
3.4562	1.8591	1.63018	37.77	37.78	-0.01	46.59
3.5966	1.8965	1.65062	38.20	38.12	+0.08	46.74
3.8959	1.9738	1.69433	38.83	38.79	+0.04	46.84
				Average	±0.06	

D. Discussion of Results

The apparent molal volume is a derived quantity, calculated in this research from the experimentally determined density and molal concentration of solutions by means of Equation 41. The accuracy of the apparent molal volumes of the rare-earth chlorides determined in this research is therefore governed by the uncertainties in the densities and concentrations of the solutions.

When a quantity, U, cannot be measured directly but must be calculated from the mean values of two or more independently measured quantities, $\bar{X}_1$, $\bar{X}_2$, ... $\bar{X}_n$, then the probable error in the mean value of U may be calculated from those of $\bar{X}_1$, $\bar{X}_2$, ... $\bar{X}_n$ with the aid of the law of propagation of precision indexes. In this method, described by Worthing and Geffner (89), the probable error in $\bar{U}$ is expressed by the equation

Table 5. Densities, apparent molal volumes, and partial molal volumes of neodymium chloride in aqueous solutions at 25° C.

m	$m^{1/2}$	d	ϕ_V	$\phi_V{}^a$ L.S.	Δ	$\bar{V}_2{}^b$
0.025985	0.16120	1.00322	13.4	13.48	-0.08	14.50
0.037182	0.19283	1.00585	13.8	13.88	-0.08	15.08
0.048954	0.22126	1.00861	14.2	14.23	-0.03	15.58
0.073320	0.27078	1.01428	15.1	14.83	+0.27	16.45
0.11599	0.34057	1.02421	15.63	15.65	-0.02	17.64
0.18668	0.43206	1.04048	16.76	16.71	+0.05	19.16
0.22257	0.47177	1.04870	17.17	17.16	+0.01	19.82
0.28528	0.53412	1.06298	17.82	17.86	-0.04	20.86
0.33423	0.57813	1.07402	18.38	18.35	+0.03	21.59
0.40038	0.63276	1.08892	18.89	18.96	-0.07	22.51
0.50921	0.71359	1.11313	19.82	19.87	-0.05	23.89
0.62558	0.79094	1.13872	20.68	20.75	-0.07	25.25
0.82591	0.90880	1.18203	22.03	22.10	-0.07	27.39
1.0224	1.0111	1.22345	23.35	23.31	+0.04	29.31
1.2393	1.1132	1.26821	24.62	24.53	+0.09	31.30
1.5409	1.2413	1.32880	26.14	26.11	+0.03	33.85
1.6938	1.3015	1.35860	26.92	26.86	+0.06	35.06
2.1610	1.4700	1.44674	28.99	29.01	-0.02	38.43
2.5811	1.6066	1.52175	30.73	30.76	-0.03	41.04
3.1132	1.7644	1.61142	32.72	32.76	-0.04	43.73
3.6138	1.9010	1.69079	34.37	34.42	-0.05	45.63
3.9292	1.9822	1.73794	35.41	35.35	+0.06	46.48
			Average		±0.06	

$^a\phi_V = 11.330 + 14.155\ m^{1/2} - 5.6661\ m + 4.3880\ m^{3/2} - 1.0331\ m^2.$

$^b\bar{V}_2 = 11.330 + 21.232\ m^{1/2} - 11.332\ m + 10.970\ m^{3/2} - 3.0992\ m^2.$

Table 6. Densities, apparent molal volumes, and partial
molal volumes of samarium chloride in aqueous
solutions at 25° C.

m	$m^{1/2}$	d	ϕ_V	$\phi_V{}^a$ L.S.	Δ	$\overline{V}_2{}^b$
0.022158	0.14886	1.00242	14.8	14.27	+0.53	15.24
0.030016	0.17425	1.00432	14.5	14.58	-0.08	15.70
0.044960	0.21240	1.00790	15.1	15.08	+0.02	16.41
0.10180	0.31906	1.02143	16.37	16.36	+0.01	18.23
0.11417	0.33789	1.02435	16.71	16.58	+0.13	18.53
0.22693	0.47638	1.05085	18.14	18.13	+0.01	20.73
0.35101	0.59246	1.07961	19.35	19.38	-0.03	22.51
0.45735	0.67628	1.10397	20.20	20.26	-0.06	23.80
0.64245	0.80153	1.14572	21.53	21.57	-0.04	25.78
0.82308	0.90724	1.18572	22.65	22.69	-0.04	27.51
0.96565	0.98267	1.21672	23.50	23.49	+0.01	28.79
1.1384	1.0670	1.25369	24.44	24.41	+0.03	30.26
1.4265	1.1944	1.31386	25.88	25.83	+0.05	32.59
1.7136	1.3090	1.37196	27.19	27.15	+0.04	34.76
1.9466	1.3952	1.41777	28.19	28.16	+0.03	36.44
2.3841	1.5441	1.50059	29.92	29.95	-0.03	39.37
2.6945	1.6415	1.55670	31.10	31.15	-0.05	41.26
3.0587	1.7489	1.61976	32.44	32.47	-0.03	43.29
3.4090	1.8463	1.67757	33.69	33.68	+0.01	45.03
3.6401	1.9079	1.71441	34.46	34.43	+0.03	46.05
				Average	±0.06	

$^a\phi_V = 12.189 + 14.908\ m^{1/2} - 7.0840\ m + 4.6026\ m^{3/2} - 0.93422\ m^2$.

$^b\overline{V}_2 = 12.189 + 22.362\ m^{1/2} - 14.168\ m + 11.506\ m^{3/2} - 2.8027\ m^2$.

Table 7. Densities, apparent molal volumes, and partial molal volumes of gadlinium chloride in aqueous solutions at 25° C.

m	$m^{1/2}$	d	ϕ_V	ϕ_V^a L.S.	Δ	$\overline{V}_2^b$
0.023050	0.15182	1.00276	16.2	16.33	-0.13	17.29
0.036376	0.19073	1.00602	16.9	16.82	+0.08	17.99
0.051437	0.22680	1.00970	17.3	17.26	+0.04	18.62
0.12354	0.35149	1.02717	18.77	18.70	+0.07	20.68
0.20505	0.45282	1.04672	19.87	19.82	+0.05	22.26
0.32080	0.56639	1.07419	20.98	21.03	-0.05	24.00
0.42474	0.65172	1.09856	21.84	21.91	-0.07	25.29
0.64112	0.80070	1.14843	23.39	23.45	-0.06	27.57
0.82366	0.90756	1.18962	24.53	24.55	-0.02	29.25
1.0011	1.0005	1.22892	25.52	25.52	0.00	30.75
1.0793	1.0389	1.24598	25.95	25.92	+0.03	31.39
1.3078	1.1436	1.29511	27.08	27.03	+0.05	33.14
1.6221	1.2736	1.36075	28.49	28.43	+0.06	35.36
1.9623	1.4008	1.42938	29.86	29.83	+0.03	37.57
2.2958	1.5152	1.49421	31.09	31.10	-0.01	39.55
2.6051	1.6140	1.55221	32.15	32.20	-0.05	41.21
2.9683	1.7229	1.61763	33.36	33.42	-0.06	42.97
3.3564	1.8320	1.68427	34.61	34.61	0.00	44.58
3.5906	1.8949	1.72291	35.34	35.29	+0.05	45.42
				Average	±0.05	

$$^a\phi_V = 14.309 + 14.165\ m^{1/2} - 5.9924\ m + 3.8494\ m^{3/2} - 0.81684\ m^2.$$

$$^b\overline{V}_2 = 14.309 + 21.247\ m^{1/2} - 11.985\ m + 9.6234\ m^{3/2} - 2.4505\ m^2.$$

Table 8. Densities, apparent molal volumes, and partial
molal volumes of dysprosium chloride in aqueous
solutions at 25° C.

m	$m^{1/2}$	d	ϕ_V	$\phi_V{}^a$ L.S.	Δ	$\bar{V}_2{}^b$
0.025036	0.15823	1.00339	15.8	15.92	-0.12	16.87
0.037732	0.19425	1.00657	16.4	16.35	+0.05	17.50
0.049460	0.22240	1.00950	16.7	16.68	+0.02	17.98
0.12118	0.34811	1.02730	18.24	18.12	+0.12	20.10
0.23862	0.48849	1.05609	19.73	19.70	+0.03	22.40
0.34630	0.58847	1.08217	20.73	20.80	-0.07	24.04
0.48745	0.69818	1.11585	21.95	22.01	-0.06	25.85
0.64737	0.80459	1.15340	23.14	23.18	-0.04	27.64
0.81840	0.90465	1.19285	24.28	24.30	-0.02	29.35
1.0551	1.0272	1.24627	25.68	25.67	+0.01	31.48
1.1240	1.0602	1.26158	26.05	26.05	0.00	32.06
1.4089	1.1870	1.32359	27.54	27.50	+0.04	34.31
1.7002	1.3039	1.38508	28.88	28.84	+0.04	36.38
1.9339	1.3907	1.43288	29.92	29.85	+0.07	37.90
2.2307	1.4936	1.49214	31.03	31.04	-0.01	39.65
2.5897	1.6093	1.56110	32.32	32.36	-0.04	41.53
2.9606	1.7206	1.62941	33.55	33.62	-0.07	43.18
3.3344	1.8260	1.69526	34.73	34.77	-0.04	44.57
3.6310	1.9055	1.74509	35.68	35.61	+0.07	45.46
				Average	±0.05	

$^a\phi_V = 13.944 + 12.968\ m^{1/2} - 3.6397\ m + 2.7826\ m^{3/2} - 0.68898\ m^2.$

$^b\bar{V}_2 = 13.944 + 19.453\ m^{1/2} - 7.2794\ m + 6.9564\ m^{3/2} - 2.0669\ m^2.$

Table 9. Densities, apparent molal volumes, and partial molal volumes of erbium chloride in aqueous solutions at 25° C.

m	$m^{1/2}$	d	ϕ_V	$\phi_V{}^a$ L.S.	Δ	$\bar{V}_2{}^b$
0.023577	0.15355	1.00318	13.8	14.00	-0.20	15.06
0.035107	0.18737	1.00614	14.5	14.46	+0.04	15.71
0.046163	0.21486	1.00898	14.9	14.82	+0.08	16.22
0.073922	0.27189	1.01607	15.7	15.55	+0.15	17.24
0.11280	0.33585	1.02596	16.40	16.33	+0.07	18.34
0.17522	0.41859	1.04174	17.25	17.30	-0.05	19.70
0.22260	0.47181	1.05361	17.95	17.90	+0.05	20.56
0.31230	0.55884	1.07599	18.78	18.87	-0.09	21.95
0.39786	0.63076	1.09709	19.62	19.66	-0.04	23.10
0.50427	0.71012	1.12309	20.49	20.52	-0.03	24.39
0.60324	0.77669	1.14703	21.21	21.25	-0.04	25.50
0.79641	0.89242	1.19305	22.50	22.53	-0.03	27.49
0.97087	0.98533	1.23379	23.59	23.57	+0.02	29.16
1.1963	1.0938	1.28535	24.87	24.82	+0.05	31.17
1.6192	1.2725	1.37873	27.01	26.93	+0.08	34.57
1.9888	1.4102	1.45696	28.64	28.60	+0.04	37.17
2.4989	1.5808	1.55991	30.61	30.67	-0.06	40.16
2.9875	1.7284	1.65300	32.33	32.40	-0.07	42.29
3.7821	1.9448	1.79389	34.75	34.71	+0.04	44.07
				Average	±0.07	

$^a\phi_V$ = 11.733 + 16.002 $m^{1/2}$ - 8.8733 m + 6.3801 $m^{3/2}$ - 1.5041 m^2.

$^b\bar{V}_2$ = 11.733 + 24.004 $m^{1/2}$ - 17.747 m + 15.950 $m^{3/2}$ - 4.5122 m^2.

Table 10. Densities, apparent molal volumes, and partial molal volumes of ytterbium chloride in aqueous solutions at 25° C.

m	$m^{1/2}$	d	ϕ_V	$\phi_V{}^a$ L.S.	Δ	$\bar{V}_2{}^b$
0.025889	0.16090	1.00398	11.9	12.10	-0.20	13.14
0.036177	0.19020	1.00669	12.8	12.48	+0.32	13.69
0.046279	0.21513	1.00938	12.6	12.79	-0.19	14.14
0.077930	0.27916	1.01770	13.7	13.58	+0.12	15.28
0.11559	0.33998	1.02758	14.32	14.31	+0.01	16.33
0.17393	0.41705	1.04278	15.20	15.22	-0.02	17.63
0.23913	0.48901	1.05964	16.04	16.04	0.00	18.83
0.34445	0.58690	1.08664	17.14	17.15	-0.01	20.45
0.44549	0.66745	1.11229	18.00	18.05	-0.05	21.79
0.55485	0.74488	1.13971	18.94	18.92	+0.02	23.10
0.67737	0.82302	1.17016	19.77	19.80	-0.03	24.45
0.87558	0.93572	1.21858	21.08	21.08	0.00	26.44
1.0857	1.0420	1.26886	22.34	22.31	+0.03	28.38
1.2780	1.1305	1.31407	23.32	23.35	-0.03	30.02
1.7397	1.3190	1.41860	25.66	25.60	+0.06	33.61
2.2400	1.4967	1.52637	27.79	27.78	+0.01	36.97
2.7681	1.6638	1.63385	29.80	29.83	-0.03	39.96
3.2336	1.7982	1.72341	31.41	31.44	-0.03	42.10
4.0028	2.0007	1.86137	33.77	33.75	+0.02	44.58
				Average	±0.06	

$^a\phi_V = 9.910 + 14.421\ m^{1/2} - 5.5761\ m + 3.9707\ m^{3/2} - 0.90444\ m^2.$

$^b\bar{V}_2 = 9.910 + 21.631\ m^{1/2} - 11.152\ m + 9.9268\ m^{3/2} - 2.7133\ m^2.$

Figure 3.   Apparent and partial molal volumes of lanthanum
            chloride in aqueous solutions at 25° C.

Figure 4.   Apparent and partial molal volumes of neodymium
            chloride in aqueous solutions at 25° C.

Figure 5.   Apparent and partial molal volumes of samarium
chloride in aqueous solutions at 25° C.

Figure 6. Apparent and partial molal volumes of gadolinium chloride in aqueous solutions at 25° C.

Figure 7. Apparent and partial molal volumes of dysprosium chloride in aqueous solutions at 25° C.

Figure 8. Apparent and partial molal volumes of erbium
chloride in aqueous solutions at 25° C.

CUBIC CENTIMETERS PER MOLE

46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10

0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0

(MOLALITY) $\frac{1}{2}$

ErCl$_3$
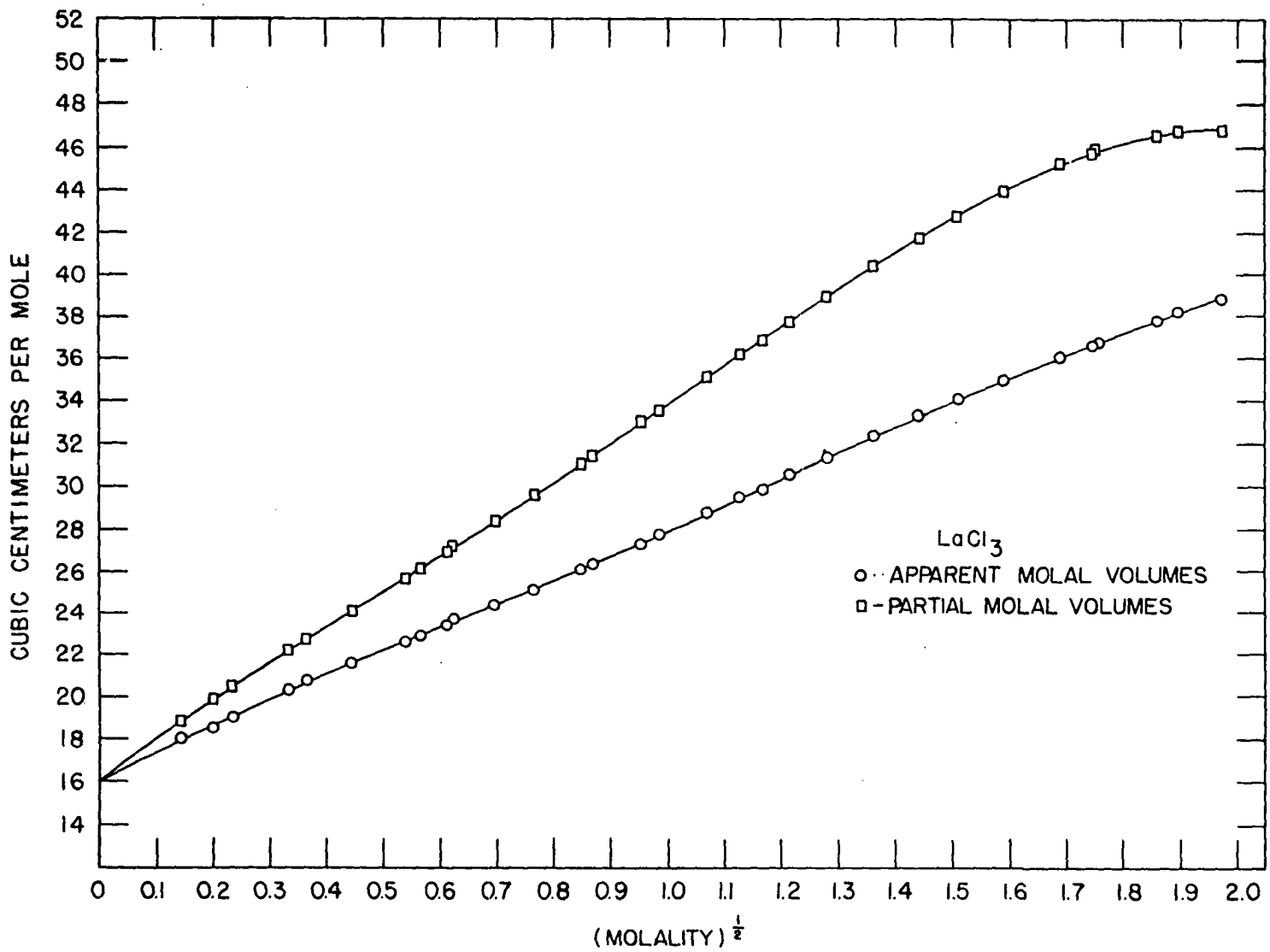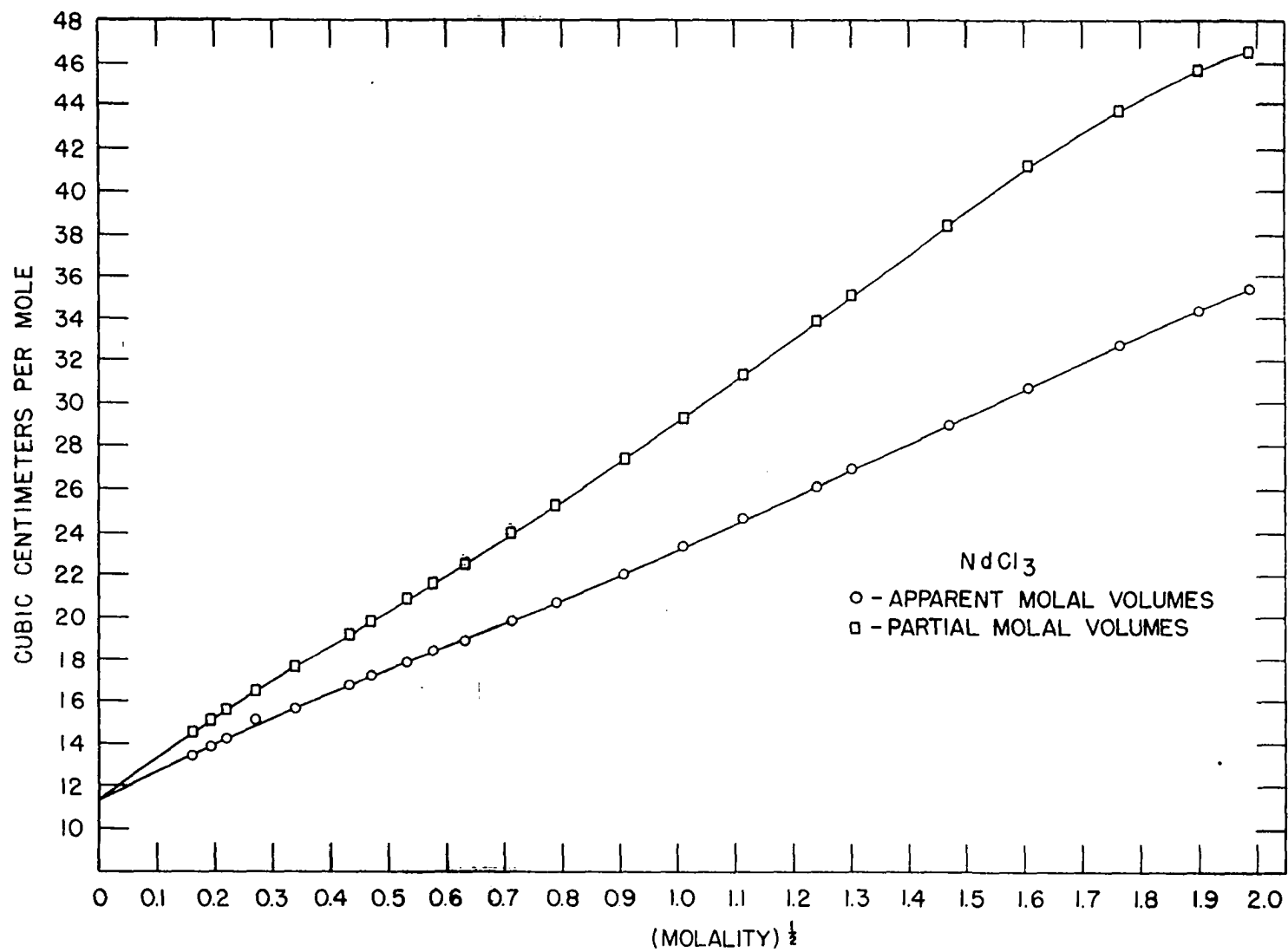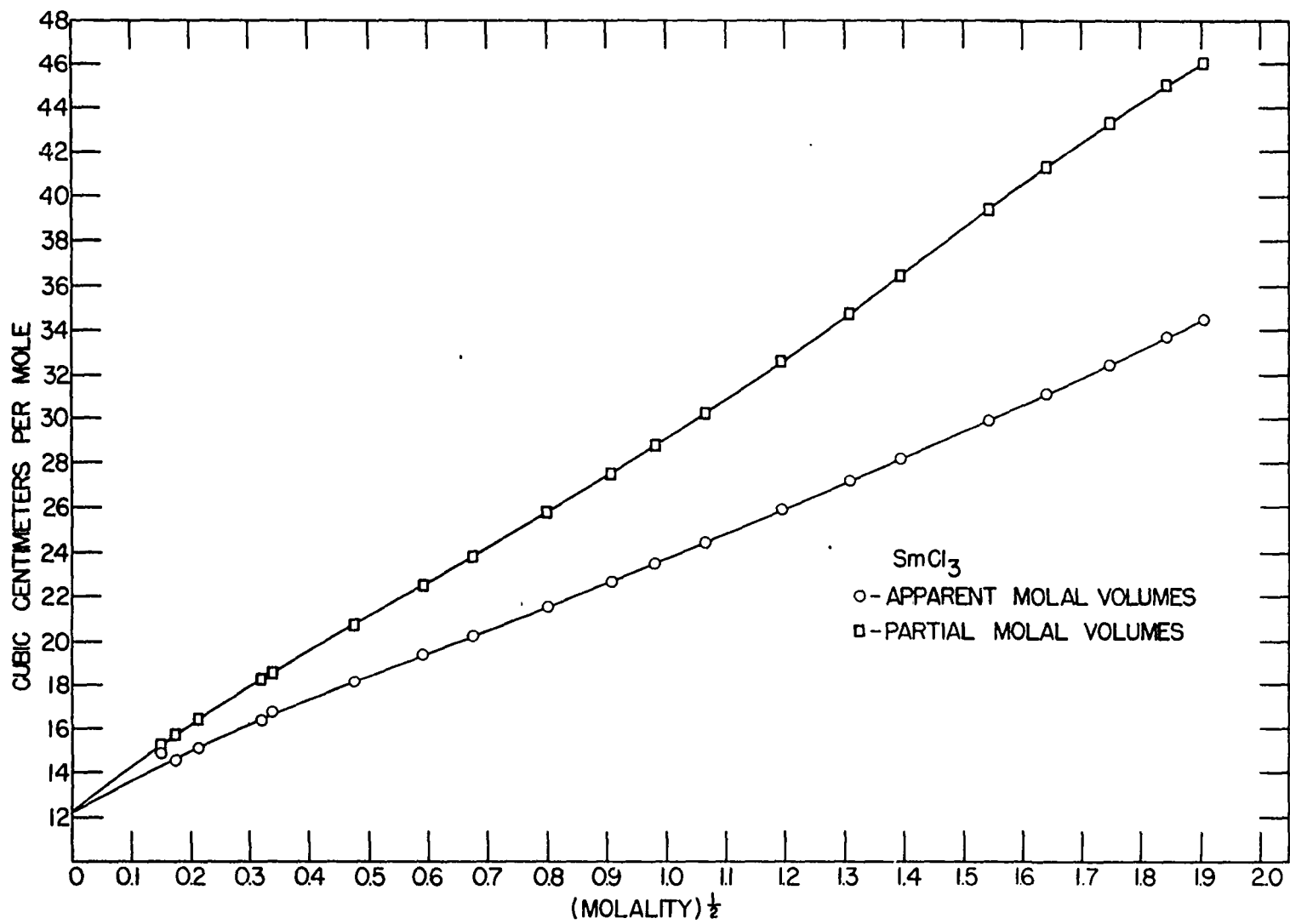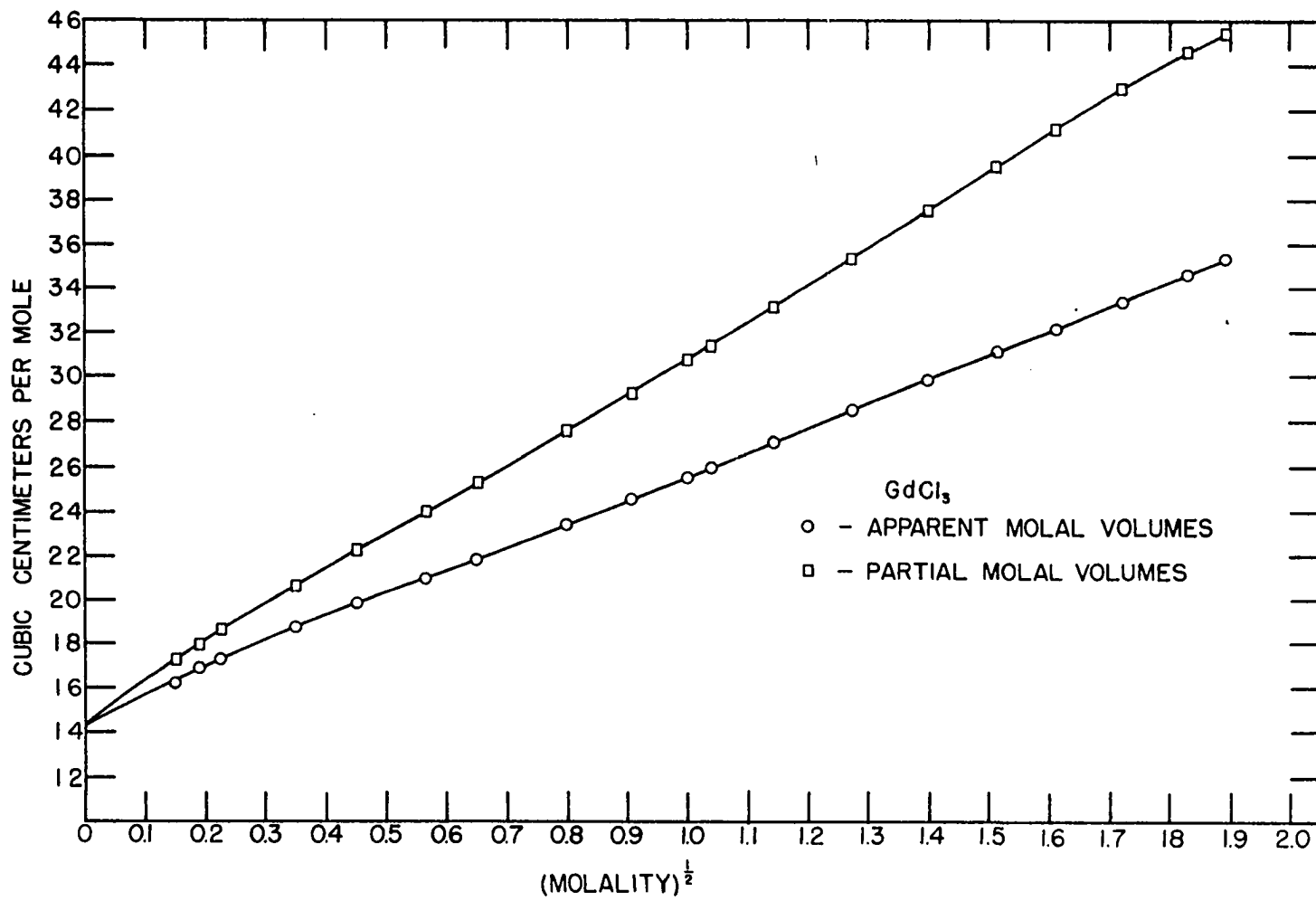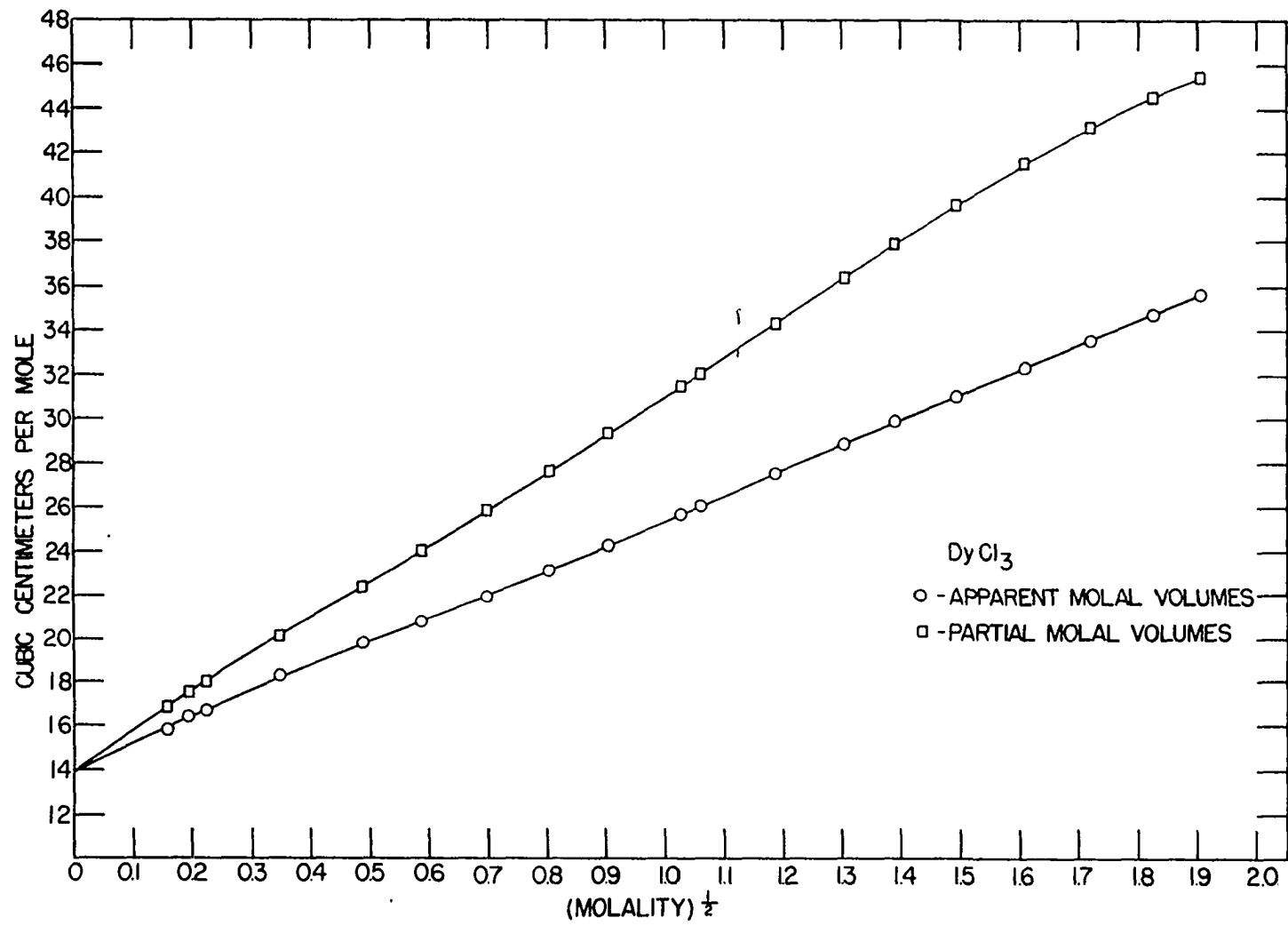o – APPARENT MOLAL VOLUMES
□ – PARTIAL MOLAL VOLUMES
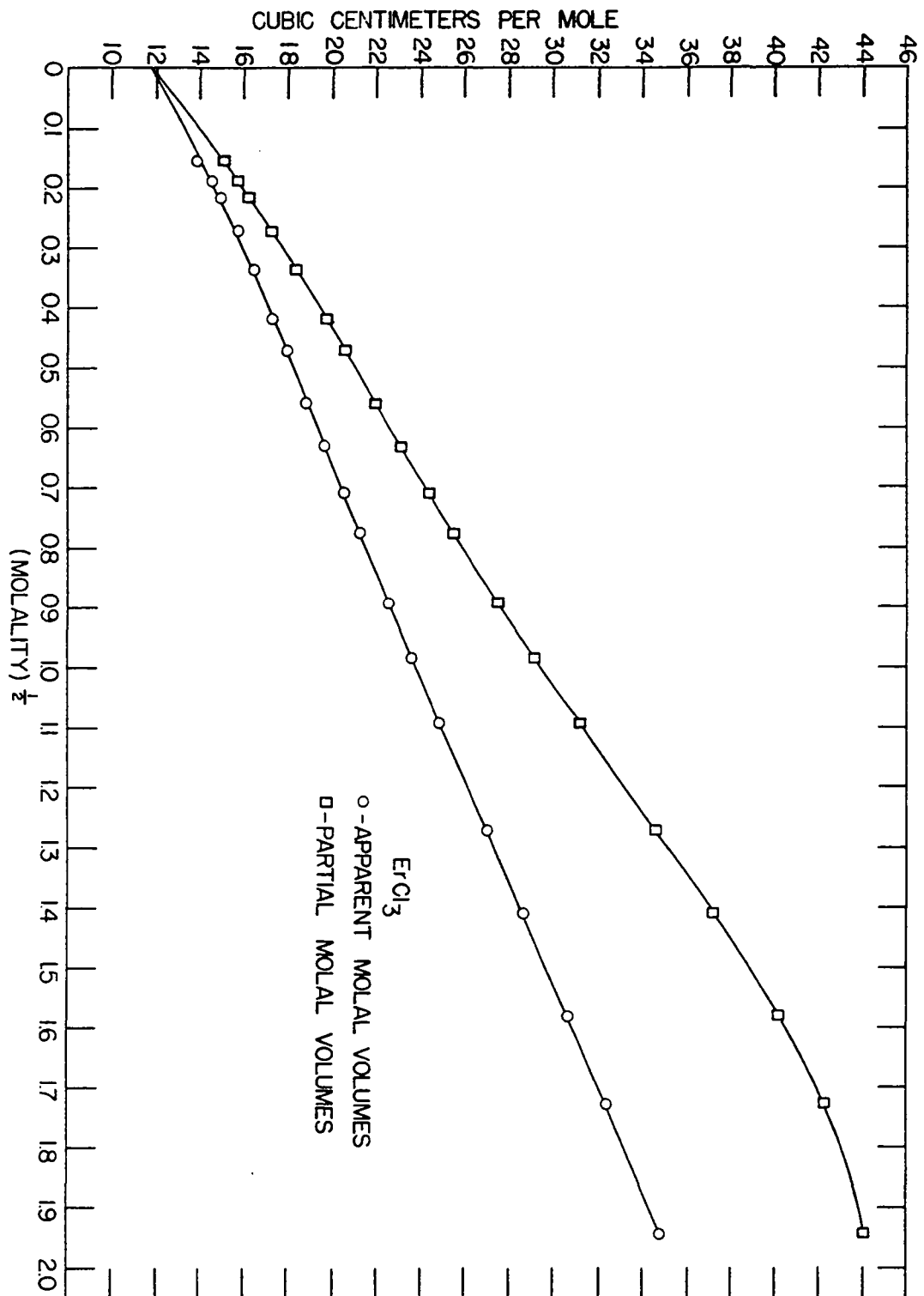
Figure 9.   Apparent and partial molal volumes of ytterbium
           chloride in aqueous solutions at 25° C.
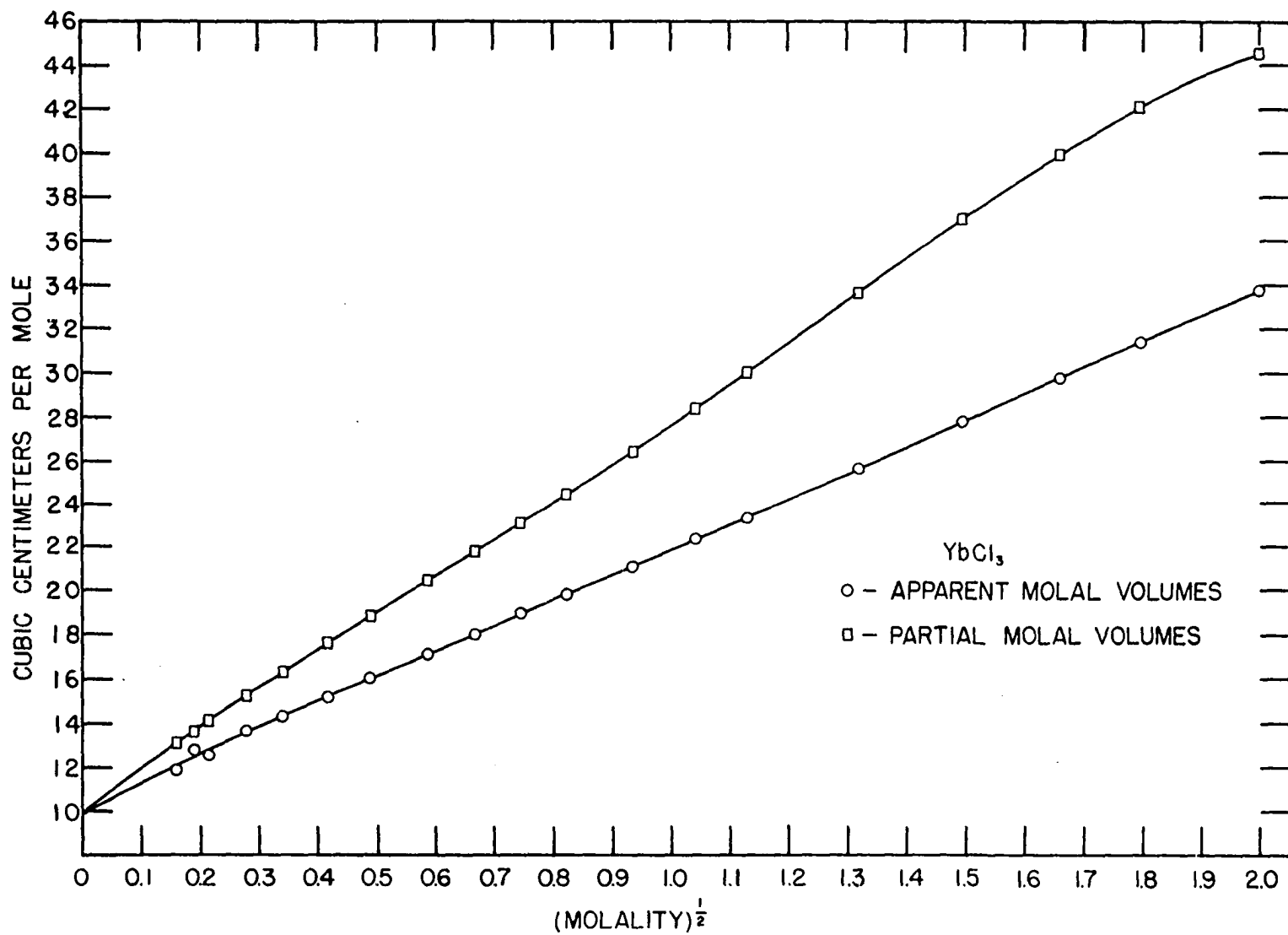
Figure 10.   Apparent molal volumes of rare-earth
             chlorides in aqueous solutions at
             25° C. as calculated from least squares
             equations
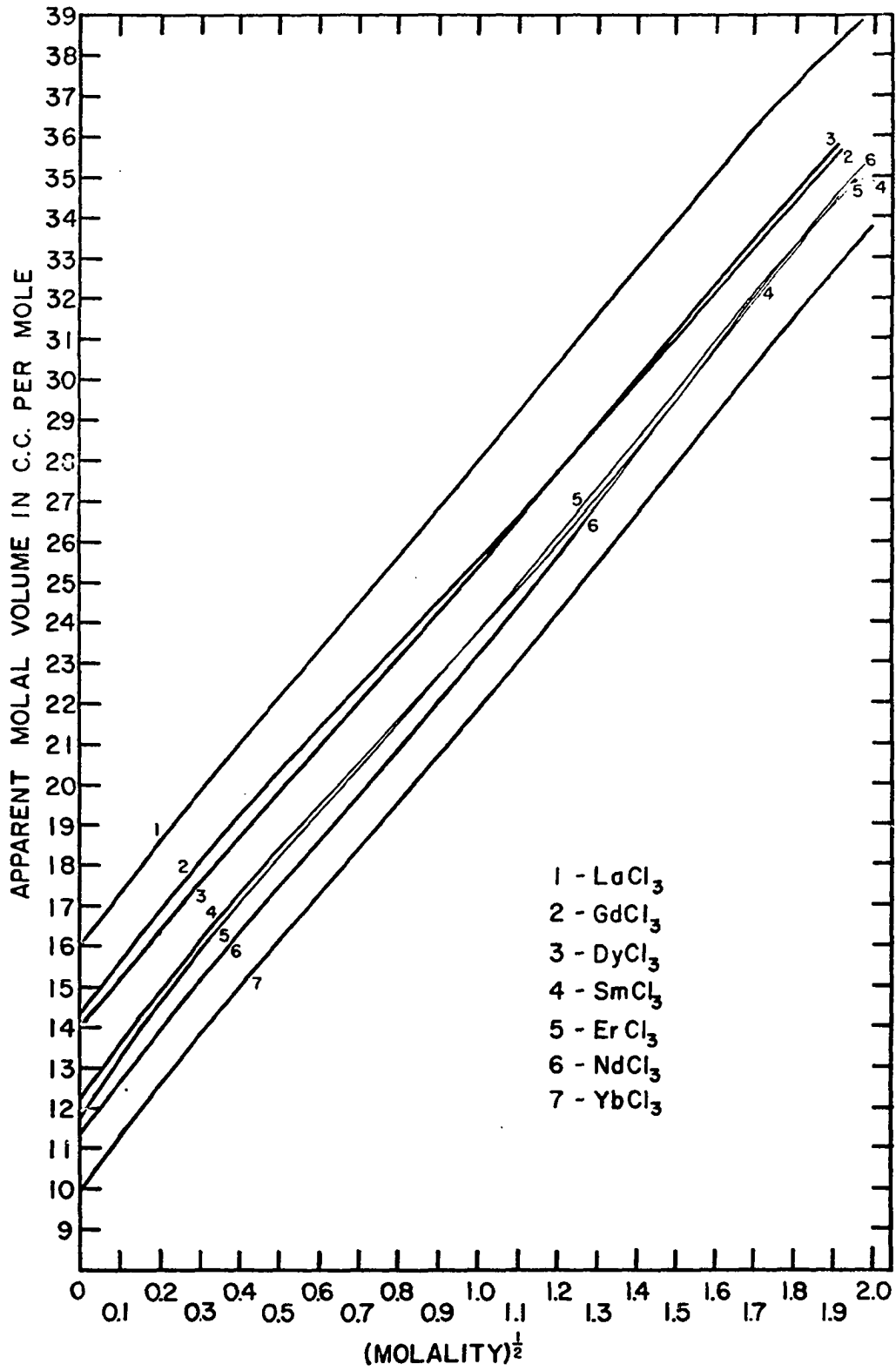
$$P_{\overline{U}}^2 = \sum_{i=1}^{n} \left(\frac{\partial U}{\partial \overline{X}_i} \right)^2 P_{\overline{X}_i}^2 \quad , \tag{59}$$

where $P_{\overline{U}}$ is the probable error in $\overline{U}$; $\overline{U}$, the mean value of the derived quantity U; $\overline{X}_i$, the mean value of the directly measured quantity X_i; and $P_{\overline{X}_i}$, the probable error in $\overline{X}_i$.

Applying Equation 59 to the apparent molal volume, $\emptyset_v$, as expressed by Equation 41, namely,

$$\emptyset_v = \frac{1000}{mdd_o}(d_o - d) + \frac{M_2}{d} \quad , \tag{41}$$

one obtains the equation

$$P_{\overline{\emptyset}_v}^2 = \left[\frac{1}{d^2} \left(\frac{1000}{m} + M_2 \right) \right]^2 P_{\overline{d}}^2 + \left[\frac{1000(d - d_o)}{m^2 dd_o} \right]^2 P_{\overline{m}}^2 \tag{60}$$

where $P_{\overline{\emptyset}_v}$ is the probable error in $\emptyset_v$; $P_{\overline{d}}$, the probable error in the density, d; and $P_{\overline{m}}$, the probable error in the molality, m.

The probable error in the molality was estimated from the precision of the analyses. The average deviations for sets of triplicate oxide analyses of rare-earth chloride solutions fell in the range ± 0.09 per cent to ± 0.001 per cent. Except in a few cases, the analytical sets had average deviations of better than ± 0.05 per cent. Since the analyses were also self-consistent, that is, the concentration of a solution as calculated from weight-dilution data

agreed with the concentration as obtained by direct analysis, within at least $\pm$ 0.05 per cent, a probable error in the molality of 0.05 per cent was assumed.

The uncertainty in the density was determined by a number of factors. These factors included temperature fluctuations in the bath, uncertainty in the volume of the pycnometers, and uncertainty in the adjustment of the solution meniscus to the calibration mark. For water at 25° C., the coefficient of cubical expansion is about 2.5×10^{-4} per degree C. A change in temperature of 0.005° C. therefore results in a change in density of about 1.3×10^{-6} gm. per ml. The average deviation of the volume calibrations for each pycnometer was less than 0.0003 milliliter. An error of this magnitude in the volume of the pycnometers introduces an uncertainty of 7.5×10^{-6} gm. per ml. in the density of dilute solutions. The uncertainty in the adjustment of the solution meniscus can only be estimated from the precision of the density determinations. Since the average deviations of the density determinations fell in the range $\pm 1 \times 10^{-5}$ to 1×10^{-6} gm. per ml., a probable error in the density of 1×10^{-5} gm. per ml. was assumed.

In Table 11, the probable error in ϕ_V for some lanthanum chloride solutions, as calculated from Equation 60 assuming $P_{\overline{d}} = 1 \times 10^{-5}$ gm. per ml. and $P_{\overline{m}} = 0.0005m$, is tabulated. The individual contributions of the density and molality to

Table 11. Probable error in $\emptyset_V$ for lanthanum chloride solutions

m	d	$(\partial\emptyset_V/\partial d)P_{\bar{d}}$	$(\partial\emptyset_V/\partial m)P_{\bar{m}}$	$P_{\bar{\emptyset}_V}$
0.020724	1.00177	0.484	0.114	0.497
0.055827	1.00966	0.178	0.112	0.210
0.13259	1.02669	0.074	0.109	0.132
0.19753	1.04096	0.049	0.107	0.118
0.29085	1.06125	0.033	0.104	0.109
0.37513	1.07937	0.025	0.102	0.105
0.48666	1.10305	0.019	0.099	0.100
0.72096	1.15182	0.012	0.093	0.094
0.90873	1.18989	0.010	0.089	0.090
1.3594	1.27780	0.006	0.081	0.081
1.8548	1.36890	0.004	0.073	0.074
2.5285	1.48478	0.003	0.065	0.065
3.0512	1.56890	0.002	0.060	0.060
3.8959	1.69433	0.002	0.053	0.053

the probable error in $\emptyset_V$ are also included. All errors are expressed in cubic centimeters per mole. It is seen from Table 11 that, except for dilute solutions, the uncertainty in $\emptyset_V$ is predominantly due to the uncertainty in the concentration. The probable error of the apparent molal volumes determined in this research thus ranges from about 0.15 cubic

centimeter at a concentration of 0.1 molal to about 0.06
cubic centimeter for the saturated solution.

The limiting value of the apparent and partial molal
volumes of the rare-earth chlorides does not show a regular
decrease with increasing atomic number of the rare earth as
might be expected from the decreasing ionic radius. As is
shown by Figure 10, the apparent molal volume of the rare-
earth chlorides at a given concentration in the dilute range
decreases in the order: lanthanum, gadolinium, dysprosium,
samarium, erbium, neodymium, and ytterbium. In the high con-
centration range, the situation is even more complex. Ex-
cept for those of lanthanum and ytterbium chlorides, the
apparent molal volume curves exhibit a general convergence
with a complex series of crossovers. All of the curves show
a slight S-shaped character.

The anomalies shown by the apparent and partial molal
volumes of rare-earth salts were first noted by Ayers (21),
who determined the apparent and partial molal volumes of the
chlorides and nitrates of lanthanum, neodymium, erbium, and
ytterbium in dilute solutions from density data obtained by
a magnetically controlled float method. In Table 12, the
empirical equations for the apparent and partial molal
volumes of these rare-earth chlorides as determined by Ayers
are given. In Tables 13 through 16, the values of the
apparent and partial molal volumes at round concentrations

Table 12. Empirical equations for apparent and partial molal volumes of some rare-earth chlorides as determined by Ayers (21)

Salt	Empirical equation[a]
$LaCl_3$	$\phi_V = 13.864 + 36.044\ m^{1/2} - 87.540\ m + 134.52\ m^{3/2} - 75.634\ m^2$
	$\bar{V}_2 = 13.864 + 54.065\ m^{1/2} - 175.08\ m + 336.31\ m^{3/2} - 226.90\ m^2$
$NdCl_3$	$\phi_V = 10.455 + 21.129\ m^{1/2} - 17.554\ m + 5.7320\ m^{3/2} - 5.3420\ m^2$
	$\bar{V}_2 = 10.455 + 31.694\ m^{1/2} - 35.108\ m + 14.330\ m^{3/2} - 16.026\ m^2$
$ErCl_3$	$\phi_V = 11.804 + 23.292\ m^{1/2} - 54.438\ m + 116.22\ m^{3/2} - 93.172\ m^2$
	$\bar{V}_2 = 11.804 + 34.938\ m^{1/2} - 108.88\ m + 290.55\ m^{3/2} - 279.52\ m^2$
$YbCl_3$	$\phi_V = 9.251 + 22.659\ m^{1/2} - 24.425\ m + 8.9836\ m^{3/2} - 12.628\ m^2$
	$\bar{V}_2 = 9.251 + 33.988\ m^{1/2} - 48.851\ m + 22.459\ m^{3/2} - 37.884\ m^2$

[a]These equations represent data obtained in the concentration range 0.001 to 0.3 molal.

Table 13. Comparison of apparent and partial molal volumes for lanthanum chloride

Molality	$\emptyset_V{}^a$	$\emptyset_V{}^b$	Δ	$\bar{V}_2{}^a$	$\bar{V}_2{}^b$	Δ
0.0	13.86[c]	15.95[c]		13.86[c]	15.95[c]	
0.05	18.86	18.89	-0.03	20.39	20.27	+0.12
0.1	20.01	20.01	0.00	21.82	21.90	-0.08
0.15	20.81	20.85	-0.04	22.97	23.11	-0.14
0.2	21.48	21.55	-0.07	24.03	24.13	-0.10
0.25	22.09	22.15	-0.06	24.98	25.02	-0.04
0.3	22.64	22.70	-0.06	25.79	25.83	-0.04

[a]Calculated from the empirical equation as given in Table 12.

[b]Calculated from the least squares equation as determined in this research and given below Table 4.

[c]Obtained by extrapolation.

Table 14. Comparison of apparent and partial molal volumes for neodymium chloride

Molality	$\emptyset_V{}^a$	$\emptyset_V{}^b$	Δ	$\bar{V}_2{}^a$	$\bar{V}_2{}^b$	Δ
0.0	10.46[c]	11.33[c]		10.46[c]	11.33[c]	
0.05	14.38	14.26	+0.12	15.99	15.63	+0.36
0.1	15.62	15.37	+0.25	17.58	17.23	+0.35
0.15	16.46	16.19	+0.27	18.66	18.42	+0.24
0.2	17.12	16.88	+0.24	19.53	19.42	+0.11
0.25	17.68	17.47	+0.21	20.32	20.29	+0.03
0.3	18.18	18.01	+0.17	21.08	21.08	0.00

[a]Calculated from the empirical equation as given in Table 12.

[b]Calculated from the least squares equation as determined in this research and given below Table 5.

[c]Obtained by extrapolation.

Table 15. Comparison of apparent and partial molal volumes
for erbium chloride

Molality	$\phi_V{}^a$	$\phi_V{}^b$	Δ	$\overline{V}_2{}^a$	$\overline{V}_2{}^b$	Δ
0.0	11.80[c]	11.73[c]		11.80[c]	11.73[c]	
0.05	15.36	14.94	+0.42	16.72	16.38	+0.34
0.1	16.47	16.09	+0.38	18.36	18.01	+0.35
0.15	17.31	16.94	+0.37	19.59	19.19	+0.40
0.2	18.00	17.63	+0.37	20.46	20.16	+0.30
0.25	18.54	18.22	+0.32	20.90	21.01	-0.11

[a]Calculated from the empirical equation as given in
Table 12.

[b]Calculated from the least squares equation as deter-
mined in this research and given below Table 9.

[c]Obtained by extrapolation.

Table 16. Comparison of apparent and partial molal volumes
for ytterbium chloride

Molality	$\phi_V{}^a$	$\phi_V{}^b$	Δ	$\overline{V}_2{}^a$	$\overline{V}_2{}^b$	Δ
0.0	9.25[c]	9.91[c]		9.25[c]	9.91[c]	
0.05	13.23	12.90	+0.32	14.75	14.29	+0.46
0.1	14.38	14.03	+0.35	16.20	15.92	+0.28
0.15	15.17	14.87	+0.30	17.24	17.13	+0.11
0.2	15.81	15.56	+0.25	18.20	18.13	+0.07
0.25	16.39	16.17	+0.22	19.21	19.01	+0.20

[a]Calculated from the empirical equation as given in
Table 12.

[b]Calculated from the least squares equation as deter-
mined in this research and given below Table 10.

[c]Obtained by extrapolation.

as calculated from the equations of Ayers and the least squares equations determined in this research are compared. The agreement between the values for lanthanum chloride is excellent, the difference between the apparent molal volume values being less than 0.1 cubic centimeter. For neodymium, erbium, and ytterbium chlorides, the agreement is less satisfactory. For these salts, the apparent molal volume values as determined by Ayers are from 0.2 to 0.4 cubic centimeter higher than those obtained in this research. This difference is greater than the experimental error estimated by Ayers for his work and that estimated for this research. Higher values of the apparent molal volume could result from either lower density values or higher molality values.

It was first suggested by Ayers (21) that the irregular order of the limiting value of the apparent and partial molal volumes of rare-earth salts with a common anion could be due to a change in the hydration number of the rare-earth ion. As the ionic radius decreases with increasing atomic number in the rare-earth series, a smaller coordination number for water may become preferable due to volume and energy requirements.

The apparent molal volume is a measure of the volume change of a solution as solute is added. The volume change includes not only the effect of the volume of solute added, but the effect of changes in the orientation and packing of

the solvent molecules. When an electrolyte, such as a rare-earth chloride, is added to water, the volume increase of the solution is less than the volume of electrolyte added implying a closer packing of the water molecules around the solute ions and a compression of these hydrated water molecules by the strong ion-dipole forces. As a result, the rather open structure of pure water is ruptured. As more and more electrolyte is added to the solution, the magnitude of the effect decreases, which is reflected by the increase of the apparent molal volume with concentration. Since the volume of a hydrated water molecule is less than that of a free water molecule, a change in coordination number should be reflected in the apparent molal volume. A lower coordination number should lead to a greater volume of the solution and hence a higher apparent molal volume.

The results obtained in this research indicate that the limiting value of the apparent and partial molal volumes decreases with atomic number for the lighter rare-earth chlorides, lanthanum through neodymium, in line with the decreasing ionic radius. A reversal, however, occurs at samarium where the limiting value begins to increase. This increase continues through gadolinium. At dysprosium, the effect of the decreasing ionic radius is again dominant, and the limiting value decreases for the remaining rare-earth chlorides.

These results seem to indicate that a shift in coordination number for water takes place over a number of rare earths in the middle of the series. For some of the rare earths, an equilibrium may therefore exist between rare-earth ions having different coordination numbers. This is possible since hydration depends both on volume and energy requirements. The behavior of some of the apparent molal volume curves in the high concentration region lends some credence to this interpretation. As the concentration increases for a given rare-earth chloride, the coordination equilibrium may shift toward the smaller coordination number, which should lead to a sharper rise in the apparent molal volume. For neodymium chloride, there is a rather pronounced upturn of the curve above a concentration of one molal. This is undoubtedly too simple a picture, since such factors as ion-pair formation, complex formation, and hydrolysis should play an important part in determining solution properties in concentrated solutions.

There is also evidence for a shift in the coordination number of the rare earth ion in the crystal form. The rare earths, lanthanum through praseodymium, form sulfates having the formula $R_2(SO_4)_3 \cdot 9H_2O$, whereas the heavier rare earths form, under similar conditions, the compounds $R_2(SO_4) \cdot 8H_2O$. X-ray measurements on lanthanum sulfate enneahydrate (90) have shown that oxygen coordination numbers of 9 and 12 exist

for lanthanum ions in the same crystal, whereas measurements
on neodymium sulfate octahydrate (91) have shown only an
oxygen coordination number of 9 for the neodymium ion. Since
there is also a change in hydration from the heptahydrate to
the hexahydrate for the rare-earth chlorides between
praseodymium and neodymium, a shift in coordination number
is also indicated.

The anomalies shown by the apparent and partial molal
volumes are exhibited in a different form by other solution
properties of the rare-earth chlorides (23). The changes
between adjacent rare-earths in the conductances and trans-
ference numbers in dilute solutions are rather small for the
first few and last few rare-earth chlorides, but are signi-
ficantly greater in the middle of the series. The apparent
and partial molal compressibilities, being volume properties,
exhibit somewhat the same irregular order as the apparent
and partial molal volumes.

Due to the very limited knowledge of ion-solvent inter-
actions and the species present in solution, no quantitative
explanation of the apparent and partial molal volumes of
rare-earth salts is possible at this time. Additional data
on both volume and heat effects in solution are needed. The
determination of the apparent and partial molal volumes
should be extended to the remaining rare-earth chlorides.
An extension to the rare-earth bromides would also be of

value in establishing the effect of anion size on these properties. Expansibility and additional compressibility measurements might also furnish valuable information.

VI. ELECTROLYTIC CONDUCTANCES

A. Introduction and Theory

A property of an electrolyte in solution that very clearly differentiates it from a non-electrolyte is its electrical conductivity. When two electrodes are immersed in a solution of an electrolyte and a voltage is impressed across them, a current is observed to flow through the solution. In contrast to metallic conductance in which the movement of electrons alone is involved, the conductance of electrolytic solutions is due to the movement of ions, both positive and negative.

Under the proper conditions the electric current passing through an electrolytic solution obeys Ohm's Law, so that it is possible to measure the specific resistance and specific conductance of the solution. The resistance, R, of a homogeneous substance of uniform cross-sectional area, A, and length, d, is given by the equation, $R = \rho \, (d/A)$, where ρ is the specific resistance of the substance. The specific resistance is thus numerically equal to the resistance between opposite sides of a unit centimeter cube of the substance. The specific conductance, L, is defined as the reciprocal of the specific resistance, i.e., $L = 1/\rho = (1/R)(d/A)$.

The specific resistance and conductance of a solution

are determined from its measured resistance across the terminals of a conductivity cell and from the geometry of the cell. In the simple case, where the electrodes form the parallel ends of a cylindrical cell of length, d, and uniform cross-sectional area, A, the specific conductance of a solution is given by $L = (1/R)(d/A) = K/R$. The quantity $K = d/A$ is a property of the particular cell, and is called the cell constant.

So that the specific conductances of solutions may be expressed on a common concentration basis, the equivalent conductance is defined as $\Lambda = 1000 \ L/C_n$, where C_n is the concentration in equivalents per liter. Since the conductance of an electrolyte is made up of contributions of the individual ions, the equivalent conductance may be expressed as the sum of ionic equivalent conductances, i.e.,

$$\Lambda = \sum_{i=1}^{k} \lambda_i \quad . \tag{61}$$

The mobility of an ion, u_i, is defined as its velocity under a potential gradient of one volt per centimeter, and is related to the ionic equivalent conductance by the equation, $\lambda_i = \mathcal{F} u_i$, where $\mathcal{F}$ is the Faraday constant. An ion will have a characteristic mobility u_i^o in the absence of all other ions for a given temperature, pressure, and solvent.

Conductance measurements have played an important role

in the development of present day theories of electrolytic solutions. The history of precise conductance measurements began with the work of Kohlrausch (92) in 1868. From 1868 to 1880, Kohlrausch and his coworkers carried out a long series of careful conductance measurements over a range of temperatures, pressures, and concentrations. Kohlrausch found that the concentration dependence of the equivalent conductance of strong electrolytes in dilute solutions was closely represented by the empirical equation

$$\Lambda = \Lambda_o - A \sqrt{C_n} \quad , \tag{62}$$

where Λ_o is the equivalent conductance at infinite dilution and A is a empirical constant. He also observed that the difference in Λ_o for pairs of salts having a common ion was always nearly constant. Kohlrausch proposed that this behavior could be readily explained if Λ_o is the sum of two independent terms, one characteristic of the anion and one of the cation, i.e.,

$$\Lambda_o = \lambda_o^+ + \lambda_o^- \quad , \tag{63}$$

where λ_o^+ and λ_o^- are the ionic equivalent conductances at infinite dilution. This is known as Kohlrausch's law of the independent migration of ions.

With the advent of the Arrhenius theory (25) in 1887, the study of conductances was given added impetus. Arrhenius

proposed that the decrease in the equivalent conductance with increasing concentration of electrolyte could be explained on the basis of incomplete dissociation, and that the degree of dissociation was given by the ratio Λ/Λ_o. However, it soon became apparent that the properties of strong electrolytes in solution could not be explained on the basis of incomplete dissociation. Among the evidence were transference number measurements which showed that the mobility of ions was a function of concentration. This contradicted a tacit assumption of the Arrhenius theory.

It was not until the introduction of the Debye-Hückel theory (1) in 1923 that the proper basis for the theoretical interpretation of conductance phenomena in dilute solutions was laid. Upon the basis of their theory, Debye and Hückel (93) were able to make an important contribution to the theory of electrolytic conductance, but it was left for Onsager (94), by developing a general treatment of the motion of ions, to derive a valid limiting law for electrolytic conductance.

According to the Debye-Hückel theory a given ion in solution is surrounded by a spherically symmetrical ionic atmosphere of opposite charge. This ionic atmosphere, it will be recalled, is due to the fact that the interionic attraction and repulsions tend to produce a slight excess of negative ions in the vicinity of a position ion, and

vice versa. Although the ionic atmosphere is treated as a reality in mathematical discussions, it actually is the result of a time average of a distribution of the ions. Each ion serves as a center of an ionic atmosphere, and the relative position of each ion with respect to other charged entities in the solution influences the atmospheres of all other ions.

In the Onsager theory of conductance, the decrease in the mobility of the ions and hence in the equivalent conductance of the electrolyte with increasing concentration is attributed to two effects of the ionic atmosphere on the motion of the central ion.

When an ion is suddenly moved under the influence of an external field, the ionic atmosphere will tend to move with it. The atmosphere, however, possesses a certain inertia, and cannot adjust to the new position instantaneously. This results in an assymetric ionic atmosphere around a moving ion or, in other words, a net accumulation of opposite charge behind the ion, which exerts an electrostatic attraction, decreasing the ionic mobility in the direction of the applied field. This effect, being purely electrostatic in nature, is independent of the viscosity of the solvent, but does depend on the limiting mobility of the ions and the ionic concentration. This effect is called the "time of relaxation effect".

The second effect which decreases the mobility of the ions is called the "electrophoretic effect". In an applied field, the ionic atmosphere, being of charge opposite to that of the central ion, will also tend to move in the opposite direction. This motion of the atmosphere imparts momentum to the solvent molecules through which the central ion is moving, giving rise to a solvent current which opposes the motion of the central ion and thus decreases its mobility. Onsager's treatment of this effect is based on the assumption that Stokes' Law for the movement of a particle through a viscous medium is valid.

From his mathematical formulation of the above effects, Onsager obtained an equation for the equivalent conductance of an ion constituent in an electrolytic solution. For an ion of valence z_1 in a solution containing C_n equivalents of a binary electrolyte per liter, the Onsager equation for the ionic equivalent conductance, λ_1, is

$$\lambda_1 = \lambda_1^o - \left[\frac{1.981 \times 10^6}{(DT)^{3/2}} \left(\frac{q}{1 + q^{1/2}} \right) |z_1 \ z_2| \lambda_1^o + \frac{29.16 \ |z_1|}{\eta \ (DT)^{1/2}} \right]$$

$$\cdot \ \sqrt{(\ |z_1| \ + |z_2| \ ) \ C_n} \ , \tag{64}$$

where D is the dielectric constant of the solvent; η, the viscosity of the solvent; T, the absolute temperature; z_1 and z_2, the valences of the positive and negative ion constituents;

$$q = \frac{|z_1 \, z_2| \, (\lambda_1^0 + \lambda_2^0)}{(|z_1| + |z_2|)(|z_1| \, \lambda_2^0 + |z_2| \, \lambda_1^0)} \quad ;$$

and λ_1^0 and λ_2^0 are the limiting equivalent conductances of the positive and negative ion constituents. The first term in the brackets of Equation 63 accounts for the "time of relaxation effect" and the second for the "electrophoretic effect".

Since the equivalent conductance of an electrolyte is the sum of ionic contributions, the Onsager equation for the equivalent conductance of a binary electrolyte is given by

$$\Lambda = \Lambda_o - S_\Lambda \sqrt{C_n} \quad , \quad (65)$$

where

$$S_\Lambda = \left[\frac{1.981 \times 10^6}{(DT)^{3/2}} \, \frac{q}{1 + q^{1/2}} \, |z_1 \, z_2| \, \Lambda_o \right.$$

$$\left. + \frac{29.16 \, (|z_1| + |z_2|)}{\eta \, (DT)^{1/2}} \right] \, (|z_1| + |z_2|)^{1/2} \quad .$$

The equivalent conductance at infinite dilution, Λ_o, is not at present a theoretically derivable constant and must be obtained by a suitable extrapolation of conductance data to infinite dilution. The Onsager equation is of the same form as Equation 62, which was arrived at empirically by Kohlrausch.

The Onsager equation is strictly valid only as a limiting

law and may be expected to hold only for very dilute solutions. In the derivation of the equation, terms higher than the first in mathematical series were neglected, and such complications as interactions between the electrophoretic and time of relaxation effects were not considered. In general, the Onsager equation provides good agreement with experimental data up to concentrations of about 0.001 normal. The range of validity is greater for uni-univalent electrolytes than for those of higher valence types, but as a limiting law the equation holds at extreme dilutions for all valence types.

Three different methods have been employed for extending the range of the Onsager equation to higher concentrations. The first method is a purely empirical one, involving the addition of terms in c, $c^{3/2}$, $c \log c$, etc., to the Onsager equation. These equations provide better agreement with experimental data at higher concentrations than the Onsager equation, but this is due to the present of arbitrary parameters. Most of the proposed equations reduce to square root equations in the limit, although the limiting slopes generally differ from the Onsager limiting slope.

The second method applies only to electrolytes for which the conductance falls below the limiting law in dilute solutions. This conductance deficiency is interpreted as being due to incomplete dissociation. Onsager (94) first

pointed out that completely dissociated electrolytes should approach the limiting tangent asymptotically from above, whereas incompletely dissociated electrolytes should approach it from below. He corrected for the conductance deficiency of partially dissociated electrolytes by introducing a term $- c \Lambda_0/K$, where K is the dissociation constant, into the limiting law. This corrected equation, however, can represent the conductance of a partially dissociated electrolyte only throughout the concentration range in which the limiting law is valid for completely dissociated electrolytes. Various procedures (95, 96, 97) for evaluating K and Λ_0 from conductance data have been extensively employed in connection with studies of ion-pair formation and the Bjerrum theory of ionic association.

The third method employed in extending the range of the Onsager equation consists of more elaborate theoretical treatments designed to include higher terms in the mathematical approximations and to introduce the distance of closest approach parameter a_0. Dye and Spedding (98) evaluated higher terms in the series expression for the electrophoretic effect by means of a graphical integration. This results in retention of the dependence on the a_0 parameter, which was dropped in the Onsager approximations. With the resulting conductance equation, good agreement with experimental data for tri-univalent electrolytes up to

concentrations of about 0.008 normal was obtained.

There have been a number of extensions and refinements in the treatment of the time of relaxation effect during the past ten years. The most important new feature in all of these is the introduction of the distance of closest approach parameter a_0. The most comprehensive treatment is that of Fuoss and Onsager (99). Their final equation, giving the contribution of both the time of relaxation effect and the electrophoretic effect, is expressed as Onsager's limiting law plus a very complicated function of the concentration, distance of closest approach parameter, ionic charge, temperature, and solvent dielectric constant. They show that the transcendental functions involved lead to a (c long c) term, although the approximations giving this form are valid only at extremely low concentrations. Notwithstanding the elaborate analysis involved in their treatment, the equation of Fuoss and Onsager has its limitations. The effects of changes in viscosity and dielectric constant with concentration were neglected, and the discontinuous nature of the solvent ignored. Since their treatment is based on the Debye-Hückel expression for the potential in the absence of an external field, the limitations of this are inherent in their result. Because of these limitations, the application of the Onsager and Fuoss equation is limited to concentrations less than 0.02 normal.

Fuoss and Onsager (99) have concluded that the problem of concentrated solutions cannot be solved by any extension of the Onsager theory based on smoothed ionic distribution. They consider that the approach must start from an adequate theory of fused salts, which must then be followed by the theoretical treatment of the effect on the distribution function of adding solvent molecules.

B. Historical Review of the Experimental Method

The measurement of the conductance of electrolytic solutions depends upon the use of a modified Wheatstone bridge. The earliest conductance measurements were made with a direct-current operated bridge, but due to polarization of the electrodes of the conductance cell, erratic results were obtained. With the introduction by Kohlrausch (92, 100) in 1868 of the use of an alternating-current Wheatstone bridge, the polarization error was largely eliminated and accurate conductance measurements became possible for the first time. The use of alternating current, however, complicates the measurement of resistance by including the effects of the capacitance of the cell, and the inductance and capacitance of various parts of the bridge network. The elimination or accurate compensation of these effects has required the ingenuity of numerous investigators.

Kohlrausch employed an alternating current of 1000

cycles per second generated by an induction coil, and a telephone earpiece to detect the balance point of the bridge. By connecting a variable capacitor in parallel with the variable resistance arm of the bridge, he was able to compensate for the effective capacitance of the conductance cell. Kohlrausch believed that when an alternating current was passed between platinum electrodes in a solution, hydrogen and oxygen were alternately deposited and that the electrolysis was chemically and thermodynamically reversible. To facilitate the reversible deposition, he plated his platinum electrodes with platinum black. To determine the cell constant, Kohlrausch actually measured the geometry of the cell. Potassium chloride reference solutions were then prepared and their specific conductances measured so that they could be used as secondary standards in determining cell constants. Kohlrausch also recognized the importance of accurate temperature control; he found that the temperature coefficient of conductance was two per cent per degree.

The first major improvement in the conductance apparatus of Kohlrausch was made in 1913 by Washburn and Bell (101). They substituted a high frequency generator for the induction coil as a source of alternating current. The advantage of the high frequency generator lay in its production of an alternating current of nearly a single frequency, practically free from the overtones present in the complex

wave system produced by the induction coil. For a detector
a telephone tuned to the frequency of the alternating cur-
rent was employed. This was more sensitive than the single
earpiece used by Kohlrausch. Washburn and Bell also employed
platinum-film resistance elements which were practically
free of inductance and capacitance effects.

In 1916 Washburn (102) presented an extensive study on
the design of conductance cells. He considered the cell to
be a resistance and a capacitor in series, shunted by a
capacitor. The series capacitance was attributed to polari-
zation, which could be minimized by the use of platinized
electrodes and a high frequency alternating current. Wash-
burn also showed that for the greatest accuracy the electrode
areas should be larger, the lower the specific conductance
of the solution being measured.

In the same year Taylor and Acree (103) made a thorough
study of the factors entering into precision conductance
measurements. They test induction coils, generators, and
Vreeland oscillators to determine which source produced
alternating current with the purest sine wave form. They
pointed out that a current of pure sine wave form was neces-
sary to prevent unsymmetrical polarization at the electrodes
and to annul the influence of harmonics in the detector.
A Vreeland oscillator was found to be the best, producing
an almost pure sine wave of constant frequency, free from

harmonics. The Vreeland oscillator works by the action of an oscillating electric current upon a double mercury vapor arc. An additional advantage of the Vreeland oscillator was that it could be adjusted to give any voltage desired. Taylor and Acree used this feature to study the validity of Ohm's Law for alternating current conductivity measurements. They found that the resistance of solutions is independent of the voltage provided the cells are scrupulously clean, and low voltages are employed to minimize heating effects in the cell.

For their bridge resistance elements, Taylor and Acree employed Curtis coils wound on porcelain spools. Such coils are practically free of inductance and capacitance. To compensate for the capacitance of the conductance cell, Taylor and Acree used both variable inductors and capacitors in the measuring arm of their bridge.

Taylor and Acree made an extensive study of conductance cells. They observed that the resistance of solutions decreased slightly with an increase in the frequency of the current used, and that this effect was most pronounced for cells having small bright electrodes. If cells with large platinized electrodes were used, this resistance variation with frequency could be made practically negligible. They reasoned that if true resistances were being measured, the ratio of resistances for any given solution in two cells,

or of two solutions in any cell, must be constant. Although they found that this was true for cells with platinized electrodes, they also observed that for an alternating current of 60 cycles per second, the ratio of resistances of two solutions in a cell with platinized electrodes differed by about two per cent from the ratio of resistances of the same solutions in a cell with bright electrodes. However, this difference in ratios was found to decrease with increasing frequency of the current, and was a minimum when the resistances were extrapolated to infinite frequency.

In 1917 Washburn and Parker (104) carried out studies of the audibility current and the sensitivity of the telephone detector. Two years later Hall and Adams (105) increased the sensitivity of the detector by employing a vacuum tube amplifier between the bridge and detector. The amplifier furnished a means of increasing the current through the telephone without changing the current through the remainder of the system, thus avoiding any increase of heating effects in the cell. Hall and Adams also substituted a vacuum tube oscillator for the Vreeland oscillator as a source of current. The advantage of the vacuum tube oscillator lay in its easily adjustable voltage and frequency.

From an intercomparison of cells, Parker (106) in 1923 found that the cell constant was not really a constant, but varied slightly with the resistance of the solution being

measured. This so-called Parker effect was also noted by other investigators (107, 108). Parker attributed this variation in cell constant to adsorption at the electrodes, but later investigators arrived at a different conclusion.

The present day designs of high-precision conductance bridges and cells stem from the principles laid down by Jones and his colleagues (109, 110, 111, 112, 113, 114) and also Shedlovsky (115).

In 1928 Jones and Josephs (109) published the results of their classic study on the design of an alternating current bridge for conductivity measurements. Among their most notable contributions were an improved method of grounding and the design of resistance boxes in which dielectric losses and energy dissipation are at a minimum. The methods of grounding previously used had been in error, as was shown by the fact that the position of balance could be changed by reversing the lead wires from the oscillator to the ends of the bridge. Like Hall and Adams (105), Jones and Josephs employed both an electronic oscillator and amplifier. They also recommended the use of oil as the bath medium, pointing out that in comparison to oil, water is a conductor. The walls of a glass cell in a water bath may act as a dielectric in a capacitor, permitting alternating current to flow into the water outside of the cell, with resultant error in the measurements.

In 1929 Jones and Bollinger (110) modified their oscil-
lator to give lower voltages to reduce heating effects of the
current on the cell, and also improved their amplifier. The
increased sensitivity of the amplifier made necessary the
addition of a wave filter in parallel to the telephone to
reduce 60-cycle hum and so-called tube noises.

Shedlovsky (115) in 1930 presented the results of his
study on bridge design. His bridge was similar to that of
Jones and Josephs (109), differing principally in the manner
of shielding. Whereas Jones and Josephs had advised against
the use of a grounded metal shield in the vicinity of the
bridge, Shedlovsky, after a theoretical analysis of his own,
concluded that an electrostatic shield could be safely used
without fear of capacitance effects. He found that a spac-
ing of 2.5 inches from any of the coils or contacts was
sufficient to make the effect of the shield capacitance on
the resistances negligible. This made enclosure of the
shield in the bridge cabinet possible. Shedlovsky pointed
out that a properly shielded bridge eliminates the change
in bridge reading caused by the changing capacitance of the
moving hands of the observer, and also permits other elec-
trical work to be in progress in the laboratory without
affecting the bridge accuracy.

The most comprehensive study on the theory and design
of conductance cells was that of Jones and Bollinger (111)

in 1931. They conclusively established that the Parker effect was due to a capacitance in parallel with the cell resistance, arising when the cell leads pass near the cell solution. Since this capacitative shunt was inherent in the design of cells then in use, Jones and Bollinger designed cells in which the capacitance between cell parts was a minimum. They concluded that the most convenient test of the quality of cells is the observation of the variation in apparent resistance with variation in frequency. Jones and Bollinger also confirmed the results of earlier investigators that the error due to polarization could be made practically negligible by a combined use of proper platinization, large electrodes, high frequency, and high resistance.

In the same year Jones and Bollinger (112) also studied the validity of Ohm's Law for electrolytic conductance measurements. They concluded that if adequate experimental precautions are taken to avoid errors due to heating, polarization, and secondary effects of inductance and capacitance, there is no measurable variation in the real resistance of electrolytic solutions with variation in the applied voltage throughout the voltage range suitable for use in the Kohlrausch method of measuring conductances.

In 1935 Jones and Christian (113) returned to the study of polarization. They found that polarization was greatly dependent on the metal used for the electrodes, and

dependent to a lessor degree on the electrolyte and temperature, but independent of the current density and the separation of the electrodes. They concluded that the least polarization resistance occurred for platinized platinum electrodes and for high frequencies of alternating current. Also in 1935 Jones and Bollinger (114) undertook a study of the various criteria as to the quality and sufficiency of platinization, concluding that the best test was the variation of the apparent resistance with frequency.

In recent years the telephone has been supplanted as the detector by the cathode-ray oscilloscope (116). The oscilloscope is a much more versatile and less nerve-racking instrument. The horizontal deflection plates are fed from the oscillator and the vertical ones from the amplifier; the out-of-balance tracing of the oscilloscope is an ellipse which becomes a horizontal straight line at balance.

In addition to the apparatus requirements, a very important factor in the accurate measurement of conductances is the calibration of the conductance cells. To avoid the necessity of constructing cells of uniform and accurately known dimensions, the cell constant is determined from the measured resistance when the cell contains a solution of known specific conductance. Since pure mercury is used in defining the international ohm, it is the primary standard for this purpose. However, because of the very high specific

conductance of mercury, solutions of potassium chloride are used as secondary standards in determining cell constants of cells designed for the study of electrolytes. Kohlrausch (117) was the first to establish potassium chloride solutions as secondary standards, and his results were used in the calibration of cells until 1924. Because of some ambiguity in the manner in which Kohlrausch described the composition of his solutions and the refinements in the measuring apparatus since his time, Parker and Parker (118) in 1924 redetermined the specific conductance of potassium chloride solutions. They eliminated an inconsistency in units by expressing the composition of their solutions in terms of the demal concentration, defining a one demal solution as one containing one gram-molecular weight of salt dissolved in one cubic decimeter of solution at 0° C.

The specific conductance values for potassium chloride solutions generally accepted today as standards are those obtained by Jones and his colleagues (119, 120). In 1933 Jones and Bradshaw (119) measured the specific conductance of solutions of the same composition employed by Parker and Parker (118), and Jones and Prendergast (120) in 1937 re-investigated the solutions described by Kohlrausch (117). The results of their measurements tend to confirm the values of Kohlrausch rather than those of Parker and Parker, but differ appreciably from both. They eliminated all sources

of ambiguity by expressing the composition of their solutions in terms of the actual weights of salt and solution in vacuo.

C. Experimental

1. Apparatus and procedure

The resistance measurements of aqueous rare-earth chloride solutions were made with a Jones conductivity bridge (Leeds and Northrup Company catalog number 4666), designed in accordance with the principles laid down by Jones and Josephs (109) and Shedlovsky (115). The construction and operation of the bridge are described by Dike (121). The alternating current source employed was an audio-frequency electronic oscillator, which provided current of frequencies 500, 1000, and 2000 cycles per second. A narrow-band, audio-frequency amplifier, which could be tuned to the frequency of the oscillator, was used to amplify the signal from the bridge. Both the oscillator and amplifier were designed and constructed by the Electronic Instrumentation Group of the Ames Laboratory; the circuit diagrams of these instruments are shown in Figure 11. A Heathkit five-inch oscilloscope was used to determine the balance point of the bridge.

The constant-temperature bath employed in the thermal equilibration of the solutions was controlled by a micro-set

1000 ～ TEE FOR AMPLIFIER

GRID ——

PIN 7
6AS6

R-1   300K   25K   25K   300K   R-2

C-1 ⊥ 0.001

50K

150K

0.0005   0.0005
C-2   C-3

—— PLATE

PIN 6
12AT7

NOTE:
ALL RESISTANCE IN OHMS, 1/2 WATT
ALL CAPACITANCE IN MICROFARADS
UNLESS SPECIFIED

	500 ～ TEE	2000 ～ TEE
R-1	310 K	310K
R-2	310 K	310K
C-1	0.002	500 μμf
C-2	0.001	250 μμf
C-3	0.001	250 μμf

OSCILLATOR

ALL FILAMENTS ARE
D.C. POWERED

AMPLIFIER

TO HEATHKIT
SCOPE BNC
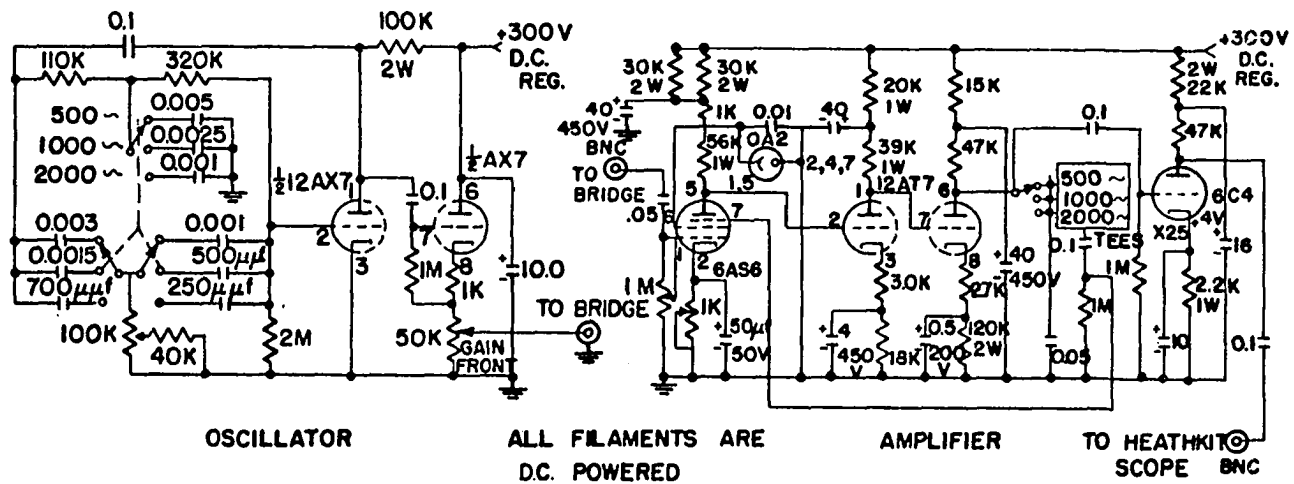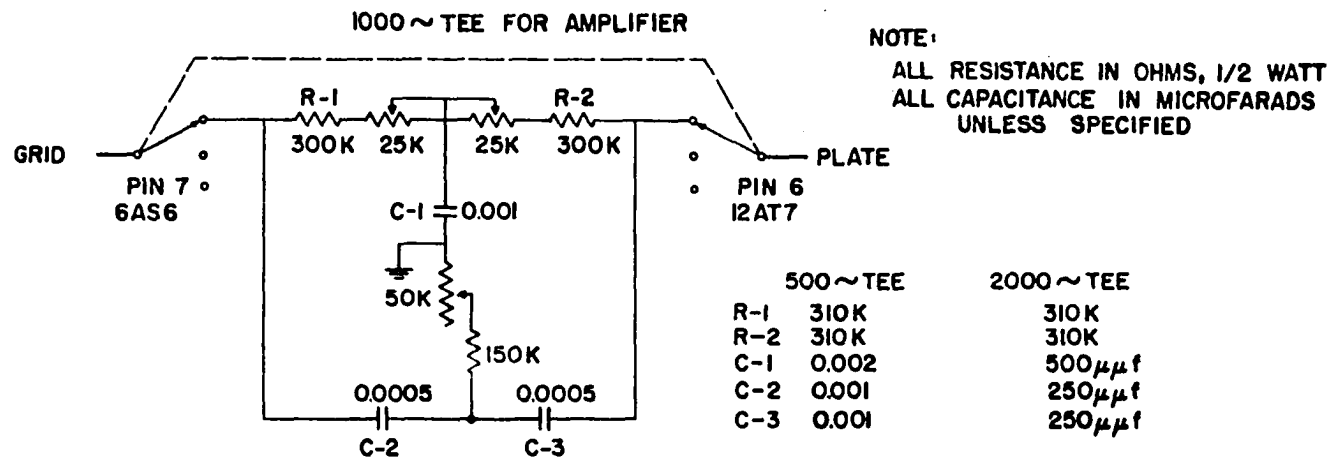
Figure 11.   Circuit diagrams for oscillator and amplifier

mercury thermoregulator in combination with an electronic
relay and 250-watt infra-red heat lamp. Cooling was provided
by tap water from a constant-head tank circulating through a
copper tube immersed in the bath. The bath was stirred by
conventional propeller-type stirrers. As the bath medium
mineral oil was employed to minimize capacitance effects,
the temperature of the medium was maintained at $25.00 \pm$
0.01° C. as determined with an Emerson calorimeter thermom-
eter, graduated in units of 0.01° C.

The conductance cells used in the measurements were of
the general design recommended by Jones and Bollinger (111).
A capillary cell, shown in Figure 12, was used in the re-
sistance measurements of the majority of solutions; a Leeds
and Northrup Type HC cell (Lees and Northrup Company catalog
number 4915) was used for-the most dilute solutions.

The capillary cell was constructed of Pyrex glass, and
had an overall length of 25 cm. and a volume of about 20 ml.
The capillary section, A, of the cell consisted of a 15-cm.
length of 3-mm. capillary tubing. The electrode chambers, B,
were constructed from 30-mm. tubing; and the filling tubes,
C, from the inner parts of 10/30 standard tapers. The fill-
ing tubes were connected near the top by a length of 8-mm.
tubing sealed at both ends, D, which gave rigidity to the
cell and served as a means of suspending the cell in the
bath. The side arms, E, into which the electrodes were sealed
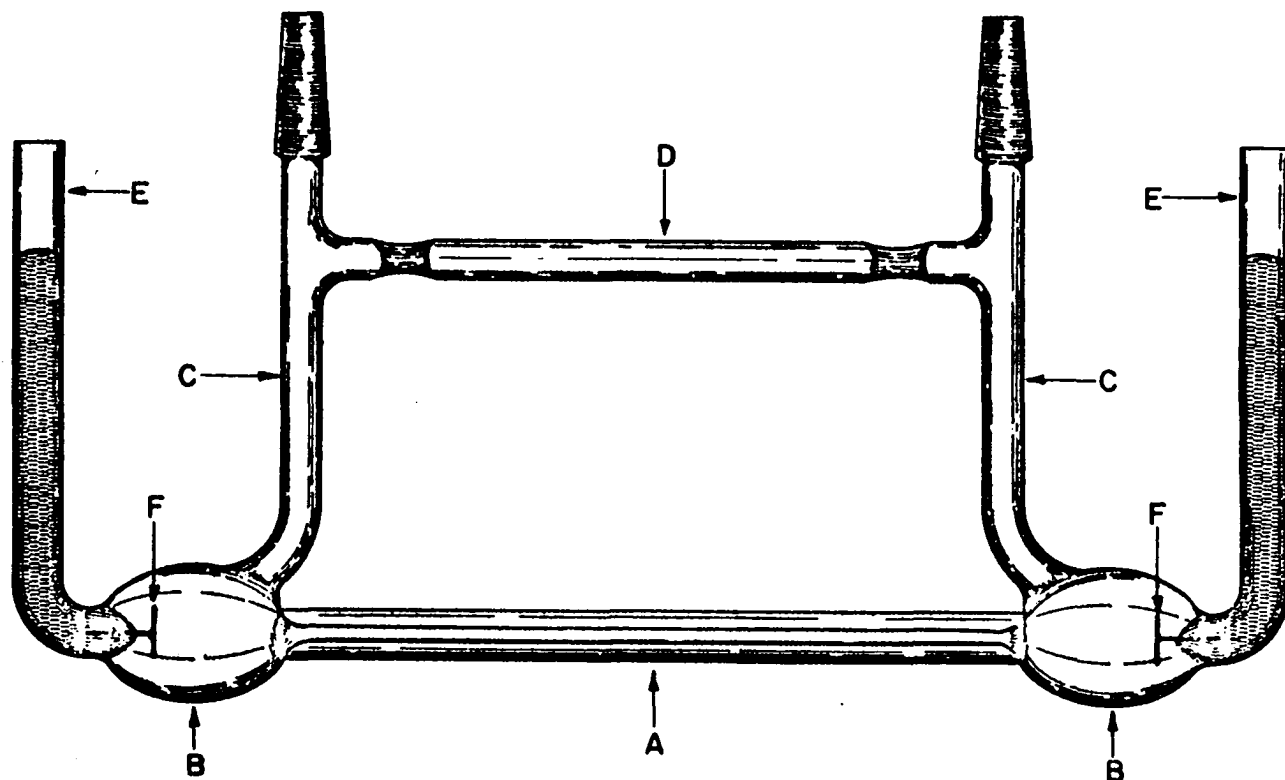
Figure 12. Capillary conductance cell

were constructed from 8-mm. tubing; electrical contact between the bridge and electrodes was made by inserting the platinum leads of the bridge into the mercury-filled side arms. Each electrode, F, consisted of a platinum disk, 1.6 cm. in diameter and 0.25 mm. thick, to which a short length of platinum wire was welded for sealing and contact purposes. The electrodes were platinized in accordance with the recommendations of Jones and Bollinger (114).

The conductance cells were calibrated with 0.1 and 1 normal potassium chloride solutions, using the specific conductance values of Jones and Prendergast (120). The potassium chloride solutions were prepared by weight using fused C. P. potassium chloride and conductivity water. No significant Parker effect was found for either cell. The cell constants of the capillary cell and Leeds and Northrup cell were found to be 253.63 cm.$^{-1}$ and 30.714 cm.$^{-1}$ respectively.

The cell used in the measurement of a particular solution was so chosen that the resistance fell within the optimum range of the bridge. The Leeds and Northrup cell was used in the concentration range 0.06 to 0.35 normal or in terms of resistance from 5000 to 1000 ohms. The capillary cell was employed in all measurements above 0.35 normal. For solutions above 0.35 normal, the resistance fell in the range 10,000 to 1400 ohms.

For a series of solutions of a given rare-earth chloride, measurements were carried out first on the solution of lowest concentration, followed by solutions of increasing concentration, in order to avoid errors due to soaking-out salt adsorbed at the electrodes. In the determination of a particular solution, the cell was thoroughly rinsed three times and allowed to soak for an hour with the solution. The cell was then rinsed once more, and a fresh sample of solution was placed in the cell. The cell was then suspended in the bath for equilibration; thermal equilibrium was generally attained within 30 minutes, as could be noted by the constancy of the resistance readings. At least two samples of solution were measured for each concentration. Resistance measurements were made at 2000, 1000, and 500 cycles per second. It was found that the average difference between the resistance at 2000 cycles per second and the resistance at infinite frequency as obtained by extrapolation was only 0.003 per cent, indicating sufficiency of platinization and making correction of the resistance to infinite frequency unnecessary.

2. Calculations and results

The resistances of aqueous solutions of lanthanum, neodymium, samarium, gadolinium, dysprosium, erbium, and ytterbium chlorides in the concentration range between 0.06

normal and saturation were determined by the method previously described.

The specific conductance due to the solute alone was calculated for each solution from the relation

$$L = (K/R) - L_{H_2O} \quad , \tag{66}$$

where L is the specific conductance of the solution due to the solute; K, the cell constant; R, the measured resistance of the solution; and L_{H_2O}, the specific conductance of the water used in preparing the solution. Over the concentration range studied in this research, the contribution of the solvent to the conductance of the solution was negligible, amounting to only 0.01 per cent for the most dilute solution studied.

The equivalent conductance for each solution was calculated from the relation

$$\Lambda = \frac{1000 \ L}{C_n} \quad , \tag{67}$$

where C_n is the normal concentration of the solution. The normal concentration was calculated from the known molality and the density of the solution by means of Equation 42.

In Tables 17 through 23, the specific and equivalent conductances of the rare-earth chlorides in aqueous solutions are given. In Figure 13 the equivalent conductances for

Table 17. Conductances of aqueous solutions of lanthanum
chloride at 25° C.

Normality	(Normality)$^{1/2}$	Specific conductance	Equivalent conductance
0.061968	0.24893	0.0064378	103.89
0.11951	0.34570	0.011624	97.264
0.16682	0.40844	0.015639	93.748
0.33111	0.57542	0.028741	86.802
0.39552	0.62890	0.033547	84.817
0.58836	0.76704	0.047224	80.264
0.86433	0.92969	0.065091	75.308
0.94893	0.97413	0.070246	74.027
1.1124	1.0547	0.079660	71.611
1.1573	1.0758	0.082129	70.966
1.4387	1.1995	0.097036	67.447
1.7285	1.3147	0.11052	63.940
2.1169	1.4550	0.12643	59.724
2.2165	1.4888	0.13005	58.674
2.6526	1.6287	0.14418	54.354
2.8290	1.6820	0.14911	52.708
3.3051	1.8180	0.15993	48.389
3.6564	1.9122	0.16580	45.345
3.9081	1.9769	0.16889	43.215
4.6653	2.1599	0.17349	37.187
5.2353	2.2881	0.17224	32.900
5.8170	2.4118	0.16756	28.805
6.3348	2.5169	0.16063	25.357
6.9513	2.6365	0.14980	21.550
7.7487	2.7836	0.13271	17.127
8.2137	2.8660	0.12140	14.780
8.2857	2.8785	0.11972	14.449
9.1476	3.0245	0.098137	10.728
9.4623	3.0761	0.090276	9.541
10.126	3.1822	0.073929	7.301

Table 18. Conductances of aqueous solutions of neodymium chloride at 25° C.

Normality	(Normality)$^{1/2}$	Specific conductance	Equivalent conductance
0.077700	0.27784	0.0079018	101.70
0.11116	0.33341	0.010912	98.165
0.14633	0.38253	0.013941	95.271
0.21908	0.46806	0.019988	91.236
0.34632	0.58849	0.029940	86.452
0.55665	0.74609	0.045191	81.184
0.66324	0.81439	0.052436	79.060
0.84903	0.92143	0.064390	75.839
0.99366	0.99682	0.073136	73.603
1.1887	1.0903	0.084133	70.777
1.5080	1.2280	0.10063	66.731
1.8474	1.3592	0.11607	62.829
2.4265	1.5577	0.13787	56.818
2.9871	1.7283	0.15386	51.508
3.5976	1.8967	0.16596	46.131
4.8462	2.2014	0.17523	36.158
6.0840	2.4666	0.16684	27.423
7.1547	2.6748	0.14910	20.839
8.4537	2.9075	0.11967	14.156
9.6186	3.1014	0.090819	9.442
10.322	3.2128	0.073981	7.167

Table 19.   Conductances of aqueous solutions of samarium
            chloride at 25° C.

Normality	(Normality)$^{1/2}$	Specific conductance	Equivalent conductance
0.066258	0.25741	0.0068228	102.97
0.089745	0.29957	0.0089662	99.908
0.13439	0.36659	0.012882	95.855
0.30399	0.55135	0.026611	87.539
0.34086	0.58383	0.029422	86.317
0.67602	0.82220	0.053002	78.403
1.0429	1.0212	0.075559	72.451
1.3556	1.1643	0.092352	68.126
1.8956	1.3768	0.11708	61.764
2.4171	1.5547	0.13619	56.344
2.8246	1.6807	0.14808	52.425
4.1154	2.0286	0.17002	41.313
4.8981	2.2132	0.17291	35.301
5.5206	2.3496	0.17035	30.857
6.6579	2.5803	0.15657	23.516
7.4382	2.7273	0.14195	19.084
8.3256	2.8854	0.12223	14.681
9.1494	3.0248	0.10258	11.212
9.6780	3.1109	0.089899	9.289

Table 20. Conductances of aqueous solutions of gadolinium
chloride at 25° C.

Normality	(Normality)$^{1/2}$	Specific conductance	Equivalent conductance
0.068922	0.26253	0.0070093	101.70
0.10874	0.32976	0.010561	97.122
0.15372	0.39207	0.014394	93.638
0.36867	0.60718	0.031179	84.572
0.61086	0.78157	0.048033	78.632
0.95319	0.97631	0.069165	72.562
1.2589	1.1220	0.085752	68.117
1.8895	1.3746	0.11414	60.408
2.4151	1.5541	0.13246	54.847
2.9201	1.7088	0.14594	49.978
3.7785	1.9438	0.16052	42.482
4.6383	2.1537	0.16576	35.737
5.5458	2.3550	0.16216	29.240
6.4110	2.5320	0.15284	23.840
7.1919	2.6818	0.13972	19.427
8.0811	2.8427	0.12147	15.031
8.9976	2.9996	0.10087	11.211
9.5340	3.0877	0.088659	9.299

Table 21. Conductances of aqueous solutions of dysprosium chloride at 25° C.

Normality	(Normality)$^{1/2}$	Specific conductance	Equivalent conductance
0.074859	0.27361	0.0074873	100.02
0.11279	0.33584	0.010818	95.913
0.14782	0.38447	0.013776	93.194
0.36168	0.60140	0.030326	83.848
0.71043	0.84287	0.053767	75.682
1.0285	1.0141	0.072308	70.304
1.4427	1.2011	0.093070	64.511
1.9079	1.3813	0.11239	58.908
2.4004	1.5493	0.12872	53.624
3.0729	1.7530	0.14484	47.135
4.0575	2.0143	0.15717	38.736
4.8483	2.2019	0.15872	32.737
5.4693	2.3387	0.15555	28.441
6.2418	2.4984	0.14714	23.573
7.1499	2.6739	0.13245	18.525
8.0577	2.8386	0.11441	14.199
8.9415	2.9902	0.095409	10.670
9.6186	3.1014	0.080886	8.409

Table 22. Conductances of aqueous solutions of erbium
chloride at 25° C.

Normality	(Normality)$^{1/2}$	Specific conductance	Equivalent conductance
0.070500	0.26552	0.0070713	100.30
0.10496	0.32398	0.010106	96.284
0.13799	0.37147	0.012895	93.449
0.22086	0.46995	0.019597	88.730
0.33678	0.58033	0.028353	84.188
0.52254	0.72287	0.041386	79.202
0.66321	0.81438	0.050485	76.122
0.92874	0.96371	0.066353	71.444
1.1809	1.0867	0.079747	67.631
1.4930	1.2219	0.094540	63.322
1.7817	1.3348	0.10660	59.830
2.3404	1.5298	0.12563	53.679
2.8393	1.6850	0.13834	48.723
3.4752	1.8642	0.14928	42.956
4.6410	2.1543	0.15601	33.616
5.6292	2.3726	0.15064	26.760
6.9450	2.6353	0.13208	19.018
8.1513	2.8550	0.10832	13.289
10.002	3.1626	0.069042	6.903

Table 23. Conductances of aqueous solutions of ytterbium chloride at 25° C.

Normality	(Normality)$^{1/2}$	Specific conductance	Equivalent conductance
0.077415	0.27824	0.0076815	99.225
0.10816	0.32888	0.010362	95.803
0.13835	0.37195	0.012916	93.357
0.23286	0.48256	0.020519	88.117
0.34518	0.58752	0.028934	83.823
0.51891	0.72035	0.041083	79.172
0.71256	0.84413	0.053481	75.055
1.0243	1.0121	0.071445	69.750
1.3220	1.1498	0.086534	65.457
1.6425	1.2816	0.10073	61.327
1.9995	1.4140	0.11433	57.179
2.5717	1.6037	0.13155	51.153
3.1710	1.7807	0.14406	45.430
3.7125	1.9268	0.15115	40.714
4.9821	2.2321	0.15395	30.901
6.3087	2.5117	0.14071	22.304
7.6506	2.7660	0.11670	15.254
8.7831	2.9636	0.092840	10.570
10.551	3.2482	0.056752	5.379

neodymium, gadolinium, and ytterbium chlorides are plotted as a function of the square root of the normality; an enlarged inset, A, gives the position of the curve at $C_n^{1/2}$ = 2.2 for all of the rare-earth chlorides studied in this research. In Figures 14 and 15, the equivalent conductance curves for lanthanum, samarium, dysprosium, and erbium chlorides are shown. The specific conductance curves for
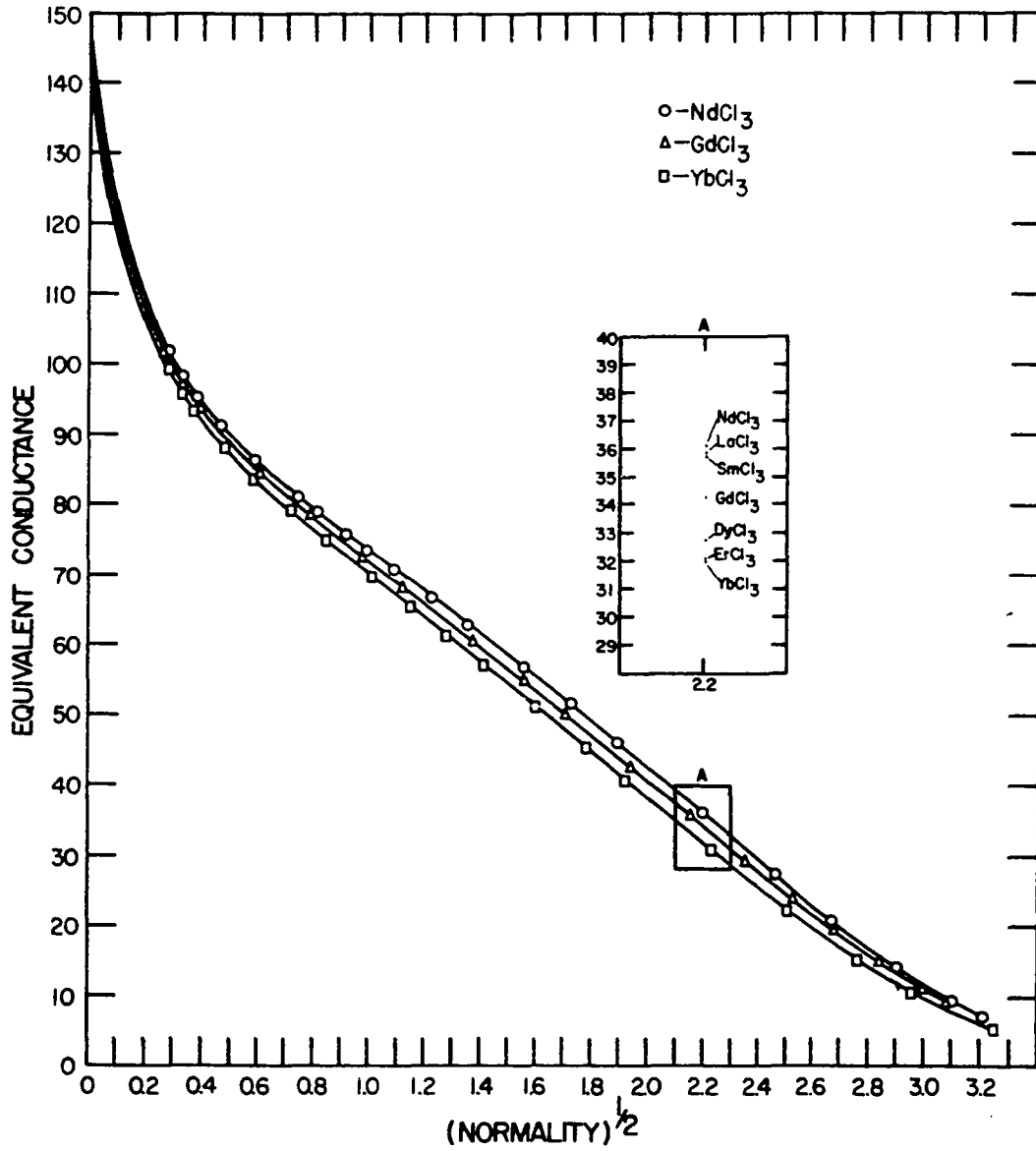
Figure 13. Equivalent conductances of neodymium, gadolinium, and ytterbium chlorides in aqueous solutions at 25° C.
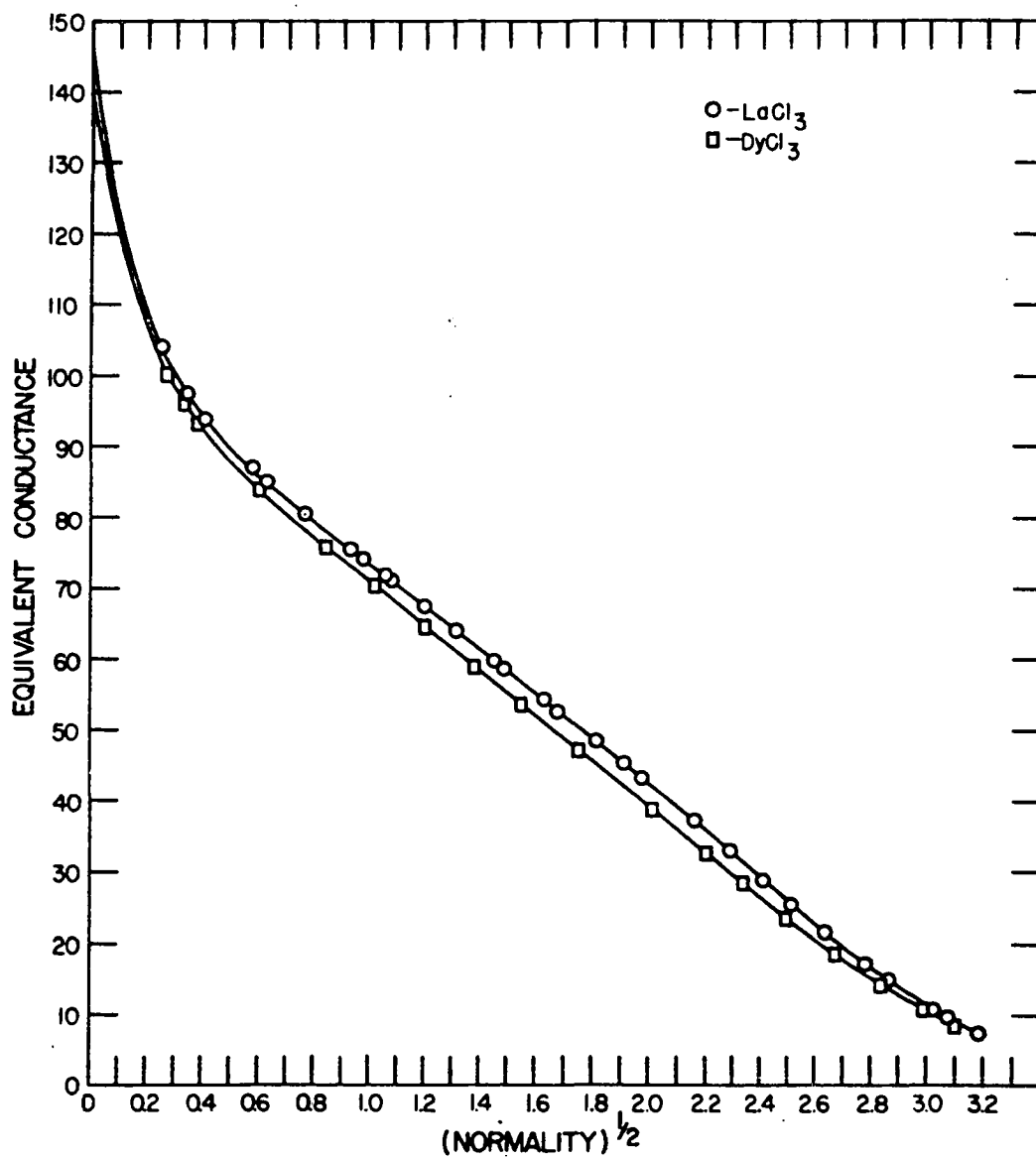
Figure 14. Equivalent conductances of lanthanum and
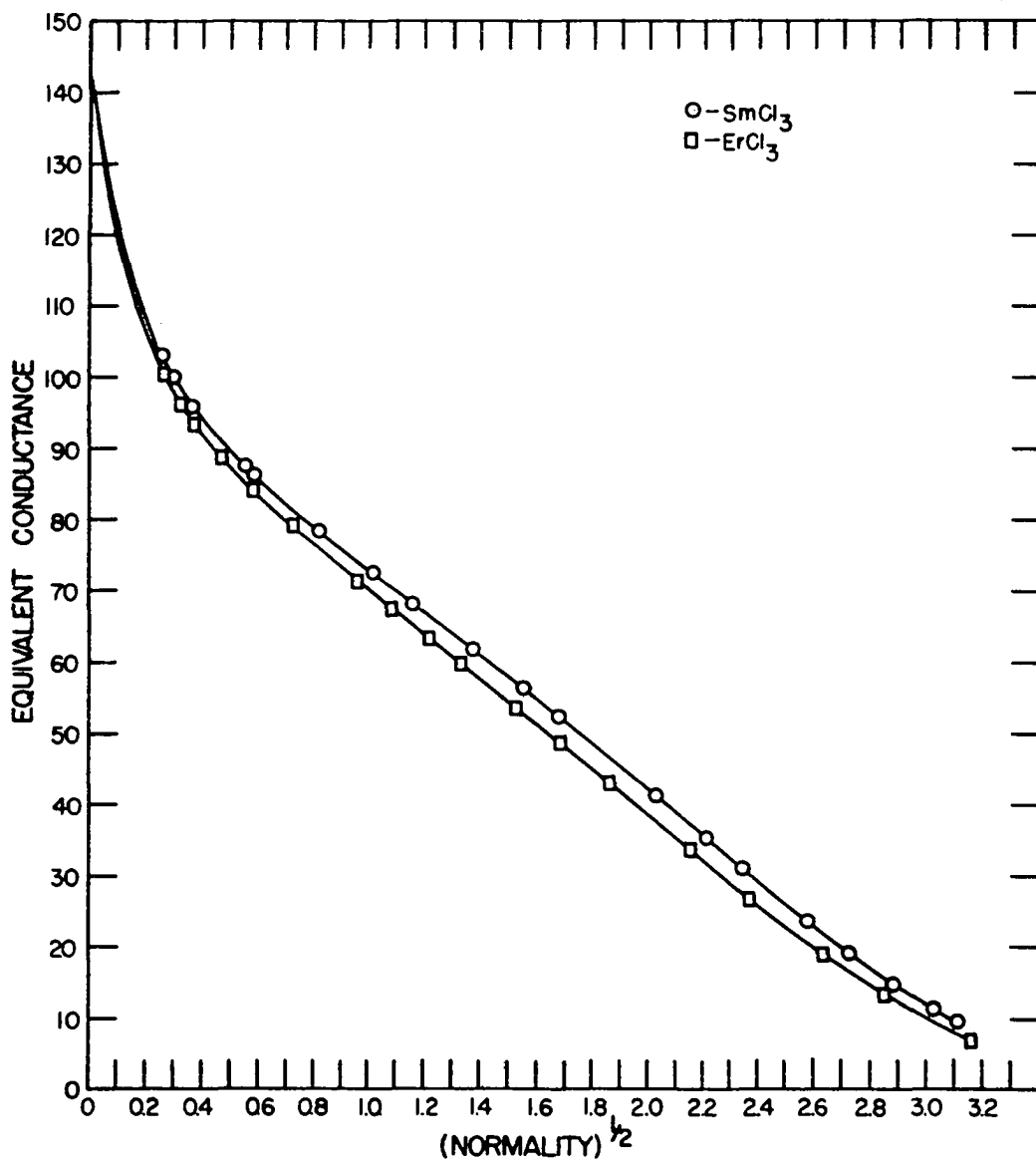   dysprosium chlorides in aqueous solutions
           at 25° C.

Figure 15. Equivalent conductances of samarium and erbium chlorides in aqueous solutions at 25° C.

the rare-earth chlorides are shown in Figures 16 and 17. The portion of the specific and equivalent conductance curves below 0.06 normal ($C_n^{1/2} = 0.24$) represent data obtained at the Ames Laboratory by other investigators (23).

D. Discussion of Results

The accuracy of the equivalent conductances determined in this research is governed by the uncertainties in the specific conductances and concentrations of the solutions. As was indicated in Section V-D of this thesis, the probable error in the concentrations was estimated to be 0.05 per cent. The probable error in the specific conductances is determined primarily by the uncertainty in the cell calibrations. Since the value of the specific conductance for a given solution as determined with the capillary cell agreed with the value for the same solution as determined with the Leeds and Northrup cell within 0.04 per cent, the probable error in the specific conductances was also estimated to be of this magnitude.

The probable error in the equivalent conductance may be estimated with the aid of the law of propagation of precision indexes as expressed by Equation 59. Applying Equation 59 to the equivalent conductance as defined by Equation 67, one obtains the relation
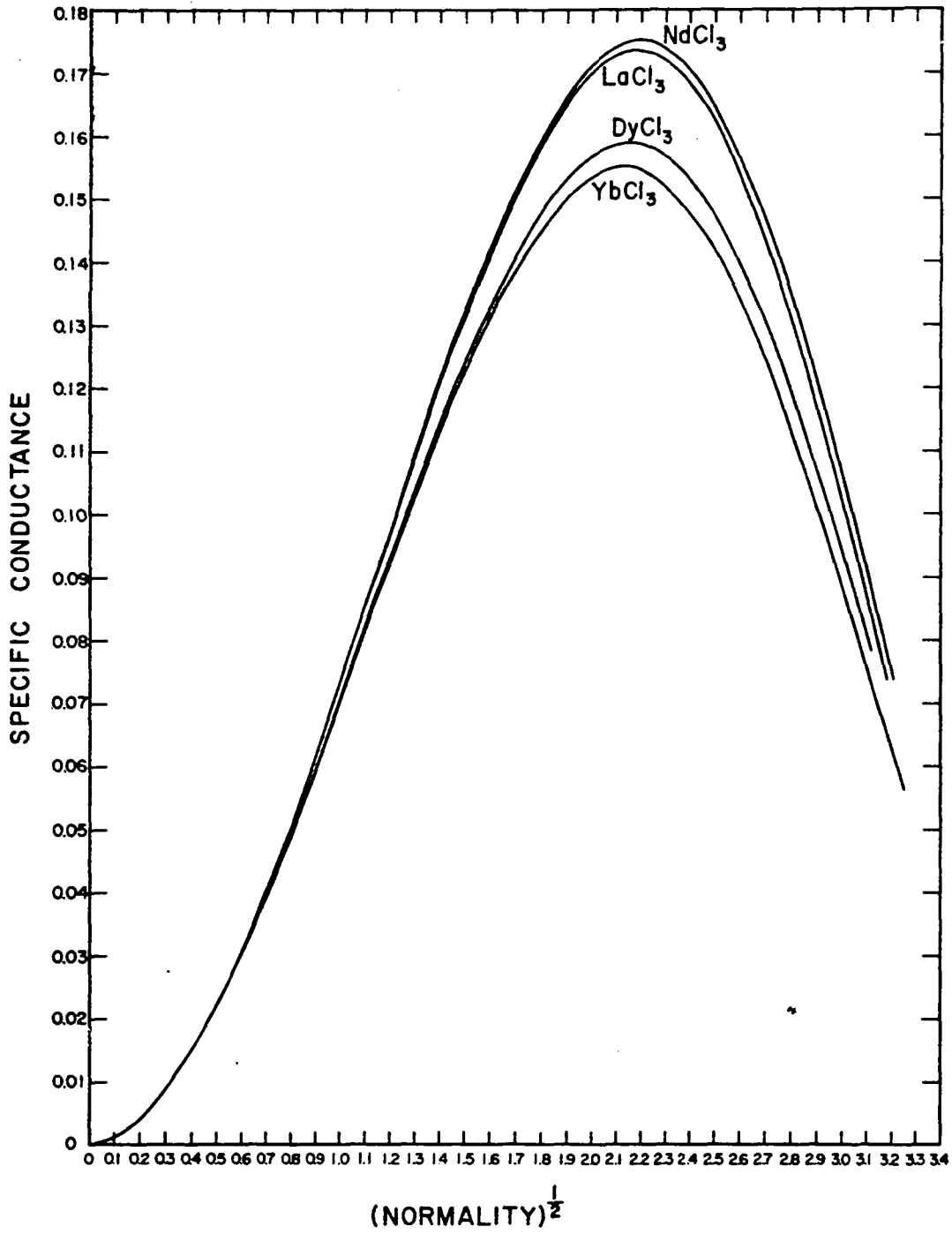
Figure 16. Specific conductances of lanthanum, neodymium, dysprosium, and ytterbium chlorides in aqueous solutions at 25° C.
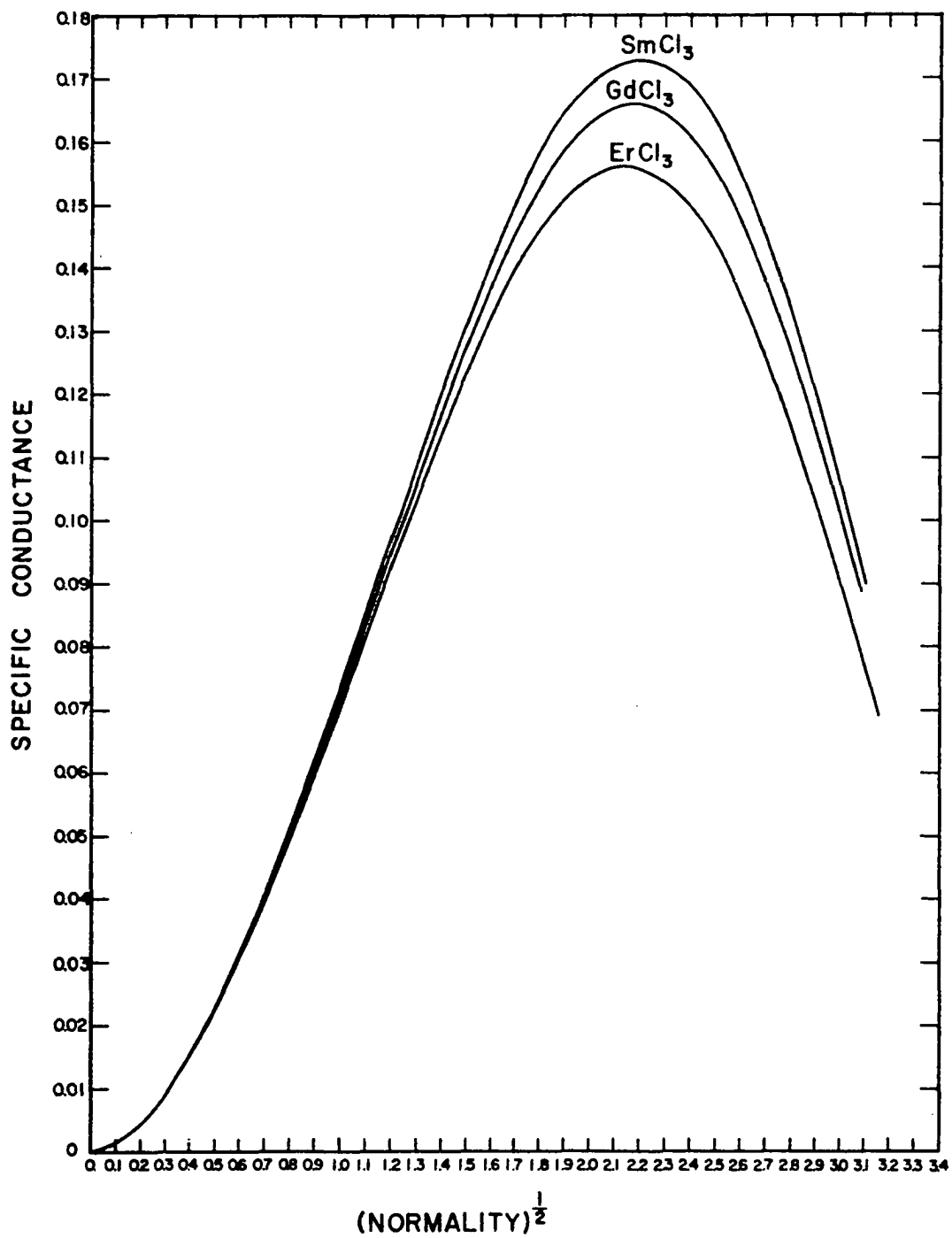
Figure 17. Specific conductances of samarium, gadolinium, and erbium chlorides in aqueous solutions at 25° C.

$$P_{\Lambda}^2 = \left[\frac{1000}{C_n}\right]^2 P_{L}^2 + \left[\frac{1000\ L}{C_n^2}\right]^2 P_{C_n}^2 \quad , \tag{68}$$

where P_{Λ} is the probable error in the equivalent conductance, Λ ; P_{L}, the probable error in the specific conductance, L; and P_{C_n}, the probable error in the normality, C_n.

For a 0.061968 normal $LaCl_3$ solution, for which L = 0.0064378 mho cm.$^{-1}$, the equivalent conductance and associated probable error as calculated from Equation 68 are 103.89 ± 0.07 mho eq.$^{-1}$ cm.^{2}. Similarly, for a 5.2353 normal $LaCl_3$ solution, for which L = 0.17224 mho cm.$^{-1}$, the equivalent conductance and associated probable error are 32.900 ± 0.021 mho eq.$^{-1}$ cm.^{2}. The probable error in the equivalent conductance thus amounts to about 0.07 per cent over the entire concentration range studied.

Prior to this research, determinations of the specific and equivalent conductances had been carried out for all of the rare-earth chlorides in the concentration region below 0.1 normal (6, 9, 10, 19, 23, 122, 123). However, only in the case of lanthanum chloride, for which Jones and Bickford (122) made measurements up to a concentration of 3.0 normal, had the conductance behavior of the rare-earth chlorides been studied beyond 0.1 normal. The results obtained by Jones and Bickford and those obtained in this research for lanthanum chloride are in agreement within 0.1 per cent.

On the whole, the results obtained below 0.1 normal by previous investigators are also in satisfactory agreement with the results obtained for the dilute concentration region in this research.

The equivalent conductance data obtained in this research show that except for the reversal in position of lanthanum and neodymium chlorides, the equivalent conductance of the rare-earth chlorides at a given concentration decreases with increasing atomic number of the rare earth. Since the ionic radius of the rare earths also decreases with increasing atomic number, this decrease in equivalent conductance is in accordance with the expectation that the ions of greatest surface charge will be most strongly hydrated and thus have the lowest mobility. As had previously been noted in the concentration region below 0.1 normal (23), the difference in the equivalent conductance between adjacent rare-earth chlorides at a given concentration is much greater in the middle of the series than at either end.

The equivalent conductance curves of the rare-earth chlorides exhibit a general divergence with increasing concentration up to a concentration between four and five normal. In this concentration region the curves begin to converge; this convergence continues until saturation is reached, as if they were approaching a common limit. A similar convergence of conductance curves was found by

Miller (124) for sodium iodide, sodium perchlorate, and sodium thiocyanate. This suggests that in these very concentrated sodium salt solutions more and more of the current is being carried by a common unit, the sodium ion, which in Miller's view is not unreasonable if quasicrystalline local order exists in these solutions. Such an interpretation for the rare-earth chlorides would mean that with increasing concentration more and more of the current is being carried by the chloride ion. In dilute solutions the anion transference number is observed to increase with increasing concentration. Transference number measurements in concentrated solutions would be necessary to clarify the situation.

It will be recalled from Section V-D of this thesis that the apparent and partial molal volume data for the rare-earth chlorides indicate that a change in coordination number for water takes place in the middle of the rare-earth series. Such a change in coordination number would undoubtedly change the effective radius of the hydrated ions and thus its mobility. However, the exact effect of the change on the mobility and equivalent conductance cannot be ascertained in the light of present knowledge. The reversal of the neodymium and lanthanum chloride curves points up the complexity in the problem of interpretation.

Accurate conductance measurements in concentrated solutions of electrolytes have been largely confined to

uni-univalent electrolytes. Stokes and Robinson (56, p. 467) have recently compiled a bibliography of conductance measurements in concentrated aqueous solutions during the past twenty years. Perhaps the most curious aspect of conductance data in concentrated solutions is the maximum in the specific conductance curve found for many electrolytes. The greatest difference in the specific and equivalent conductances between adjacent rare-earth chlorides occurs at the concentration of the maximum. In addition, the concentration at which the maximum occurs decreases slightly with increasing atomic number of the rare-earth. The existence of the maximum in the specific conductance must be due either to ionic association or to a marked decrease in the mobility of the ions, or what is probably more likely a combination of both.

In concentrated solutions of the rare-earth chlorides, it is likely that most solvent molecules are tightly held by the ions with little or no free water. This should produce, as it does, a large increase in the viscosity of the solution. The increase in viscosity decreases the mobility of the ions, but the exact relation between mobility and the change in viscosity remains unanswered. In order to determine this, one would need an exact treatment of the interionic effects which also change the mobility.

The interpretation of conductance behavior beyond the

very dilute range is thus a very complicated and as yet un-solved problem. Additional data for non-equilibrium pro-perties in electrolytic solutions and fused-salt systems are needed before even a qualitative picture may be obtained.

VII. OSMOTIC AND ACTIVITY COEFFICIENTS

A. Introduction and Theory

The importance of the chemical potential and activity in the characterization of solution behavior has been emphasized in previous sections. A complete thermodynamic description of a solution can be expressed in terms of the temperature, pressure, composition, and the chemical potentials of the various components. All other thermodynamic functions can be derived from these.

There are various types of experimental measurements from which activities may be determined. In general, the methods of determining the solute activity in an electrolytic solution fall into two classifications: methods dependent on the determination of the activity of the solvent and calculation of the solute activity from the Gibbs-Duhem equation, and methods which determine the solute activity directly.

Under the first classification, one may include vapor-pressure measurements and measurements of the freezing point depression, boiling point elevation, osmotic pressure, and other colligative properties of the solution. The vapor pressure measurements may be sub-divided into the static, dynamic, and isopiestic methods. In the second classification, the activity of the solute is usually determined by

measuring the potentials of electrochemical cells with or without liquid junctions. Other more exotic methods, such as sedimentation measurements in an ultracentrifuge, have found only limited use in the determination of activities.

Since the isopiestic comparison method was employed in this research, it will be discussed in detail. For the theory and literature references pertaining to the other methods, the treatises on electrolytic solutions by Harned and Owen (36) and Stokes and Robinson (56) may be consulted.

The isopiestic comparison method is a comparative technique depending on the principle that in a closed system the common solvent in solutions of different non-volatile solutes will distill from one to the other until their concentration are such that the solutions have equal vapor pressure. If the activity of one solute is known as a function of concentration, then the activities of other solutes whose solutions are in vapor-pressure and thermal equilibrium can be calculated by thermodynamic reasoning.

In this research solutions of some rare-earth chlorides were brought to thermal and vapor-pressure equilibrium in a closed chamber with solutions of a reference salt, either potassium chloride or calcium chloride. At equilibrium the chemical potential of the solvent was the same in each of the three phases present: rare-earth chloride solution, reference salt solution, and vapor phase. From the

equilibrium concentration of each solution and known activity
data for the reference salt, the rare-earth chloride
activities could be computed by the Gibbs-Duhem equation.
The theoretical considerations in this calculation will now
be considered.

At the attainment of thermodynamic equilibrium between
a rare-earth chloride solution and a solution of the refer-
ence salt, e.g., potassium chloride, the chemical potential
of the solvent in each solution is the same:

$$(\mu_{H_2O})_{RCl_3} = (\mu_{H_2O})_{KCl} \quad . \tag{69}$$

Since the chemical potential of the water can be expressed
in terms of activity by the relation

$$\mu_{H_2O} = \mu^0_{H_2O} + RT \ln (a_{H_2O}) \quad , \tag{70}$$

the equilibrium condition can be expressed as

$$(a_{H_2O})_{RCl_3} = (a_{H_2O})_{KCl} \quad . \tag{71}$$

It is convenient to express further developments in
terms of a new function of the chemical potential. The con-
cept of osmotic coefficient was introduced by Bjerrum (125)
to obtain a more sensitive measure of the non-ideality of
solutions in terms of the solvent. For aqueous solutions
the rational osmotic coefficient, g, is defined by

$$\mu_{H_2O} = \mu^O_{H_2O} + gRT \ln N_{H_2O} \quad , \tag{72}$$

and the practical or molal osmotic coefficient, $\emptyset$, by

$$\mu_{H_2O} = \mu^O_{H_2O} - \emptyset RT \, \frac{\nu \, m \, M_{H_2O}}{1000} \quad , \tag{73}$$

where N_{H_2O} is the mole fraction concentration of water; M_{H_2O}, the molecular weight of water; m, the molal concentration of solute; and ν, the number of moles of ions resulting from the dissociation of one mole of solute.

Equating Equations 70 and 73 for the chemical potential, one obtains the relation between the activity of water and the molal osmotic coefficient:

$$\ln (a_{H_2O}) = - \emptyset \, \nu \, m \, M_{H_2O}/1000 \quad . \tag{74}$$

The equilibrium condition in terms of the molal osmotic coefficient then becomes

$$(\emptyset \, \nu \, m)_{RCl_3} = (\emptyset \, \nu \, m)_{KCl} \tag{75}$$

or since ν equals 4 for a rare-earth chloride and 2 for potassium chloride

$$\emptyset_{RCl_3} = \frac{2m_{KCl}}{4m_{RCl_3}} \, \emptyset_{KCl} \quad . \tag{76}$$

Similar reasoning for a calcium chloride reference solution leads to the relation

$$\phi_{RCl_3} = \frac{3m_{CaCl_2}}{4m_{RCl_3}} \phi_{CaCl_2} \quad . \quad (77)$$

For a binary solution composed of a solute and water at constant temperature and pressure, the Gibbs-Duhem equation, Equation 18, may be expressed as

$$n_{H_2O} \, d \, \mu_{H_2O} + n_{solute} \, d \, \mu_{solute} = 0 \quad . \quad (78)$$

Utilizing the relation between the chemical potential and activity, and the definition of mole fraction, $N_i = n_i/\Sigma n_i$, the Gibbs-Duhem equation becomes

$$N_{H_2O} \, d \, \ln(a_{H_2O}) + N_{solute} \, d \, \ln (a_{solute}) = 0 \quad . \quad (79)$$

Since

$$N_{H_2O} = \frac{1000/M_{H_2O}}{1000/M_{H_2O} + m} \quad (80)$$

and

$$N_{solute} = \frac{m}{1000/M_{H_2O} + m} \quad , \quad (81)$$

the Gibbs-Duhem equation may be expressed in terms of the molality by

$$\frac{1000}{M_{H_2O}} \, d \, \ln (a_{H_2O}) + m \, d \, \ln (a_{solute}) = 0 \quad . \quad (82)$$

Differentiation of Equation 74 and substitution of the

differential into Equation 82 gives the relation

$$-\nu d(\phi m) + m \ d \ \ln(a_{solute}) = 0 \quad . \qquad (83)$$

But

$$a_{solute} = (a_{m\pm})^{\nu} = (m_{\pm} \gamma_{\pm})^{\nu} = [m(\nu_{+}^{\nu_{+}} \nu_{-}^{\nu_{-}})]^{\nu} (\gamma_{\pm})^{\nu} \ , \qquad (84)$$

so that

$$-d(\phi m) + dm + m \ d \ \ln(\gamma_{\pm}) = 0 \qquad (85)$$

or

$$d(\phi m) = dm + m \ d \ \ln(\gamma_{\pm}) \quad . \qquad (86)$$

The integral form of Equation 86 is

$$\int_{\phi m=0}^{\phi m} d(\phi m) = \int_{m=0}^{m} dm + \int_{\ln(\gamma_{\pm})=0}^{\ln(\gamma_{\pm})} m \ d \ \ln(_{\pm}) \ , \qquad (87)$$

where the lower limit of integration is the standard state of infinite dilution and the upper limit a solution of molal concentration m, activity coefficient $\gamma_{\pm}$, and osmotic co-efficient ϕ. Integration of Equation 87 then gives

$$\phi = 1 + \frac{1}{m} \int_{0}^{\ln(\gamma_{\pm})} m \ d \ \ln(\gamma_{\pm}) \quad . \qquad (88)$$

The remaining integral is evaluated graphically. Knowing

the activity coefficient of a solute as a function of concentration, the osmotic coefficient at various concentrations can be determined from Equation 88.

The reverse procedure of determining activity coefficients from molal osmotic coefficients requires a different approach. The Gibbs-Duhem equation in the form of Equation 86 can be expressed in the following way:

$$d(\phi m) = m \, d\phi + \phi \, dm = dm + m \, d \ln (\gamma_{\pm}) \quad . \tag{89}$$

Rearrangement of Equation 89 gives

$$d \ln(\gamma_{\pm}) = d\phi - (1 - \phi) \frac{dm}{m} \quad . \tag{90}$$

As a simplification the divergence function, h, is defined as

$$h = 1 - \phi \; ; \; dh = - d\phi \quad . \tag{91}$$

Substitution of the divergence function into Equation 90 then gives

$$d \ln(\gamma_{\pm}) = -dh - h \frac{dm}{m} \tag{92}$$

or in integral form

$$\int_{\ln(\gamma_{\pm})=0}^{\ln(\gamma_{\pm})} d \ln(\pm) = - \int_{h=0}^{h} dh - \int_{m=0}^{m} h \frac{dm}{m} \quad , \tag{93}$$

where the limits of integration are the same as for Equation 87. Therefore

$$\ln(\gamma_\pm) = -h - \int_{m=0}^{m} h\,\frac{dm}{m} \quad . \tag{94}$$

In order to take advantage of a function which approaches the m=0 axis more rapidly, Equation 94 is written in the form:

$$\log(\gamma_\pm) = -\frac{h}{2.3026} - \frac{2}{2.3026} \int_{\sqrt{m}=0}^{\sqrt{m}} \frac{h}{\sqrt{m}}\,d\sqrt{m} \quad . \tag{95}$$

From this equation by means of a graphical integration, the activity coefficient at various concentrations can be computed from osmotic coefficient data. This is the graphical method as set forth by Randall and White (126).

B. Historical Review of Isopiestic Comparison Method

The isopiestic comparison method as an indirect method for the determination of activities has been one of the most useful and widely applicable techniques for the thermodynamic investigation of solutions. Bousfield (127) in 1918 was the first to propose and utilize such a method for the indirect determination of vapor pressures of solutions, but it was not until 1933 that Sinclair (128) established many of

the experimental principles necessary to make the method capable of a high degree of accuracy. In the decade after the work of Sinclair, the method was applied to approximately a hundred salts. During this period various modifications in the apparatus and procedure were devised by numerous investigators. Before reviewing some of the contributions of these investigators, it would be useful to consider the basic experimental principles which have been established.

Assuming that accurate activity data for the reference solute exists, the success of the isopiestic method in determining activities is dependent on the ability of the experimental technique to bring about thermal and vapor-pressure equilibrium between solutions as rapidly as possible and to permit accurate determination of the concentrations of these solutions at equilibrium. On the basis of these objectives, the general experimental principles of the method may be considered.

1. The transfer of solvent between solutions by evaporation and condensation results in energy and hence temperature changes in the solutions, so that the attainment of equilibrium is dependent on the equalization of the solution temperatures. To achieve rapid equalization of temperature, good thermal contact between various solutions must be provided. This has usually been accomplished by placing silver cups containing the solutions in close

contact with a thick copper block. The high thermal conductivities of silver and copper reduce the thermal resistance between the solutions to a small value. The importance of good thermal contact cannot be overemphasized. Since the value of (dP/dT) at 25° C. is 1.4 mm. of Hg per degree for water and about the same for dilute aqueous solutions, a temperature difference of 0.0007° C. between solutions corresponds to a vapor-pressure difference of 0.001 mm. To achieve the same precision as is possible in direct vapor-pressure measurements, it is essential, therefore, that the solutions must not differ in temperature, when equilibrium is attained, by more than 0.0007° C.

2. The necessity for the close approach to temperature equality between solutions does not imply that the bath temperature must be controlled within the same limits. If the chamber containing the copper block and the solution cups is thick-walled and the area of contact between the block and chamber is kept small, an effective thermal buffer is formed which tends to damp out the fluctuations in bath temperature, usually controlled to 0.01° C.

3. Since the equilibration process involves both concentration and temperature changes in the solutions, two factors of importance in the attainment of equilibrium are the diffusion of solute and the conduction of heat through the solutions themselves. These processes can be accelerated

by some method of stirring and by keeping the depth of solution in the cups shallow. The stirring, however, must not be vigorous enough to cause local heating effects or the splattering of solution from the cups.

4. To effect the concentration changes involved in the equilibration process, adequate diffusion of water vapor in the gaseous phase is necessary. This is accomplished by complete evacuation of air from the solution chamber. The evacuation of the chamber must be carried out slowly to prevent splattering of the solutions.

5. The determination of the equilibrium concentration of each solution simply involves determination of the weight of solute or solution of known concentration initially added to the cup and the weight of solution after equilibrium has been attained. From these quantities the equilibrium molal concentration can easily be calculated. The cups must be provided with caps during weighings to eliminate any error due to evaporation. The size of the solution samples should be as small as is compatible with accuracy in weighing so that the amount of solvent which has to distill may be kept at a minimum.

6. The isopiestic method is most suitable for measurements on concentrated solutions, since the time required for equilibrium to be attained increases greatly with decreasing concentration. The lower practical limit for the isopiestic

method is a concentration of 0.1 molal.

As was previously mentioned, many of the experimental principles just outlined were established by the work of Sinclair (128) in 1933. Sinclair used a set of four silver-plated copper dishes, 1-1/2 inches square by 3/4 inch deep, which fitted neatly together. Two-cubic-centimeter samples of a potassium chloride reference solution were weighed into two of the dishes, and similar-sized samples of a solution of the salt under investigation were weighed into the remaining dishes. The four dishes were then mounted in a square formation on a silver-plated copper block, one inch thick. To improve the thermal contact between solutions, Sinclair placed sodium hydroxide solution in the crevices between the dishes. The block and dishes were mounted in a desiccator which was evacuated to about 20 mm. of Hg before being placed in a thermostat controlled to 0.01° C. For stirring, the desiccator was rocked back and forth in the thermostat with a period and angle of oscillation of about one second and 20° respectively. The time allowed for equilibrium to be attained varied from one day for solutions above a concentration of 0.5 molal to three days for 0.1 molal solutions. The use of the sodium hydroxide contact solution necessitated the washing and drying of the outside of the dishes before the final weighings could be made at the end of the equilibration period.

Robinson and Sinclair (129) in 1934 modified the isopiestic apparatus by employing gold-plated silver dishes fitted with flap-lids. The flap-lids were held open during an experiment by a wire bridge attached to the exit tube of the desiccator, so arranged that at the conclusion of the experiment the lids could be allowed to fall by rotating the exit tube through a small angle without opening the desiccator. The vast majority of the activity determinations by the isopiestic method has been done by Robinson and his colleagues (130, 131, 132), using essentially the same apparatus and method employed by Robinson and Sinclair (129).

In 1938 Scatchard, Hamer, and Wood (133) made extensive modifications in the apparatus and method of Robinson and Sinclair. They employed a set of six platinum cups, each cup consisting of a cylinder, 3.5 cm. high and 2.5 cm. in diameter, the top of which was constricted to 1.8 cm. A nickel ring, 0.5 cm. high, was silver-soldered to the outside of the constriction; the outside of the ring was ground with a 3° taper to fit a nickel lid. The bottom and lower 2 cm. of the cups were lined with platinum gauze to increase the surface and aid in the stirring and heat conduction. The six cups fitted snugly in cylindrical holes arranged symmetrically in a gold-plated copper block. The block in turn fitted into a stainless steel vessel, the cover of which had a conical valve through which the vessel was

evacuated. During an equilibration the vessel sat on a table in the thermostat which rotated around an axis inclined at 45°. The thermostat was controlled to within 0.001° C. over an interval of several hours and within 0.005° C. over a twenty-four hour period. Great care was exercised to ensure complete evacuation of air from the vessel. After an initial evacuation to the vapor pressure of water, the vessel was evacuated ten additional times. One-gram solution samples were employed in measurements with concentrated solutions; and 0.5 gm. samples, with dilute solutions. The allowed equilibration time varied from one to three days.

In the period from 1936 to 1941, Mason (134, 135, 136) carried out an extensive investigation on the activities of trivalent metal chlorides in aqueous solutions by the isopiestic method. He employed ordinary glass-stoppered weighing bottles for his concentrated solutions, and gold-plated silver bottles in the concentration range below 0.5 molal. Platinum gauze in the form of a strip folded like a bellows was placed in each of the bottles to aid in stirring and heat conduction. His desiccator was constructed of monel metal and was fitted with a brass needle valve for evacuation purposes. The thermostat, controlled to 0.01° C., was equipped with a shaking device to rock the desiccator back and forth about 45 times a minute. An equilibration

period of about 48 hours was generally employed in his determinations.

Phillips, Watson, and Felsing (137) in 1942 employed nickel cups in their activity determinations. To improve the thermal contact between solutions, liquid mercury was placed between and around the cups which were mounted on a heavy steel plate in a steel desiccator. The inside of the cups was gold-plated, and the gold-plated walls were lacquered to prevent amalgamation of the gold.

In 1943 Gordon (138) by some refinements in the apparatus attempted to extend the lower concentration limit of the isopiestic method down to 0.03 molal. He improved the thermal contact between solutions by employing gold-plated silver cups with a double-cup arrangement in which a cup of one solution rested inside a larger cup of the reference solution. The outer cup was covered with a loosely-fitting silver lid. A glass bead was placed inside the inner cup to aid in the stirring. This double-cup arrangement fitted snugly into a glass vacuum desiccator, 4.2 cm. in diameter, which in turn fitted in a copper box. The copper box was placed in a Dewar flask, packed tightly with glass wool, which rested in a large glass vacuum desiccator, 25 cm. in diameter. The large desiccator was mounted on a rocking table in a double-walled water bath which was controlled to $\pm$ 0.003° C. as far as individual fluctuations with a

maximum drift over a 48-hour period of 0.01° C. Gordon found that the most serious experimental difficulty was the complete removal of air from the desiccator. He employed a lengthy procedure to achieve this, involving evacuation of the desiccator in a number of steps between which the assembly was rocked in the bath. For equilibration of the solutions, a period of from 7 to 18 days was allowed. At the end of the equilibration period, the assembly of chambers was dismantled, and dry air was slowly admitted to the small desiccator. Immediately after opening the desiccator, ground-glass stoppers were inserted into the cups. Both cups were first weighed together, and then the inner cup, after its outer surface had been washed and dried, was weighed singly. Although acceptable precision for solutions of sodium and potassium chloride was obtained, the complexity of the apparatus and its limitation to a single pair of solutions restrict the applicability of Gordon's technique.

C. Experimental

1. Apparatus and procedure

The isopiestic apparatus employed in the osmotic and activity coefficient determinations for the rare-earth chlorides consisted of twenty-four gold-plated sterling-silver equilibration cups, three rectangular stainless-steel

equilibration chambers with a copper block in each, a
constant-temperature bath, and a device for rocking the
chambers.

The gold-plated sterling-silver equilibration cups were
manufactured by the Randahl Company of Skokie, Illinois.
The cups were cylindrical in shape, 3.5 cm. high and 2.6 cm.
in diameter, with a wall thickness of 0.5 mm. At a height
of 2.5 cm., the walls of the cups were constricted to give
a diameter at the top of 2.0 cm. A silver ring, 0.5 cm.
high and ground on the outside to a 3° taper, was silver-
soldered to the outside of the uppermost part of the cups.
The base of the cups extended about 0.5 cm. beyond the walls
forming a flange by which the cups were secured to the
copper block. Polyethylene caps, which were of such a size
as to just snap on over the soldered ring around the cup
opening, were used to cover the cups during weighings. No
detectable loss of weight due to evaporation over a period
of an hour was noted with use of these caps on the solution-
containing cups.

The copper block contained in each equilibration chamber
served the dual purpose as a thermal buffer and as a means
of mounting the cups in good thermal contact. Each copper
block was about 25 cm. long, 11 cm. wide, and 3 cm. high.
Eight cylindrical holes, 1.6 cm. deep and of a diameter
slightly larger than the base of the cups, were drilled in

each block to serve as mountings for the cups. The upper half of the walls of each hole was threaded to fit a brass collar. When the brass collar was screwed firmly against a Bakelite collar which sat on the flange of the cup, good thermal contact between the base of the cup and the copper block was obtained. This arrangement, shown in Figure 18, was essentially the same as that employed by Mason (135). To prevent corrosion and to provide a gold-to-gold contact between the cups and block, the surfaces of the holes were gold-plated. The outer surface of each block was polished and heavily lacquered.

Each stainless steel equilibration chamber, also shown in Figure 18, was 28 cm. long, 14 cm. wide, and 11 cm. high with a wall thickness of 1 cm. The copper block was mounted in each chamber on two parallel ridges, 0.5 cm. wide and 0.5 cm. high, which extended the length of the chamber bottom. Eight projections from the walls of the chamber positioned the block in the center of the chamber. The larger copper block and the thick-walled chamber with the limited contact between them formed an effective thermal buffer. Around the top of each chamber was a flat flange which served as a seat for a stainless steel cover. A Neoprene gasket was used between the flange and cover. The cover was tightly fastened to the chamber by means of twelve stud bolts with wing-nuts. The cover of each chamber was fitted with a

ARM OF ROCKING DEVICE

NEEDLE VALVE

CHAMBER COVER

NEOPRENE GASKET

— BRASS COLLAR
— BAKELITE COLLAR

CUP IN POSITION

— EQUILIBRATION CUP

ROCKING AXIS

COPPER BLOCK

COPPER BLOCK SUPPORTS

BATH WALL

BATH WALL

154

NOT DRAWN TO SCALE
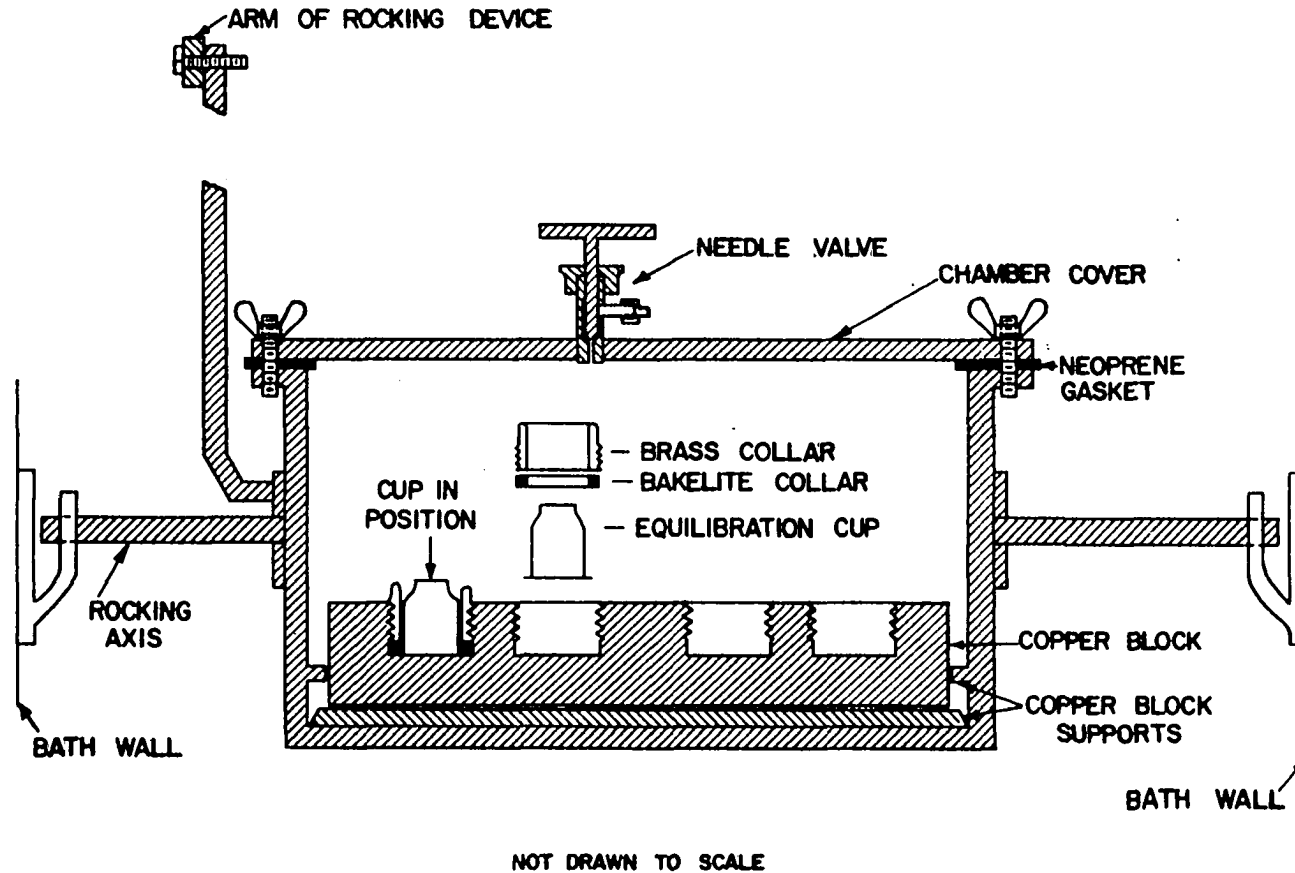
Figure 18. Cross-sectional view of chamber for isopiestic equilibrations

Hoke No. RF-275 stainless steel needle valve through which evacuation of the chamber was carried out. When the chamber was immersed in the bath, the hollow metal connector used to join the valve to the vacuum line was replaced by a similar connector which had been soldered shut to keep water out of the valve.

To the center of each end of a chamber was attached a steel rod about 10 cm. long and 1.5 cm. in diameter, extending outward perpendicular to the end of the chamber. When the ends of the two rods were placed in brackets mounted on opposite walls of the constant-temperature bath, each chamber was free to rock about an axis through the rods. To one end of each chamber was also attached a steel bar about 50 cm. long, bent to a vertical position. When the chamber was mounted in the bath, the bar extended about 4 inches above the top of the bath. The top end of the bar of each chamber could be set by means of a pin in a bearing on a horizontal arm which traversed the length of the bath. This horizontal arm was driven back and forth by a wheel and crank device, powered by an electric motor through a Graham variable speed transmission. By means of this, the chambers could be rocked back and forth with any frequency of oscillation from zero to 70 cycles per minute. The radius of crank could also be adjusted to give any amplitude of rocking from 10° to 60° from the vertical. In Figure 19, the rocking device and a
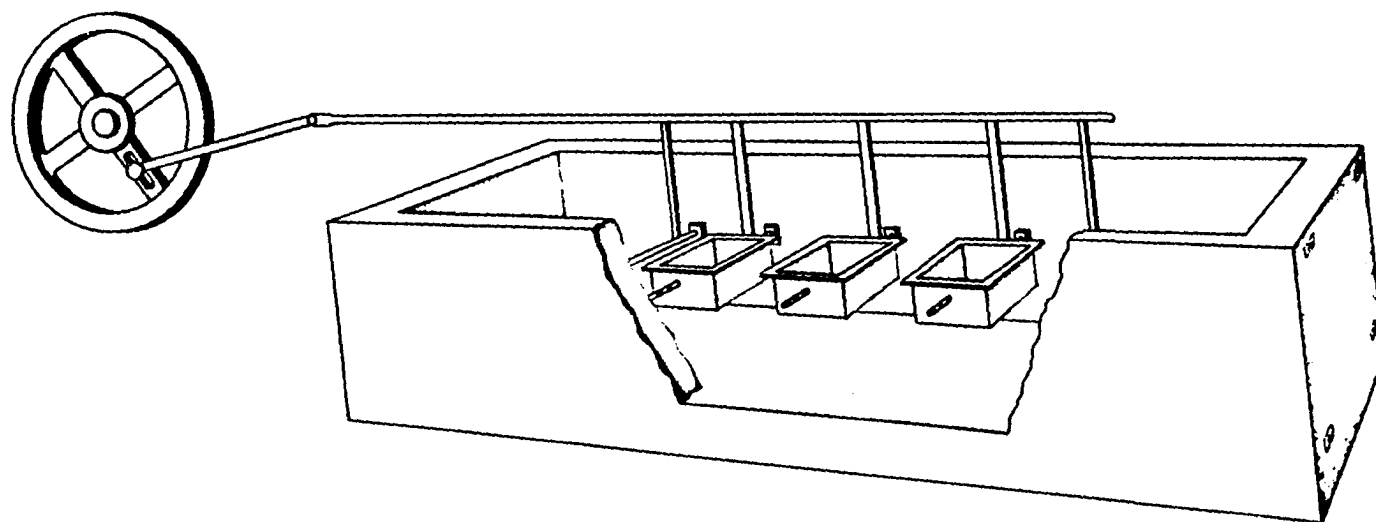
Figure 19. Constant-temperature bath and rocking device for the equilibration chambers

cutaway view of the constant-temperature bath are shown.

The constant-temperature bath was a double-walled tank consisting of an inner stainless steel tank and outer galvanized iron tank. The three-inch space between the inner and outer tanks was filled with blown-mica insulation. The inner tank was 53 inches long, 20 inches wide, and 20 inches deep. Its walls in the long dimension were structurally reinforced to hold the brackets by which the equilibration chambers were suspended in the bath. At each end of the bath was mounted a centrifugal stirrer (Central Scientific Company catalog number 18850) with a pumping capacity of 100 gallons per minute. The bath was controlled by a microset mercury thermoregulator in combination with an electronic relay and two infra-red heat lamps. The heat lamps were mounted at opposite ends of the bath in such a manner that they never shone directly on the chambers. Cooling was provided by the circulation of tap water through a copper U-tube immersed in the bath; the flow of cooling water was regulated by means of a constant-head tank. The temperature of the bath was maintained constant and uniform throughout at $25.00 \pm 0.01^\circ$ C. as read from two Emerson calorimeter thermometers positioned in different regions of the bath. These thermometers, graduated in units of 0.01° C., were checked against a platinum resistance thermometer calibrated by the National Bureau of Standards.

The equilibration chambers were evacuated with a Welch Duo-Seal vacuum pump in combination with a trichloroethylene-dry-ice trap to remove water vapor from the vacuum line. All weighings of the equilibration cups were made on an Ainsworth type BB analytical balance using a set of Ainsworth Class S certified weights.

As was previously stated, two different reference salts, potassium chloride and calcium chloride, were employed in the isopiestic comparisons. Potassium chloride was used as the reference salt up to its solubility limit, 4.8 molal, which corresponds to a rare-earth chloride concentration of about 1.5 molal. For more concentrated rare-earth chloride solutions calcium chloride was employed. The stock solutions of potassium chloride were prepared by weight from the fused C. P. salt and conductivity water. Two calcium chloride solutions were prepared by dissolving Mallinckrodt Primary Standard calcium carbonate in C. P. hydrochloric acid with boiling to expel the carbon dioxide. This is the method of preparation recommended by Robinson and Stokes (56, p. 213). Additional stock solutions were prepared from these by weight dilution. The concentrations of the calcium chloride solutions were determined from chloride analyses by the standard gravimetric method. For each of the rare-earth chlorides, a set of about eight stock solutions of widely differing concentrations was employed. These were

selected from among the solutions prepared for the density
and conductance measurements. From the sets of rare-earth
chloride and reference salt solutions, solutions of appro-
priate concentrations could be chosen for making up the
samples so that the sample weights fell in the optimum
range.

The procedure for an isopiestic equilibration experiment
was as follows:

1. The gold-plated sterling-silver equilibration cups
were first cleaned with "Quik-Dip" silver cleaner. After
a thorough rinsing with distilled and then conductivity
water, the cups were dried at 60° C. in an oven. A strip
of platinum screen folded in the form of a bellows, which
had been cleaned and rinsed similarly and then ignited in
the flame of a Meker burner, was placed in the bottom of
each equilibration cup.

2. After the empty weight of each cup with its plati-
num bellows and polyethylene cap had been determined, the
appropriate volume of stock solution was pipetted into the
cup, and the cup reweighed. A sufficient quantity of con-
ductivity water was then added to bring the concentration
of the solution to the desired initial value. The weight
of the solution samples was generally about 2 grams. For
each salt equilibrated in an experiment, two cups of solu-
tion were weighed out. The two solutions for each salt

were made up so that there was an initial concentration difference of about 5 per cent between them. Solutions of as many as three different rare-earth chlorides were equilibrated with the same reference salt solutions in a single chamber.

3. After completion of the weighings, the cups were mounted in the copper block in the equilibration chamber. The cups were so arranged in the block that a cup containing a solution of a given salt had as its nearest neighbors cups containing solutions of different salts. The caps were then removed and stored in the same arrangement as that of the cups in the block to facilitate rapid covering of the cups at the end of the equilibration period. Several drops of water were placed in the various recesses of the chamber, so that their evaporation during the evacuation of the chamber would sweep out the air and replace solvent lost from the cups. No water was ever found remaining in the chamber outside of the cups at the end of an equilibration experiment.

4. Before bolting the chamber cover in place, the Neoprene gasket was coated on both sides with Apiezon T grease. After the cover had been tightly fastened, the chamber was evacuated to a pressure of 30 mm. Hg. The solutions were then allowed to degas at this pressure for a 12-hour period while rocking in the bath. The chamber was

temporarily removed from the bath at the end of this period, and the pressure was reduced to the vapor pressure of the solutions. The evacuation was carried out in this two-step process to avoid splattering of the solutions.

5. An equilibration was considered complete above a rare-earth chloride concentration of 0.2 molal when the concentrations of the two solutions of the same salt had come within 0.1 per cent of the average for that salt. In the majority of experiments, the concentration of each member of a pair was brought to within 0.05 per cent of the average. Below a concentration of 0.2 molal, a concentration approach to within 0.15 per cent of the average was considered satisfactory, since further equilibration did not improve the results to any degree. For rare-earth chloride solutions above a concentration of one molal, the necessary rocking equilibration time was from three to four days. Below a concentration of one molal, the equilibration time increased until in the concentration range below 0.2 molal, about two weeks were necessary.

6. At the conclusion of the equilibration period, clean dry air was slowly admitted to the chamber through traps of anhydrous calcium chloride and glass wool. Within 60 seconds after removal of the cover, the caps had been placed on all of the cups. By experiment it was found that no more than 0.2 mg. of water would evaporate during this

period. The cups were then weighed.

7. From the vacuum-corrected weights of solution and the known molalities of the stock solutions, the isopiestic molalities were calculated by means of the reations

$$\text{Weight of solution} = \text{Weight of solute} + \text{Weight of solvent} \qquad (96)$$

and

$$\text{Molality} = \frac{\text{Weight of solute/Molecular-weight of solute}}{\text{Weight of solvent/1000}} \cdot \qquad (97)$$

2. Isopiestic standards

In order to calculate osmotic and activity coefficients from isopiestic molality data, it is necessary to have a set of osmotic coefficient (or activity coefficient) data for the reference salt. For potassium chloride the osmotic coefficients as reported by Robinson (139) were selected as the standard. These osmotic coefficients are based on numerous isopiestic comparisons with sodium chloride. For calcium chloride the osmotic coefficient data of Stokes (131, 140) were employed as the standard. These osmotic coefficients are based on isopiestic comparison with sodium chloride and sulfuric acid solutions, and are anchored at 0.1 molal by the osmotic coefficient data of McLeod and Gordon (141).

The values of the osmotic coefficient for the reference salts at the experimental molalities were calculated from the values given at round concentrations by means of the interpolation formulae of Bessel, Stirling, and Newton as described by Scarborough (142).

To check the preparation of the calcium chloride solutions, several isopiestic equilibrations between potassium chloride and calcium chloride solutions were carried out. In Table 24, the osmotic coefficients of some calcium chloride solutions as calculated from the potassium chloride osmotic coefficient data of Robinson (139) and the isopiestic molalities are given. In the last column of Table 24, the osmotic coefficients of the same calcium chloride solutions as obtained by interpolation of the data of Stokes (131) are given.

3. Osmotic and activity coefficient calculations and results

Isopiestic equilibrations between solutions of a reference salt, potassium chloride or calcium chloride, and solutions of lanthanum, neodymium, samarium, gadolinium, and dysprosium chlorides were carried out in the rare-earth chloride concentration range between 0.1 molal and saturation. From the isopiestic molality data and the osmotic coefficient data for the reference salt, the osmotic coefficients for the rare-earth chlorides were calculated by means

Table 24.   Comparison of osmotic coefficients for calcium chloride

m_{CaCl_2}	m_{KCl}	ϕ_{KCl}	$\phi_{CaCl_2}{}^a$	$\phi_{CaCl_2}{}^b$
2.1264	4.6202	0.9830	1.4239	1.4223
2.0222	4.3152	0.9741	1.3857	1.3841
1.9152	4.0066	0.9649	1.3457	1.3456
1.7850	3.6454	0.9544	1.2994	1.2998
1.7462	3.5388	0.9514	1.2854	1.2865
1.7294	3.4950	0.9502	1.2803	1.2807
1.5958	3.1406	0.9405	1.2339	1.2356

[a]Calculated from isopiestic molalities and potassium chloride osmotic coefficients.

[b]Obtained by interpolation of the calcium chloride osmotic coefficient data of Stokes (131).

of the isopiestic equilibrium condition as expressed by Equations 76 and 77.   In Tables 25 through 34, the isopiestic molalities and osmotic coefficients for these rare-earth chlorides and reference salts are given.

In order to calculate the activity coefficient at a molality m from osmotic coefficient data by means of Equation 95, a graphical integration of a plot of $h/\sqrt{m}$ vs. $\sqrt{m}$ between the limits zero and $\sqrt{m}$ must be carried out.   The isopiestic method, however, does not yield precise data below a concentration of 0.1 molal.   On the other hand, the

Table 25. Isopiestic molalities and osmotic coefficients for $LaCl_3$ and KCl

m_{LaCl_3}	m_{KCl}	ϕ_{KCl}	ϕ_{LaCl_3}
0.69550	1.5314	0.9030	0.9942
0.83581	1.9542	0.9114	1.0655
0.93855	2.2882	0.9188	1.1200
1.1256	2.9443	0.9352	1.2232
1.1772	3.1406	0.9405	1.2545
1.2690	3.4950	0.9502	1.3086
1.2799	3.5388	0.9514	1.3153
1.3959	4.0066	0.9649	1.3848
1.5406	4.6202	0.9830	1.4740

Table 26. Isopiestic molalities and osmotic coefficients for $LaCl_3$ and $CaCl_2$

m_{LaCl_3}	m_{CaCl_2}	ϕ_{CaCl_2}	ϕ_{LaCl_3}
1.1256	1.5206	1.2106	1.2265
1.1772	1.5958	1.2356	1.2562
1.2468	1.6974	1.2698	1.2966
1.2690	1.7294	1.2807	1.3090
1.2799	1.7462	1.2865	1.3164
1.3959	1.9152	1.3456	1.3846
1.5214	2.0956	1.4110	1.4577
1.5406	2.1264	1.4223	1.4723
1.6441	2.2734	1.4780	1.5328
1.7322	2.4010	1.5279	1.5884
1.9190	2.6668	1.6378	1.7070
2.0211	2.8138	1.7013	1.7764
2.0664	2.8760	1.7267	1.8024
2.0934	2.9152	1.7437	1.8212
2.2167	3.0864	1.8150	1.8953

Table 26 (continued)

m_{LaCl_3}	m_{CaCl_2}	ϕ_{CaCl_2}	ϕ_{LaCl_3}
2.3060	3.2102	1.8648	1.9470
2.3380	3.2526	1.8822	1.9639
2.5290	3.5112	1.9855	2.0675
2.5963	3.6000	2.0211	2.1018
2.7043	3.7410	2.0777	2.1556
2.7852	3.8456	2.1197	2.1950
2.7854	3.8442	2.1192	2.1936
3.0128	4.1329	2.2357	2.3002
3.1284	4.2798	2.2950	2.3548
3.2115	4.3830	2.3363	2.3914
3.2817	4.4667	2.3711	2.4205
3.3346	4.5339	2.3964	2.4437
3.4561	4.6816	2.4543	2.4934
3.4725	4.7000	2.4613	2.4985
3.6286	4.8859	2.5321	2.5572
3.6339	4.8924	2.5346	2.5592
3.6818	4.9541	2.5573	2.5807
3.7690	5.0538	2.5934	2.6082
3.8196	5.1172	2.6157	2.6283
3.8672	5.1742	2.6353	2.6445
3.8944	5.2098	2.6475	2.6564

Table 27.   Isopiestic molalities and osmotic coefficients
for $NdCl_3$ and KCl

m_{NdCl_3}	m_{KCl}	ϕ_{KCl}	ϕ_{NdCl_3}
0.10720	0.18276	0.9146	0.7797
0.12034	0.20604	0.9125	0.7811
0.17420	0.30533	0.9066	0.7945
0.23873	0.42947	0.9007	0.8102
0.29128	0.53689	0.8983	0.8279
0.38929	0.74856	0.8968	0.8623
0.43789	0.86088	0.8971	0.8818
0.48713	0.97920	0.8973	0.9019
0.69374	1.5314	0.9030	0.9967
0.83317	1.9542	0.9114	1.0689
0.84939	2.0044	0.9125	1.0767
0.93542	2.2882	0.9188	1.1238
0.98740	2.4682	0.9231	1.1537
1.1205	2.9443	0.9352	1.2287
1.1716	3.1406	0.9405	1.2605
1.2626	3.4950	0.9502	1.3152
1.2734	3.5388	0.9514	1.3221
1.3875	4.0066	0.9649	1.3932
1.5300	4.6202	0.9830	1.4842

Table 28.   Isopiestic molalities and osmotic coefficients
for $NdCl_3$ and $CaCl_2$

m_{NdCl_3}	m_{CaCl_2}	ϕ_{CaCl_2}	ϕ_{NdCl_3}
1.1205	1.5206	1.2106	1.2321
1.1716	1.5958	1.2356	1.2622
1.2626	1.7294	1.2807	1.3156
1.2734	1.7462	1.2865	1.3232
1.3875	1.9152	1.3456	1.3930
1.5106	2.0956	1.4110	1.4681

Table 28 (continued)

m_{NdCl_3}	m_{CaCl_2}	ϕ_{CaCl_2}	ϕ_{NdCl_3}
1.5300	2.1264	1.4223	1.4825
1.6309	2.2734	1.4780	1.5452
1.7171	2.4010	1.5279	1.6024
1.8980	2.6668	1.6378	1.7259
1.9974	2.8138	1.7013	1.7975
2.0408	2.8760	1.7267	1.8250
2.0670	2.9152	1.7437	1.8444
2.2303	3.1501	1.8406	1.9498
2.2712	3.2102	1.8648	1.9768
2.3748	3.3570	1.9245	2.0403
2.5459	3.5977	2.0202	2.1411
2.5472	3.6000	2.0211	2.1424
2.7218	3.8442	2.1192	2.2448
2.7237	3.8456	2.1197	2.2446
2.7842	3.9278	2.1529	2.2779
2.8919	4.0740	2.2118	2.3369
3.0418	4.2798	2.2950	2.4218
3.0588	4.3003	2.3032	2.4285
3.1194	4.3830	2.3363	2.4620
3.2564	4.5632	2.4079	2.5307
3.3438	4.6816	2.4543	2.5772
3.3599	4.7000	2.4613	2.5822
3.5003	4.8859	2.5321	2.6509
3.5060	4.8924	2.5346	2.6526
3.6288	5.0538	2.5934	2.7089
3.6637	5.1016	2.6103	2.7262
3.7180	5.1742	2.6353	2.7507
3.7833	5.2607	2.6648	2.7791
3.8583	5.3567	2.6968	2.8080
3.9031	5.4180	2.7165	2.8280
3.9286	5.4503	2.7270	2.8374
3.9307	5.4530	2.7279	2.8382

Table 29. Isopiestic molalities and osmotic coefficients
for $SmCl_3$ and KCl

m_{SmCl_3}	m_{KCl}	ϕ_{KCl}	ϕ_{SmCl_3}
0.10686	0.18276	0.9146	0.7821
0.12004	0.20604	0.9125	0.7831
0.14578	0.25359	0.9090	0.7906
0.23781	0.42947	0.9007	0.8133
0.29002	0.53689	0.8983	0.8315
0.38668	0.74586	0.8968	0.8681
0.43534	0.86088	0.8971	0.8870
0.48391	0.97920	0.8973	0.9079
0.60440	1.2942	0.8996	0.9632
0.68854	1.5314	0.9030	1.0042
0.76702	1.7636	0.9074	1.0431
0.82730	1.9542	0.9114	1.0765
0.84312	2.0044	0.9125	1.0847
0.93376	2.3073	0.9192	1.1356
0.98004	2.4682	0.9231	1.1624
1.1046	2.9141	0.9344	1.2327
1.2234	3.3757	0.9470	1.3065
1.2994	3.6788	0.9553	1.3523
1.3928	4.0686	0.9668	1.4120

Table 30. Isopiestic molalities and osmotic coefficients
for $SmCl_3$ and $CaCl_2$

m_{SmCl_3}	m_{CaCl_2}	ϕ_{CaCl_2}	ϕ_{SmCl_3}
1.2312	1.6974	1.2698	1.3130
1.4996	2.0956	1.4110	1.4789
1.6191	2.2734	1.4780	1.5565
1.7048	2.4010	1.5279	1.6139
1.8844	2.6668	1.6378	1.7384
1.9843	2.8138	1.7013	1.8094
2.0267	2.8760	1.7267	1.8377
2.0534	2.9152	1.7437	1.8566
2.1708	3.0864	1.8150	1.9354
2.2566	3.2102	1.8648	1.9896
2.2851	3.2526	1.8822	2.0093
2.4678	3.5112	1.9855	2.1187
2.5308	3.6000	2.0211	2.1562
2.5478	3.6241	2.0306	2.1663
2.6298	3.7410	2.0777	2.2167
2.7058	3.8442	2.1192	2.2581
2.7080	3.8456	2.1197	2.2576
2.9185	4.1329	2.2357	2.3745
3.0250	4.2798	2.2950	2.4352
3.1027	4.3830	2.3363	2.4753
3.1669	4.4667	2.3711	2.5082
3.3250	4.6792	2.4533	2.5892
3.3712	4.7389	2.4764	2.6107
3.4587	4.8530	2.5198	2.6518
3.5438	4.9667	2.5619	2.6929
3.6414	5.0952	2.6081	2.7371

Table 31. Isopiestic molalities and osmotic coefficients for $GdCl_3$ and KCl

m_{GdCl_3}	m_{KCl}	ϕ_{KCl}	ϕ_{GdCl_3}
0.10632	0.18276	0.9146	0.7861
0.11944	0.20604	0.9125	0.7870
0.14513	0.25359	0.9090	0.7942
0.17258	0.30533	0.9066	0.8020
0.23625	0.42947	0.9007	0.8187
0.28779	0.53689	0.8983	0.8379
0.43148	0.86088	0.8971	0.8949
0.59730	1.2942	0.8996	0.9746
0.68014	1.5314	0.9030	1.0166
0.75801	1.7636	0.9074	1.0555
0.83191	2.0044	0.9125	1.0993
0.92022	2.3073	0.9192	1.1523
0.96612	2.4682	0.9231	1.1791
1.0882	2.9141	0.9344	1.2512
1.2047	3.3757	0.9470	1.3268
1.2792	3.6788	0.9553	1.3737
1.3710	4.0686	0.9668	1.4345
1.4272	4.3152	0.9741	1.4726
1.5240	4.7520	0.9868	1.5386

Table 32. Isopiestic molalities and osmotic coefficients
for $GdCl_3$ and $CaCl_2$

m_{GdCl_3}	m_{CaCl_2}	ϕ_{CaCl_2}	ϕ_{GdCl_3}
1.4272	2.0222	1.3841	1.4709
1.5240	2.1694	1.4382	1.5354
1.5508	2.2066	1.4524	1.5500
1.6416	2.3485	1.5072	1.6172
1.7385	2.4948	1.5659	1.6854
1.8151	2.6099	1.6135	1.7400
1.9183	2.7661	1.6797	1.8165
2.0070	2.8984	1.7363	1.8806
2.1498	3.1098	1.8244	1.9793
2.1778	3.1501	1.8406	1.9968
2.2474	3.2526	1.8822	2.0430
2.3188	3.3570	1.9245	2.0896
2.4859	3.5977	2.0202	2.1928
2.5856	3.7410	2.0777	2.2546
2.7176	3.9278	2.1529	2.3338
2.8124	4.0574	2.2052	2.3861
2.8226	4.0740	2.2118	2.3943
2.9872	4.3003	2.3032	2.4867
3.0349	4.3646	2.3291	2.5123
3.1799	4.5632	2.4079	2.5916
3.1921	4.5788	2.4142	2.5972
3.2655	4.6792	2.4533	2.6364
3.3106	4.7389	2.4764	2.6585
3.3943	4.8530	2.5198	2.7021
3.4799	4.9667	2.5619	2.7423
3.5898	5.1172	2.6157	2.7965

Table 33. Isopiestic molalities and osmotic coefficients for $DyCl_3$ and KCl

m_{DyCl_3}	m_{KCl}	ϕ_{KCl}	ϕ_{DyCl_3}
0.10605	0.18276	0.9146	0.7881
0.11892	0.20604	0.9125	0.7904
0.14490	0.25359	0.9090	0.7954
0.17254	0.30533	0.9066	0.8022
0.23534	0.42947	0.9007	0.8218
0.38151	0.74856	0.8968	0.8799
0.47609	0.97920	0.8973	0.9228
0.59284	1.2942	0.8996	0.9820
0.67523	1.5314	0.9030	1.0240
0.75024	1.7636	0.9074	1.0665
0.82554	2.0044	0.9125	1.1078
0.91286	2.3073	0.9192	1.1616
0.95764	2.4682	0.9231	1.1896
1.0781	2.9141	0.9344	1.2630
1.1930	3.3757	0.9470	1.3398
1.2661	3.6788	0.9553	1.3879
1.3561	4.0686	0.9668	1.4503
1.4119	4.3152	0.9741	1.4886
1.5070	4.7520	0.9868	1.5559

Table 34. Isopiestic molalities and osmotic coefficients for $DyCl_3$ and $CaCl_2$

m_{DyCl_3}	m_{CaCl_2}	ϕ_{CaCl_2}	ϕ_{DyCl_3}
1.4119	2.0222	1.3841	1.4868
1.5070	2.1694	1.4382	1.5528
1.5322	2.2066	1.4524	1.5688
1.6208	2.3485	1.5072	1.6380
1.7163	2.4948	1.5659	1.7072
1.7906	2.6099	1.6135	1.7638

Table 34 (continued)

m_{DyCl_3}	m_{CaCl_2}	ϕ_{CaCl_2}	ϕ_{DyCl_3}
1.8918	2.7661	1.6797	1.8419
1.9769	2.8984	1.7363	1.9093
2.1008	3.0864	1.8150	1.9999
2.1156	3.1098	1.8244	2.0113
2.1446	3.1501	1.8406	2.0277
2.2818	3.3570	1.9245	2.1235
2.3840	3.5112	1.9855	2.1932
2.4438	3.5977	2.0202	2.2306
2.6312	3.8713	2.1301	2.3505
2.6693	3.9278	2.1529	2.3760
2.7592	4.0574	2.2052	2.4321
2.7706	4.0740	2.2118	2.4393
2.9300	4.3003	2.3032	2.5353
2.9765	4.3646	2.3291	2.5616
3.1164	4.5632	2.4079	2.6444
3.1292	4.5788	2.4142	2.6494
3.2003	4.6792	2.4533	2.6901
3.2020	4.6816	2.4543	2.6913
3.2434	4.7389	2.4764	2.7136
3.3247	4.8530	2.5198	2.7587
3.4074	4.9667	2.5619	2.8007
3.4975	5.0952	2.6081	2.8497
3.5562	5.1742	2.6353	2.8758
3.6196	5.2607	2.6648	2.9047
3.6302	5.2766	2.6702	2.9111

nature of the $h/\sqrt{m}$ curve makes any extrapolation to zero concentration very uncertain without the aid of points below 0.1 molal.

For the rare-earth chlorides studied in this research,

the activity coefficients up to a concentration of about

0.03 molal had been determined from electromotive force

measurements on concentration cells with transference. These

determinations were carried out for lanthanum and samarium

chlorides by Spedding, Porter, and Wright (8), for gadolin-

ium chloride by Spedding and Yaffe (9), and for neodymium

and dysprosium chlorides by Spedding and Dye (10).

In this research the activity coefficient at various

molalities for each rare-earth chloride was calculated rela-

tive to the activity coefficient value obtained for the

highest concentration studied in the electromotive force

measurements. The $h/\sqrt{m}$ isopiestic curve for each rare-

earth chloride could be extrapolated quite easily to the

$h/\sqrt{m}$ value corresponding to this reference concentration.

The $h/\sqrt{m}$ value and hence osmotic coefficient for the refer-

ence concentration were calculated from the activity coeffi-

cient data by means of Equation 88, namely,

$$\emptyset = 1 + \frac{1}{m} \int_0^{\ln(\gamma_{\pm})} m \; d \; \ln(\gamma_{\pm}) \quad . \tag{88}$$

The integral was evaluated graphically using a Keuffel and

Esser compensating polar planimeter. For neodymium,

samarium, gadolinium, and dysprosium chlorides, the $h/\sqrt{m}$

vs. $\sqrt{m}$ graphical integration was then carried out from

this reference concentration to the concentration of interest using the planimeter. The procedure for lanthanum chloride was slightly different. The osmotic and activity coefficients of lanthanum chloride had previously been determined up to a concentration of 1·1 molal by Heiser (20) using the isopiestic method. Since the osmotic coefficient data of Heiser and that obtained in this research were in good agreement down to 0.7 molal, measurements were not extended below this concentration. The $h/\sqrt{m}$ vs. $\sqrt{m}$ graphical integration was carried out starting with a concentration of 0.7 molal. The activity coefficients were then calculated relative to the value at the reference concentration employed by Heiser, which was the highest concentration studied in the electromotive force measurements of Spedding, Porter, and Wright (8).

To calculate the activity coefficient at a concentration m relative to the value at the reference concentration, Equation 95 was expressed in the following manner:

$$\log(\gamma_\pm)_m = \frac{-h - 2\int_0^{\sqrt{m_r}} h/\sqrt{m}\ d\sqrt{m} - 2\int_{\sqrt{m_r}}^{\sqrt{m}} h/\sqrt{m}\ d\sqrt{m}}{2.30258} \quad . \quad (98)$$

Since

$$\log(\gamma_\pm)_{m_r} = \frac{-(h)_{m_r} - 2\int_0^{\sqrt{m_r}} h/\sqrt{m}\, d\sqrt{m}}{2.30258} \quad , \quad (99)$$

$$[\log(\gamma_\pm)_{m_r} - \log(\gamma_\pm)_m] = \frac{-(h)_{m_r} + h + 2\int_{\sqrt{m_r}}^{\sqrt{m}} h/\sqrt{m}\, d\sqrt{m}}{2.30258} . \quad (100)$$

Thus the activity coefficient at a molality m, relative to the value at the reference concentration, is given by

$$\log(\gamma_\pm)_m = - [\log(\gamma_\pm)_{m_r} - \log(\gamma_\pm)_m] + \log(\gamma_\pm)_{m_r}. \quad (101)$$

In Tables 35 through 39 are given the values of the molal osmotic coefficient, ϕ, at round concentrations as read from the $h/\sqrt{m}$ vs. $\sqrt{m}$ plots; the measured values of the integral term of Equation 100; the logarithm differences for the activity coefficients as calculated from Equation 100; and values of the mean molal activity coefficient, $\gamma_\pm$, as calculated from Equation 101. The first entry in each column of the tables gives the value of the quantity at the reference concentration, while the last entry gives the value for the saturated solution. In Table 35 for lanthanum chloride, the data up to a concentration of 0.7

Table 35. Molal osmotic and activity coefficients for lanthanum chloride at round concentrations

m	ϕ	$\int_{\sqrt{m_r}}^{\sqrt{m}} h/\sqrt{m}\ d\sqrt{m}$	$[\log(\gamma_\pm)_{m_r} - \log(\gamma_\pm)_m]$	$\gamma_\pm$
0.031186	0.7955	0.0	0.0	0.4319
0.1	0.7724	0.12817	0.12136	0.3266
0.2	0.7967	0.20409	0.17675	0.2875
0.3	0.8277	0.24241	0.19657	0.2747
0.4	0.8636	0.26501	0.20061	0.2721
0.5	0.9050	0.27795	0.19387	0.2764
0.6	0.9494	0.28477	0.18051	0.2850
0.7	0.9950	0.28699	0.16263	0.2970
0.8	1.0468	0.28565	0.13897	0.3136
0.9	1.0992	0.28139	0.11252	0.3333
1.0	1.1537	0.27477	0.08310	0.3567
1.1	1.2096	0.26614	0.05132	0.3838
1.2	1.2669	0.25580	0.01746	0.4149
1.3	1.3270	0.24389	-0.01899	0.4512
1.4	1.3871	0.23070	-0.05655	0.4920
1.5	1.4468	0.21631	-0.09497	0.5375
1.6	1.5066	0.20092	-0.13431	0.5884
1.7	1.5681	0.18463	-0.17517	0.6465
1.8	1.6328	0.16745	-0.21819	0.7138
1.9	1.6979	0.14946	-0.26209	0.7897
2.0	1.7628	0.13074	-0.30653	0.8748
2.2	1.8847	0.09147	-0.39358	1.069
2.4	1.9982	0.05048	-0.47848	1.300
2.6	2.1034	0.00837	-0.56074	1.571
2.8	2.2021	-0.03435	-0.64072	1.888
3.0	2.2967	-0.07747	-0.71925	2.263
3.2	2.3864	-0.12077	-0.79582	2.699
3.4	2.4707	-0.16409	-0.87006	3.202
3.6	2.5470	-0.20726	-0.94069	3.768
3.8	2.6211	-0.25010	-1.01008	4.420
3.8944	2.6563	-0.27020	-1.04283	4.767

Table 36. Molal osmotic and activity coefficients for
neodymium chloride at round concentrations

m	ϕ	$\int_{\sqrt{m_r}}^{\sqrt{m}} h/\sqrt{m}\ d\sqrt{m}$	$[\log(\gamma_{\pm})_{m_r} - \log(\gamma_{\pm})_m]$	$\gamma_{\pm}$
0.03352	0.7892	0.0	0.0	0.4178
0.1	0.7768	0.12296	0.11219	0.3227
0.2	0.7996	0.19679	0.16641	0.2848
0.3	0.8311	0.23471	0.18567	0.2725
0.4	0.8662	0.25663	0.18947	0.2701
0.5	0.9075	0.26941	0.18263	0.2744
0.6	0.9531	0.27587	0.16844	0.2835
0.7	1.0008	0.27771	0.14932	0.2962
0.8	1.0508	0.27605	0.12616	0.3125
0.9	1.1040	0.27154	0.09914	0.3325
1.0	1.1603	0.26461	0.06867	0.3567
1.1	1.2186	0.25561	0.03553	0.3850
1.2	1.2775	0.24486	0.00062	0.4172
1.3	1.3382	0.23256	-0.03643	0.4544
1.4	1.3999	0.21890	-0.07509	0.4967
1.5	1.4622	0.20405	-0.11504	0.5445
1.6	1.5256	0.18813	-0.15641	0.5989
1.7	1.5906	0.17123	-0.19932	0.6611
1.8	1.6579	0.15340	-0.24403	0.7328
1.9	1.7275	0.13468	-0.29052	0.8156
2.0	1.7976	0.11506	-0.33800	0.9098
2.2	1.9303	0.07397	-0.43132	1.128
2.4	2.0557	0.03069	-0.52338	1.394
2.6	2.1731	-0.01413	-0.61330	1.715
2.8	2.2858	-0.05945	-0.70161	2.102
3.0	2.3961	-0.10571	-0.78969	2.574
3.2	2.5034	-0.15257	-0.87699	3.147
3.4	2.6031	-0.19976	-0.96128	3.822
3.6	2.6967	-0.24678	-1.04277	4.610
3.8	2.7849	-0.29391	-1.12201	5.533
3.9307	2.8383	-0.32457	-1.17183	6.206

Table 37. Molal osmotic and activity coefficients for samarium chloride at round concentrations

m	ϕ	$\int_{\sqrt{m}_r}^{\sqrt{m}} h/\sqrt{m}\ d\sqrt{m}$	$[\log(\gamma_\pm)_{m_r} - \log(\gamma_\pm)_m]$	$\gamma_\pm$
0.03646	0.7811	0.0	0.0	0.4105
0.1	0.7785	0.11375	0.09993	0.3261
0.2	0.8029	0.18679	0.15278	0.2888
0.3	0.8350	0.22401	0.17116	0.2768
0.4	0.8734	0.24523	0.17292	0.2757
0.5	0.9142	0.25721	0.16561	0.2804
0.6	0.9611	0.26296	0.15023	0.2905
0.7	1.0092	0.26418	0.13040	0.3040
0.8	1.0608	0.26190	0.10601	0.3216
0.9	1.1159	0.25670	0.07757	0.3434
1.0	1.1741	0.24908	0.04567	0.3695
1.1	1.2325	0.23945	0.01194	0.3994
1.2	1.2921	0.22805	-0.02384	0.4337
1.3	1.3532	0.21515	-0.06158	0.4730
1.4	1.4155	0.20089	-0.10103	0.5180
1.5	1.4792	0.18548	-0.14208	0.5694
1.6	1.5442	0.16894	-0.18467	0.6280
1.7	1.6100	0.15150	-0.22840	0.6946
1.8	1.6791	0.13309	-0.27440	0.7722
1.9	1.7492	0.11378	-0.32161	0.8608
2.0	1.8198	0.09367	-0.36974	0.9617
2.2	1.9541	0.05142	-0.46477	1.197
2.4	2.0788	0.00721	-0.55732	1.481
2.6	2.1973	-0.03834	-0.64835	1.827
2.8	2.3114	-0.08482	-0.73828	2.247
3.0	2.4214	-0.13196	-0.82699	2.756
3.2	2.5256	-0.17951	-0.91355	3.364
3.4	2.6248	-0.22728	-0.99812	4.087
3.6	2.7183	-0.27508	-1.08025	4.938
3.6414	2.7370	-0.28496	-1.09695	5.132

Table 38. Molal osmotic and activity coefficients for gadolinium chloride at round concentrations

m	$\emptyset$	$\displaystyle\int_{\sqrt{m}_r}^{\sqrt{m}} h/\sqrt{m}\, d\sqrt{m}$	$[\log(\gamma_\pm)_{m_r} - \log(\gamma_\pm)_m]$	$\gamma_\pm$
0.03515	0.7897	0.0	0.0	0.4172
0.1	0.7835	0.11553	0.10304	0.3291
0.2	0.8087	0.18700	0.15417	0.2925
0.3	0.8418	0.22288	0.17096	0.2814
0.4	0.8808	0.24312	0.17161	0.2810
0.5	0.9254	0.25405	0.16173	0.2875
0.6	0.9749	0.25871	0.14428	0.2993
0.7	1.0281	0.25865	0.12112	0.3157
0.8	1.0826	0.25502	0.09430	0.3358
0.9	1.1396	0.24852	0.06390	0.3601
1.0	1.1988	0.23964	0.03048	0.3889
1.1	1.2595	0.22875	-0.00534	0.4224
1.2	1.3224	0.21612	-0.04363	0.4613
1.3	1.3877	0.20193	-0.08431	0.5066
1.4	1.4536	0.18635	-0.12647	0.5582
1.5	1.5205	0.16957	-0.17010	0.6172
1.6	1.5891	0.15168	-0.21543	0.6851
1.7	1.6584	0.13278	-0.26194	0.6626
1.8	1.7297	0.11295	-0.31013	0.8521
1.9	1.8029	0.09224	-0.35991	0.9555
2.0	1.8745	0.07074	-0.40968	1.072
2.2	2.0112	0.02583	-0.50806	1.344
2.4	2.1409	-0.02102	-0.60508	1.680
2.6	2.2632	-0.06914	-0.69999	2.091
2.8	2.3808	-0.11810	-0.79359	2.594
3.0	2.4939	-0.16775	-0.88583	3.208
3.2	2.6018	-0.21765	-0.97604	3.948
3.4	2.7043	-0.26783	-1.06414	4.836
3.5898	2.7967	-0.31535	-1.14554	5.833

Table 39. Molal osmotic and activity coefficients for dysprosium chloride at round concentrations

m	ϕ	$\int_{\sqrt{m}_r}^{\sqrt{m}} h/\sqrt{m}\ d\sqrt{m}$	$[\log(\gamma_\pm)_{m_r} - \log(\gamma_\pm)_m]$	$\gamma_\pm$
0.03456	0.7808	0.0	0.0	0.4090
0.1	0.7875	0.12438	0.10513	0.3211
0.2	0.8107	0.19543	0.15676	0.2851
0.3	0.8448	0.23070	0.17259	0.2749
0.4	0.8865	0.25036	0.17156	0.2755
0.5	0.9347	0.26047	0.15940	0.2833
0.6	0.9857	0.26414	0.14044	0.2960
0.7	1.0378	0.26329	0.11708	0.3124
0.8	1.0935	0.25894	0.08911	0.3331
0.9	1.1534	0.25172	0.05682	0.3588
1.0	1.2156	0.24204	0.02140	0.3893
1.1	1.2790	0.23028	-0.01635	0.4247
1.2	1.3447	0.21666	-0.05671	0.4660
1.3	1.4117	0.20152	-0.09896	0.5137
1.4	1.4804	0.18500	-0.14314	0.5687
1.5	1.5498	0.16724	-0.18871	0.6316
1.6	1.6227	0.14831	-0.23681	0.7056
1.7	1.6960	0.12837	-0.28597	0.7901
1.8	1.7713	0.10740	-0.33688	0.8884
1.9	1.8487	0.08543	-0.38958	1.003
2.0	1.9259	0.06272	-0.44283	1.134
2.2	2.0697	0.01513	-0.54662	1.440
2.4	2.2026	-0.03432	-0.64729	1.816
2.6	2.3324	-0.08505	-0.74773	2.288
2.8	2.4568	-0.13671	-0.84662	2.873
3.0	2.5762	-0.18908	-0.94397	3.595
3.2	2.6900	-0.24172	-1.03911	4.475
3.4	2.7974	-0.29463	-1.13171	5.539
3.6	2.8920	-0.34687	-1.21817	6.769
3.6302	2.9116	-0.35537	-1.23407	7.011

molal are those obtained by Heiser (20). In Figure 20, the osmotic coefficients for these rare-earth chlorides are plotted as function of the molality. The activity coefficients are likewise plotted as a function of molality in Figure 21.

4. Simultaneous determination of solubility and osmotic coefficient

The isopiestic method can be adapted to the simultaneous determination of solubility and the osmotic coefficient for the saturated solution of a salt. The following procedure was employed in such determinations for the rare-earth chlorides. Into two of the equilibration cups an unweighed quantity of near-saturated solution of a rare-earth chloride was added to about a gram of the solid rare-earth chloride hydrate. Two additional cups of a rare-earth chloride solution of known concentration less than saturated were weighed out. A third pair of cups contained a weighed quantity of a calcium chloride reference solution. The solutions were then equilibrated in one of the chambers using the procedure previously outlined. At equilibrium the concentration of the rare-earth chloride solutions not in contact with a solid phase must be the same as that in the solutions in equilibrium with the solid phase. The calculated isopiestic molality is thus identical with the
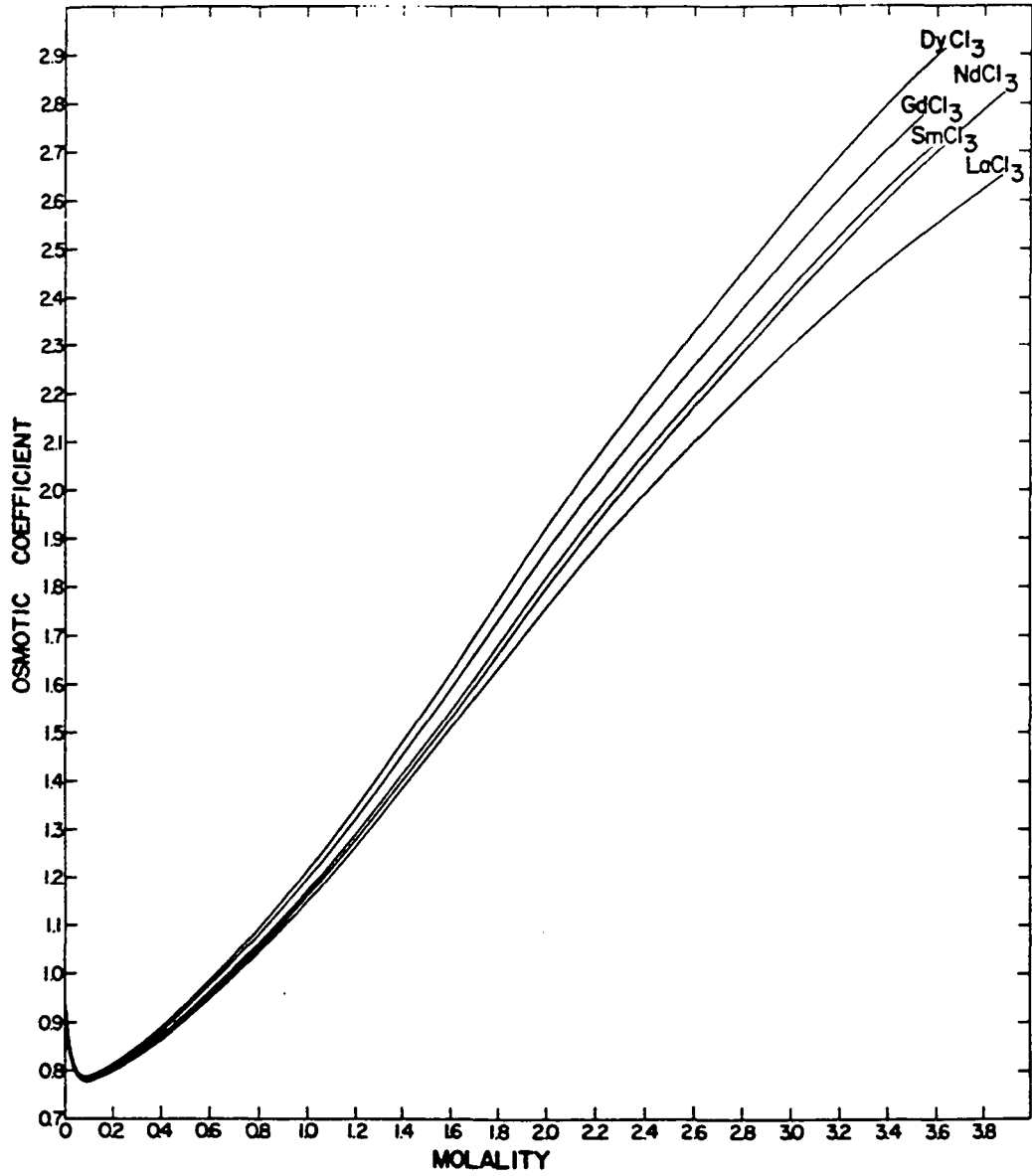
Figure 20.   Molal osmotic coefficients of some rare-
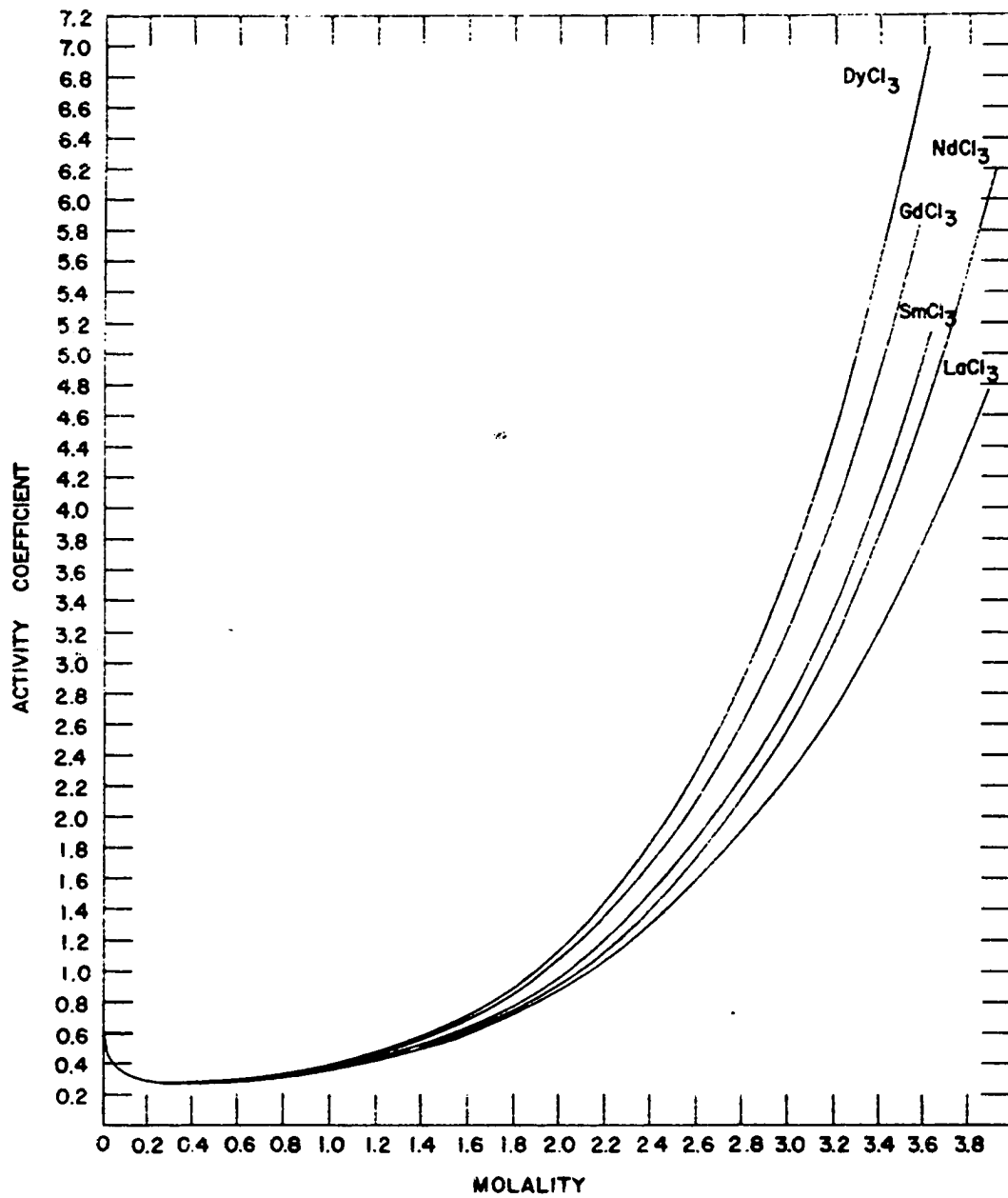earth chlorides in aqueous solutions
at 25° C.

Figure 21. Molal activity coefficients of some rare-earth chlorides in aqueous solutions at 25° C.

solubility. The solubility was thus determined without separation of the solution and solid phases. This method of measuring solubility is particularly convenient for cases of high solubility varying rapidly with temperature, and with viscous saturated solutions. The molal solubilities determined by this method are given in Table 2. They are in agreement with the solubilities determined by direct analysis within 0.05 per cent. The osmotic coefficient for the saturated solutions was calculated from the isopiestic molalities and the osmotic coefficient of the calcium chloride solution by means of Equation 77. The osmotic and activity coefficient values for the saturated solutions are included in Tables 35 through 39.

D. Discussion of Results

The accuracy of the activity coefficients determined in this research depends on the uncertainty in the osmotic coefficient values used to plot the $h/\sqrt{m}$ vs. $\sqrt{m}$ curves, the accuracy with which the areas under the curves could be measured, and the uncertainty in the reference value employed. The uncertainty in the osmotic coefficient data is determined by the uncertainties in the experimental isopiestic molalities and the osmotic coefficient data for the reference salt. As has been previously stated, the probable error in the concentrations of the stock solutions

was estimated to be 0.05 per cent. An equilibration was considered complete when the concentrations of a pair of solutions of the same salt approached from opposite sides within 0.1 per cent of the average for that salt at rare-earth chloride concentrations above 0.2 molal. Below 0.2 molal an approach within 0.15 per cent was considered satisfactory. The precision of the osmotic coefficient data is thus at worst 0.15 per cent for concentrations above 0.2 molal, and 0.2 per cent below 0.2 molal. The accuracy of the osmotic coefficient data depends upon that of the reference data.

The areas under the curves were measured with a Keuffel and Esser compensating polar planimeter, accurate to 0.1 cm.^{2} on a 100 cm.^{2} standard circle or square. The planimeter could be manipulated with a reproducibility of $\pm$ 0.2 cm.^{2} on an irregular figure. The curves were so plotted that an error of 5.0 cm.^{2} in the area measurement would produce only a 0.1 per cent change in the activity coefficient for the saturated solution. The precision of the activity coefficient values is thus estimated to be about $\pm$ 0.2 per cent.

Osmotic and activity coefficient determinations had previously been carried out by the isopiestic method for lanthanum chloride in the concentration range between 0.1 and 2.0 molal by Robinson (143, 144), Mason (134, 135, 136),

and as previously stated Heiser (20). The results obtained
by these investigators and in this research are on the whole
in good agreement. In Figure 22, the osmotic coefficient
data obtained by Mason, Heiser, and in this research are
plotted as a function of the molality. Mason (135, 136)
also carried out osmotic and activity coefficient determina-
tions for neodymium and samarium chlorides up to a concen-
tration of 2.0 molal. In Figures 23 and 24, the osmotic
coefficient data for neodymium and samarium chlorides
obtained by Mason and in this research are shown. It is
seen that the deviation of Mason's data from those obtained
in this research increases in going from lanthanum to
neodymium to samarium chloride. While the osmotic coeffi-
cient data obtained in this research show negligible scatter,
the data of Mason, especially those for samarium chloride,
exhibit considerable scatter. The osmotic coefficient and
hence activity coefficient values of Mason are generally
higher than those obtained in this research. For neodymium
chloride the smoothed osmotic coefficient values at round
concentrations obtained by Mason differ by from 0.1 to 0.8
per cent from the corresponding values obtained in this
research. For samarium chloride the differences are greater.
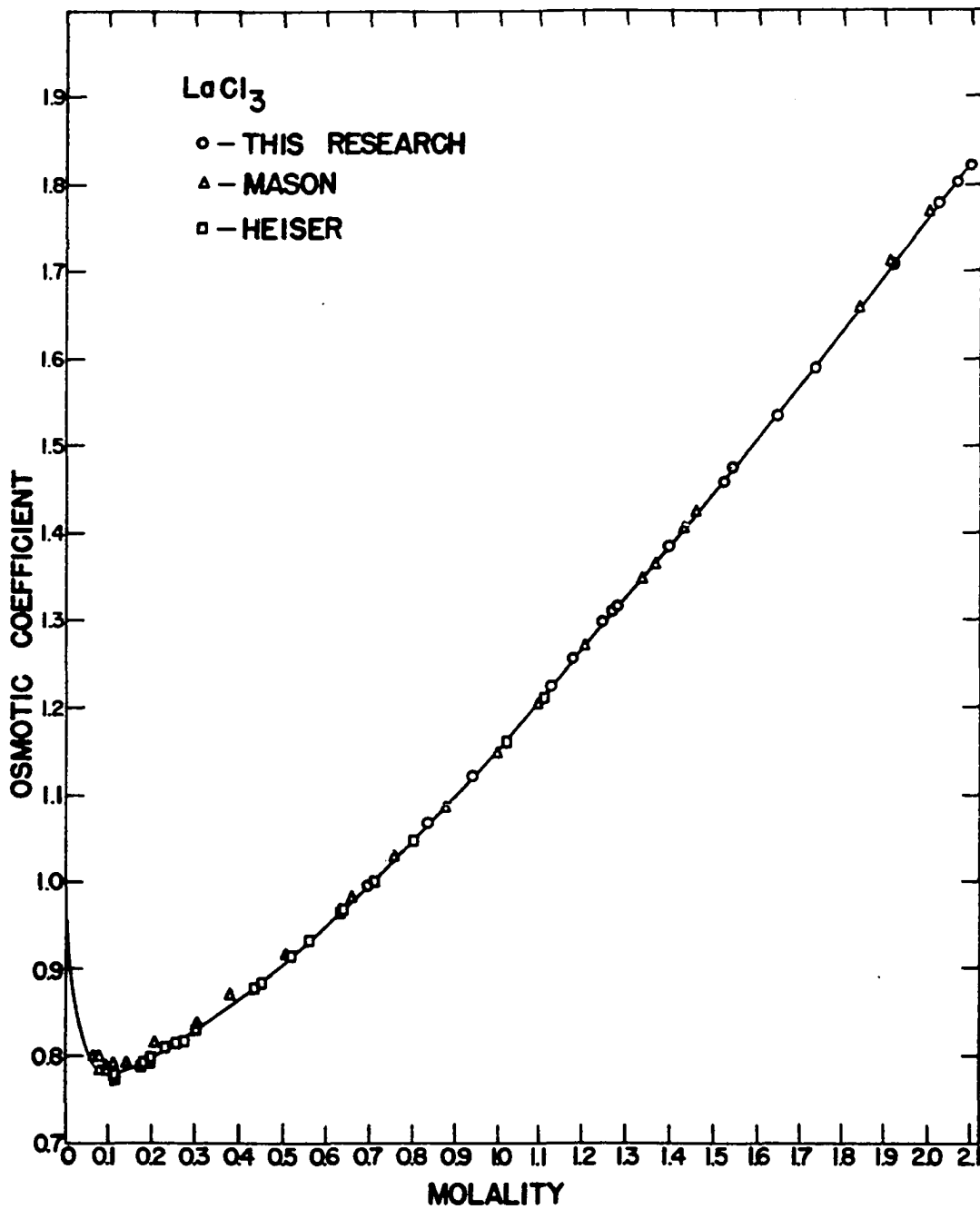While the differences in osmotic coefficient values are

Figure 22. Molal osmotic coefficients for lanthanum
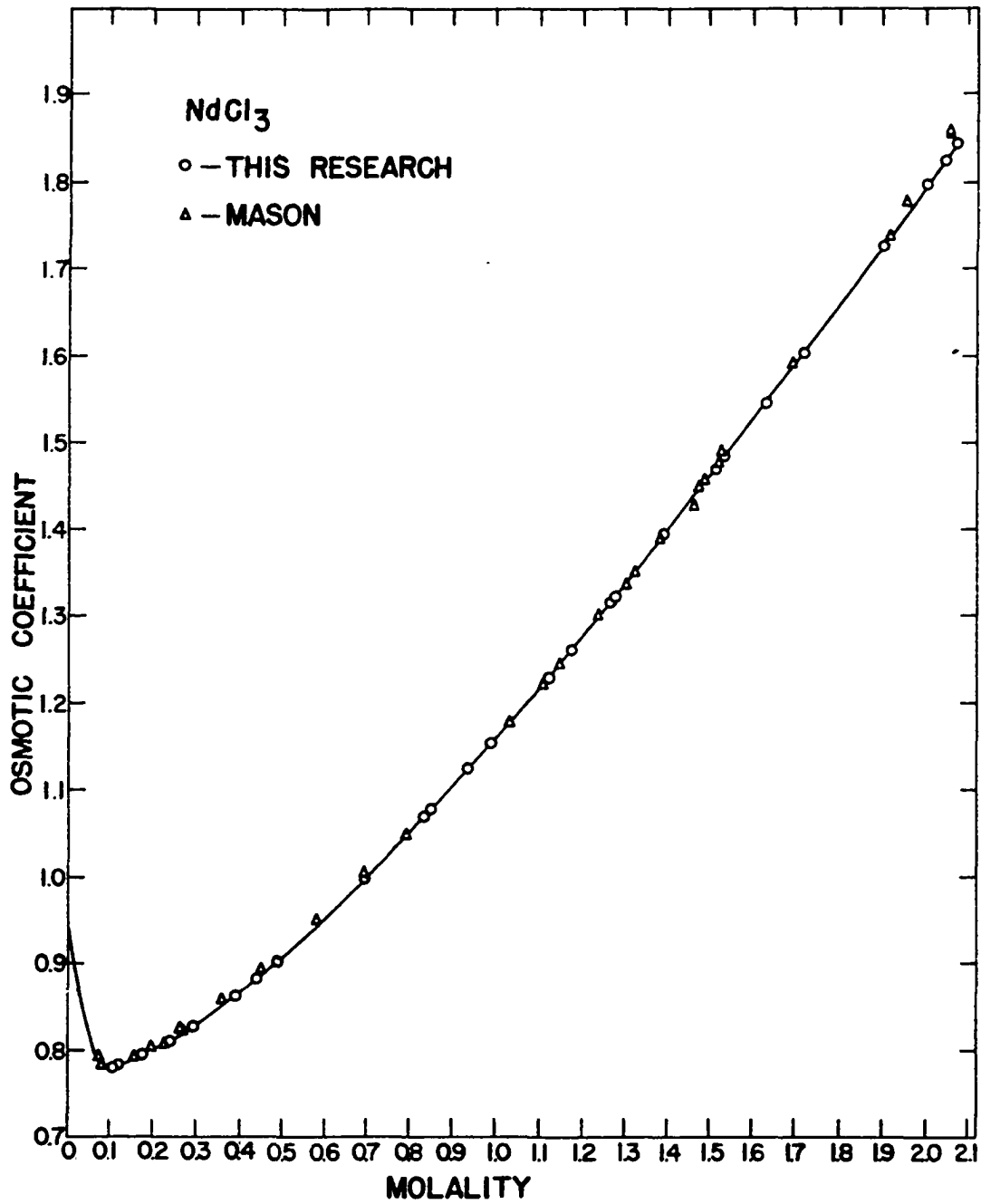chloride in aqueous solutions at 25° C.

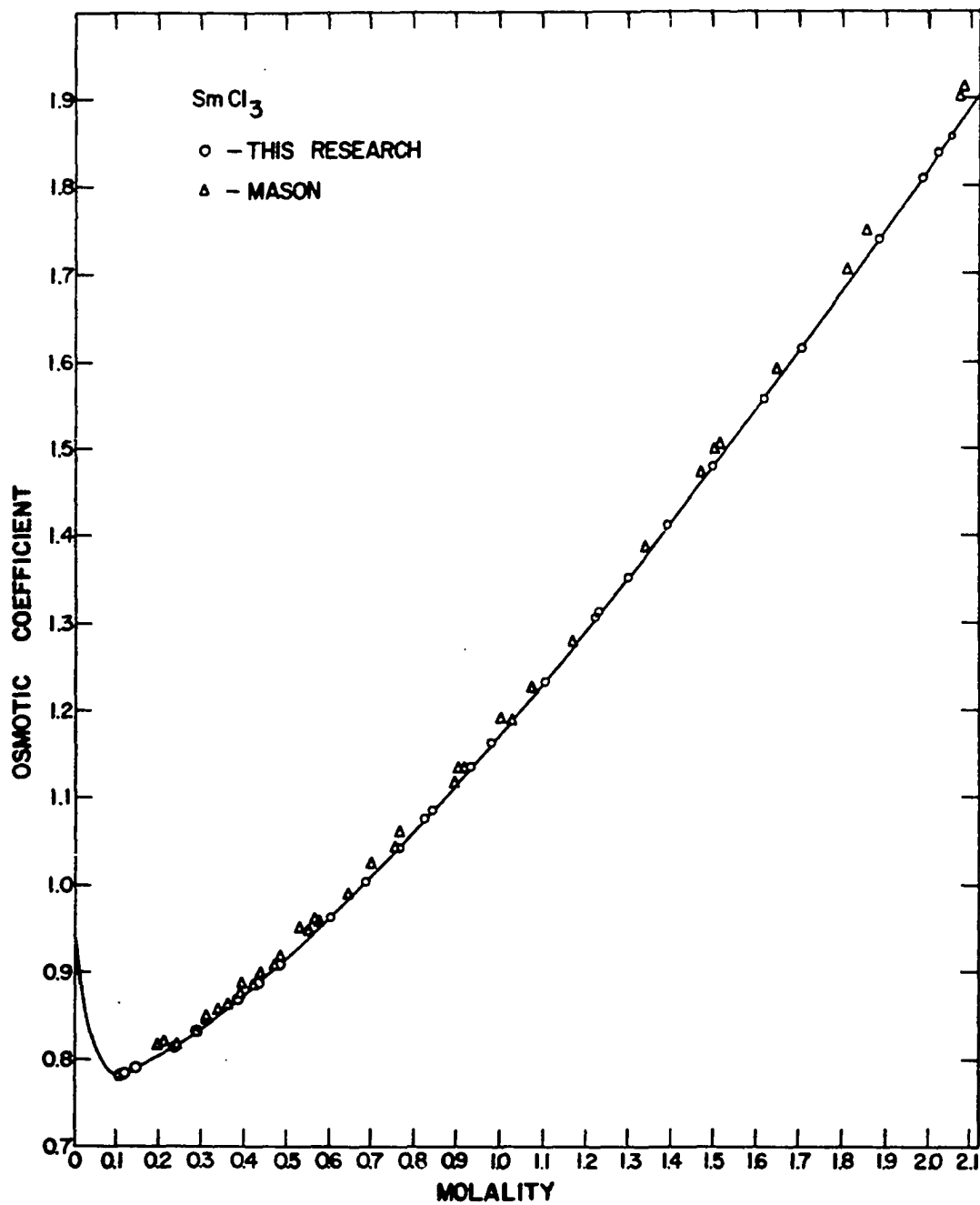Figure 23. Molal osmotic coefficients for neodymium chloride in aqueous solutions at 25° C.

Figure 24. Molal osmotic coefficients for samarium
chloride in aqueous solutions at 25° C.

_not large, they are outside the supposed limit of error.

Since the deviation of Mason's data increases with in-
creasing atomic number of the rare earth, it would seem most
likely that the composition of his solutions is the source
of the discrepancy. Mason prepared his solutions from the
hydrated salt which had been previously dried in a current
of warm air at 50° to 70° C. Such treatment could quite
conceivably cause oxychloride formation, the tendency in-
creasing with increasing atomic number of the rare earth.
The method of preparation employed in this research has al-
ready been described in Section III.

At a given concentration, the osmotic and activity co-
efficients of the rare-earth chlorides increase with in-
creasing atomic number of the rare earth. The osmotic
coefficient curves, shown in Figure 20, are the activity
coefficient curves, shown in Figure 21, are similar in
shape for the rare-earth chlorides studied in this research.
The activity coefficient curves drop steeply from unity at
infinite dilution, pass through a rather flat minimum in
the concentration range between 0.2 and 0.6 molal, and then
rise markedly with increasing concentration. High values
of the activity coefficient in concentrated solutions are
generally considered to be due to hydration effects. The
ion-solvent interactions tend to hold the solvent in solu-
tion, with a consequent decrease in the solvent vapor

pressure from the ideal value, and a corresponding increase in the activity coefficient of the solute.

VIII. GENERAL SUMMARY

The aqueous solution behavior of some rare-earth chlorides has been investigated at 25° C. in the concentration range between 0.02 molal and saturation. Density measurements on solutions of lanthanum, neodymium, samarium, gadolinium, dysprosium, erbium, and ytterbium chlorides were carried out by a pycnometric method with an estimated accuracy of 1×10^{-5} gm. per ml. From the density data the apparent molal volumes for these rare-earth chlorides were calculated. The apparent molal volume data for each rare-earth chloride were expressed as a function of the square root of the molality by a five-parameter power series from which partial molal volumes were calculated. Conductance measurements on solutions of these rare-earth chlorides were carried out over the same concentration range using the conventional alternating-current technique. In addition, the solubilities of the rare-earth chlorides at 25° C. were determined.

Osmotic and activity coefficient determinations for solutions of lanthanum, neodymium, samarium, gadolinium, and dysprosium chlorides were carried out in the concentration range between 0.1 molal and saturation by the isopiestic comparison method using potassium chloride and calcium chloride reference solutions. The solubilities of

these salts at 25° C. were also determined by an adaptation of the isopiestic method.

The apparent and partial molal volumes of the rare-earth chlorides at a given concentration do not show a regular decrease with increasing atomic number of the rare-earth as might be expected from the decreasing ionic radius. This irregular order can be explained qualitatively on the basis of a change in the water coordination number for the rare-earth ion occurring in the middle of the rare-earth series.

The specific and equivalent conductances at a given concentration were found to decrease with increasing atomic number of the rare earth except for the reversal in position of lanthanum and neodymium chlorides. The general trend is in line with the expectation that the smallest ions will be the most heavily hydrated and thus have the lowest mobility. The change in the specific and equivalent conductances at a given concentration between adjacent rare-earth chlorides is much greater in the middle of the series than at either end. It is likely that this behavior together with the reversal in position of the lanthanum and neodymium chloride curves are related to the indicated change in coordination number, since such a change would undoubtedly alter the effective radius of the ions and hence their mobility. The specific conductance curves exhibit a maximum, the concentration at the maximum decreasing

slightly with increasing atomic number of the rare earth.
The equivalent conductance curves show a general divergence
with increasing concentration up to a concentration between
four and five normal; the curves begin to converge in this
region with a seeming approach toward a common limit as
saturation is reached.

The osmotic and activity coefficients for the rare-earth
chlorides at a given concentration show a general increase
with increasing atomic number of the rare-earth. The osmotic
coefficient curves are very similar in shape, as is also the
case for the activity coefficient curves. The activity co-
efficient curves drop steeply from unity at infinite dilu-
tion, pass through a rather flat minimum between 0.2 and 0.6
molal, and then rise markedly with increasing concentration.
The rather marked rise in the high concentration region is
generally interpreted in terms of the extensive hydration
of the cations.

The solubility data for the rare-earth chlorides indi-
cate that the solubility rises to a maximum for cerium or
praseodymium chloride, reaches a minimum at europium
chloride, and continues to increase for the heavier rare-
earth chlorides.

Before more than a very qualitative interpretation of
the many irregularities noted for solution properties of
rare-earths salts can be made, additional data on the

properties measured in this research and other solution prop-
erties are needed.

IX. BIBLIOGRAPHY

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