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Apparent molal volumes of some dilute aqueous rare earth salt solutions at 25°C

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RARE EARTH SALT SOLUTIONS AT 25° C.

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APPARENT MOLAL VOLUMES OF SOME DILUTE
AQUEOUS RARE EARTH SALT SOLUTIONS AT 25° C

by

Peter Francis Cullen

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
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DOCTOR OF PHILOSOPHY

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Approved:

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1969

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I. INTRODUCTION

The interactions occurring in an electrolytic solution may be generally classified into two categories: 1) ion-solvent interactions, and 2) ion-ion interactions. An understanding of these two types of interactions is the goal of all basic studies on solutions of electrolytes. Often the nature of the pure solvent, itself, is not well known. Water, the most common of all solvents from the standpoint of usage, is one of the most uncommon from the standpoint of properties. To date, no theoretical model has satisfactorily accounted for all the properties of liquid water. Ion-ion interactions may be somewhat artificially classified into long range electrostatic interactions and short range interactions characterized by the formation of complexes which are often covalent in nature. Of course, there are many complexes which are predominantly electrostatic in nature. Also, an ion pair, an aggregate of two ions separated by at least one solvent molecule, would seem to fall somewhere in between the long range and short range classifications. Furthermore, the interactions of an ion with a polar solvent molecule such as water is, in many cases, really little different in character from the complex formation of two ions. The utility of the classifications, then, is not in that they are totally inclusive, which they are not, but that they bring some order to the study and understanding of electrolytic solutions.

Successful theoretical treatment of these solutions is thus far limited to dilute solutions where the predominant ion-ion interactions are long range, electrostatic in nature and where the solvent may be considered a structureless continuum. Tests of these theories, particularly for higher valence type electrolytes, are often more informative by their deviations from theoretical behavior than from their conformity to the theory.

Previous studies of the apparent molal volumes of rare earth chlorides and nitrates have revealed two interesting facts (1, 2, 3). First, while all of the chlorides studied and also Er and Yb nitrate appeared to conform to the Debye-Hückel solution theory in the dilute range (<0.05 molal), La and Nd nitrate did not. Ayers suggested that this might be due to the formation of an appreciable amount of a nitrate complex of La and Nd in the concentration range studied (1). Second, the apparent molal volumes at infinite dilution for a given rare earth anion series did not decrease regularly with decreasing rare earth ionic radius as one might infer, but seemed to fall into two decreasing series with Sm and Gd falling in between. Ayers suggested a change in the coordination of the solvent molecules about the rare earth ions to explain this behavior. Pikal found that, for the chlorides, the change was very likely occurring in the region of Sm and Gd (3).

This study had the objective to investigate a third rare earth anion series where the assumption that no complex formation is occurring can be made. The rare earth perchlorate salts were chosen for this purpose. This allowed a further check on whether or not the rare earth salts approached the Debye-Hückel limiting law in dilute solution. The data could also be tested against the Debye-Hückel theory when the effect of the α parameter is included. This study also sought to determine which of the other nitrates deviated markedly from the Debye-Hückel theory at low concentrations. This could be compared with the variation of the stability constants of the rare earth nitrates. Furthermore, the nitrate series, as a whole, could be compared with the chlorides, which complex to a lesser extent than the nitrates, and the perchlorates, which do not complex at all. Lastly, it was desired to determine if the trends in the apparent molal volumes at infinite dilution found by Ayers and Pikal persisted for all the chlorides and nitrates and extended to the perchlorates.

Therefore, the apparent molal volumes of aqueous solutions of Eu, Tm and Lu chlorides; Pr, Sm, Eu, Gd, Tb, Dy, Ho, Tm and Lu nitrate; and La, Nd, Gd and Lu perchlorate were determined at 25^o C from 0.0015 to about 0.15 molal. It is hoped that in the future this data will also be useful in testing a more complete theory of electrolytic solutions capable of predicting changes in the coordination of ions, formation of

complexes and changes in solvent characteristics. Furthermore, while this data is limited to dilute solutions, it is necessary to any thermodynamic theory of concentrated solutions since it provides an accurate extrapolation to infinite dilution. It will be shown that the partial molal volume at infinite dilution is equal to the partial molal volume in a standard state often chosen for electrolytic solutions.

II. THEORY

A. Introduction

Let Y be an extensive thermodynamic property of a solution which is a function of temperature, pressure, and the amounts of the several constituents. A partial molal value of Y for the i th component is defined by the equation

$$\bar{Y} = \left(\frac{\partial Y}{\partial n_i} \right)_{T, P, n_j, n_k, \dots} \quad (2.1)$$

where

n_i is the number of moles of component i ;

T is the temperature;

P is the pressure;

n_j, n_k, \dots are the number of moles of each of the other components.

The subscripts indicate that T, P, n_j, n_k, \dots are held constant during the differentiation. It is evident that the partial molal quantity is an intensive property and not dependent on the total amount of the i th component. It is, however, dependent upon the relative amounts of the various constituents.

For a multi-component system at constant pressure and temperature

$$Y = f(n_1, n_2, n_3, \dots)$$

Since Y is a homogenous equation of degree one, using Euler's

theorem

$$\begin{aligned}
 Y &= n_1 \left(\frac{\partial Y}{\partial n_1} \right)_{T,P,n_2,n_3,\dots} + n_2 \left(\frac{\partial Y}{\partial n_2} \right)_{T,P,n_1,n_3,\dots} \\
 &+ n_3 \left(\frac{\partial Y}{\partial n_3} \right)_{T,P,n_1,n_2,\dots} + \dots
 \end{aligned}
 \tag{2.2}$$

For a two component system, this may be written in the form of the partial molal quantities

$$Y = n_1 \bar{Y}_1 + n_2 \bar{Y}_2
 \tag{2.3}$$

For the volume of an electrolytic solution the expression becomes

$$V = n_1 \bar{V}_1 + n_2 \bar{V}_2
 \tag{2.4}$$

where the subscript 1 denotes the solvent and subscript 2 denotes the electrolyte.

Another quantity which is more conveniently related to experimental quantities is the apparent molal volume. It is defined as

$$\phi_v = \frac{V - n_1 \bar{V}_1^{\circ}}{n_2}
 \tag{2.5}$$

where \bar{V}_1° is the partial molal volume of the solvent in the standard state, usually taken as the pure solvent. Rearranging Equation 2.5 for V and taking the partial derivative with respect to n_2 yields

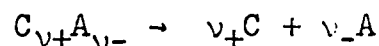
$$\bar{V}_2 = \left(\frac{\partial V}{\partial n_2} \right)_{T,P,n_1} = \phi_v + n_2 \left(\frac{\partial \phi_v}{\partial n_2} \right)_{T,P,n_1} \quad (2.6)$$

As the solution approaches infinite dilution, n_2 approaches 0 and

$$\bar{V}_2^\circ = \phi_v^\circ \quad (2.7)$$

where the superscript \circ denotes infinite dilution.

Suppose an electrolyte dissociates into ions in a solvent according to the reaction



where C and A denote the cations and anions, respectively and ν_+ and ν_- are the number of moles of cations and anions, respectively, given by the dissociation of one mole of electrolyte. The chemical potential of the electrolyte may be given in the notation of Harned and Owen (4) by the expression

$$\begin{aligned} \mu_2 - \mu_2^\circ &= RT \ln a_2 \\ &= \nu RT \ln f_{\pm} + \nu RT \ln N_{\pm} \end{aligned} \quad (2.8)$$

where

μ_2 is the chemical potential of the solute at concentration N_{\pm} ;

μ_2° is the chemical potential of the solute in the standard state;

a_2 is the activity of the electrolyte;

ν is the number of moles of ions given by one mole of electrolyte (equal to $\nu_+ + \nu_-$ for the electrolyte $C_{\nu_+}A_{\nu_-}$);

N_{\pm} is the mean ionic mole fraction defined by $(N_+^{\nu_+} \cdot N_-^{\nu_-})^{1/\nu}$ with N_+ and N_- the mole fractions of cations and anions, respectively;

f_{\pm} is the rational activity coefficient.

The partial molal volume may be obtained by taking the partial derivative with respect to pressure at constant T and N_{\pm}

$$\begin{aligned} \left(\frac{\lambda(\mu_2 - \mu_2^0)}{\partial P} \right)_{T, N_{\pm}} &= \bar{V}_2 - \bar{V}_2^0 \\ &= \nu RT \left(\frac{\lambda(\ln f_{\pm})}{\partial P} \right)_{T, N_{\pm}} \end{aligned} \quad (2.9)$$

Since the solution approaches an ideal solution as the concentration approaches infinite dilution, $f_{\pm} \rightarrow 1$ as $N_{\pm} \rightarrow 0$ at all T and P . Therefore,

$$\bar{V}_2^{\infty} = \bar{V}_2^0 \quad (2.10)$$

That is, the partial molal volume at infinite dilution is equal to the partial molal volume in the standard state.

The choice of the standard state is, of course, arbitrary.

However, for a two component system of electrolyte and solvent, the standard state for the electrolyte is usually

defined as a hypothetical 'ideal' solution at a concentration of unity and activity coefficient equal to 1 at all temperatures and pressures (5). Comparing Equation 2.10 with Equation 2.7 yields

$$\bar{V}_2^0 = \phi_v^0 \quad (2.11)$$

Returning to Equation 2.5 and substituting

$$V = 1000 \text{ ml}$$

$$\bar{V}_1^0 = \frac{M_1}{d_0} \text{ ml/mole}$$

$$n_1 = \frac{1000d - cM_2}{M_1} \text{ moles}$$

yields

$$\phi_v = \frac{1000}{c} \left(1 - \frac{d}{d_0}\right) + \frac{M_2}{d_0} \quad (2.12)$$

where

d is the density of the solution;

d_0 is the density of the solvent;

c is the molar concentration;

M_1 and M_2 are the molecular weights of the solvent and solute, respectively.

The apparent molal volume of a dilute solution, then, can be calculated from a knowledge of the density of the solution and the pure solvent.

B. Electrolytic Solution Theory

The goal of modern electrolytic solution theory is to successfully predict the macroscopic and microscopic properties of an electrolytic solution from a calculation of the distribution, degree of complexing, and hydration of the ions, the properties of the solvent, and the variation of these quantities with concentration, temperature, and pressure. The complexity of the problem is testified to by the fact that the dissociation of an electrolyte into ions in solution was first recognized by Arrhenius in 1887. In spite of much effort by many workers since then, no unified theory has emerged to characterize the properties of electrolytic solutions over a broad concentration range.

The first quantitative theories have been restricted to the area of very dilute solutions in an attempt to eliminate the difficulties due to short range ion-ion interactions such as complexing and to avoid any changes in ion-solvent interactions which might occur at higher concentrations. The problem for dilute solutions is to calculate the change in electrical free energy which occurs when an electrolyte is diluted from one concentration to another as a function of concentration, temperature and pressure. From this function, all of the other thermodynamic properties may be calculated.

In 1912, Milner made the first attempt at solving this problem (6). His treatment involved a laborious numerical

summation of interaction energies for all configurations of ions. Though the result was not easily compared with experimental data, it gave essentially the correct form for dilute solutions. Little further progress was made until the theory of Debye-Hückel was published in 1923 (7).

1. The Debye-Hückel theory

The present theory of electrolytic solutions is based on a greatly simplified picture of an ionic solution. Due to the electroneutrality of the solution, the time average of the charge density at any fixed reference point in solution is, of course, zero. However, the authors assumed that, if a moving coordinate system centered on a particular ion was chosen, this central ion would be surrounded by a charged atmosphere composed of the other ions in the solution. Each positive ion would be surrounded with an "atmosphere" containing on the average more negative ions and less positive ions than the bulk solution, thus inducing a negative charge density in its neighborhood. Similarly, each negative ion would be surrounded with a positively charged atmosphere. The authors sought to calculate the potential as a function of the distance r from the central ion resulting from the central ion and its atmosphere. This potential could be evaluated at $r = a$, the "surface" of the central ion, and the electrostatic contribution to the chemical potential of the solution could be found by calculating the electrical

work done on charging the ions described by the potential function from 0 to their full charge.

In this discussion, the emphasis will be on considering the assumptions and approximations made in the theory and their effect on the final equations. Rigorous derivations are presented in virtually all the standard texts on electrolytic solutions and many texts on statistical thermodynamics (4,5,8,9).

The assumptions contained in the Debye-Hückel theory are:

1. The electrolyte is completely dissociated into non-polarizable spherical ions. Furthermore, none of the ions may approach each other closer than an average distance \bar{a} .

2. The solvent is a continuous, structureless medium with dielectric constant D . The dielectric constant is not a function of the concentration.

3. The electrostatic properties of the central ion and its atmosphere obey Poisson's equation.

4. The distribution of the ions about the central ion may be represented by Boltzmann's distribution law.

5. The system obeys the theorem of the linear superposition of fields.

6. The departure of dilute solutions from ideal behavior is due solely to the electrostatic interaction of the ions.

For a given configuration of ions, the potential about the j th ion, $\psi_j(r)$, may be related, using Poisson's equation,

to the charge density surrounding the j th ion, $\rho(r)$, by the expression

$$\nabla^2 \psi_j(r) = -4\pi \rho(r)/D \quad (2.13)$$

where r is the distance from the j th ion. In the absence of outside influence, the symmetry of the ionic atmosphere about the j th ion will be spherical. By summing Equation 2.13 for all the configurations of ions, $\psi_j(r)$ and $\rho(r)$ may be replaced by their average values, $\bar{\psi}_j(r)$ and $\bar{\rho}(r)$.

The average charge density about the j th ion is given by the expression

$$\rho(r) = \sum_{i=1}^s n_{ji} z_i \epsilon \quad (2.14)$$

where

n_{ji} is the concentration of i ions in the vicinity of the j th ion;

z_i is the valence of the i ions;

ϵ is the electronic charge;

and, the summation is made over all the types of ions in the solution. Then, using the Boltzmann formula,

$$n_{ji} = n_i \exp(-U_{ji}/kT) \quad (2.15)$$

where

n_i is the concentration of the i ions in the bulk solution;

U_{ji} is the potential energy of the i ions in the electric potential $\bar{\psi}_j(r)$.

A critical step in the theory was the assumption of linear superposition of fields which allowed the potential energy, U_{ji} , to be calculated from the equation

$$U_{ji} = z_i \epsilon \bar{\psi}_j(r) \quad (2.16)$$

Furthermore, it follows that

$$U_{ji} = U_{ij} \quad (2.17)$$

The potential energy given by Equation 2.16 is assumed small compared to kT . The exponential term in Equation 2.15 may be represented by the expansion

$$\exp(-U_{ji}/kT) = 1 - U_{ji}/kT + (U_{ji}/kT)^2/2! - \dots \quad (2.18)$$

and for

$$U_{ji}/kT \ll 1 \quad (2.19)$$

Equation 2.18 may be terminated after the linear term. This approximation is necessary for the theory to remain self-consistent because it makes $\bar{\psi}(r)$ proportional to $\bar{\psi}_j(r)$, a requirement of the linear superposition of fields.

Collecting Equations 2.13 through 2.18, terminated after the linear term, and recognizing that

$$\sum_{i=1}^s n_i z_i \epsilon = 0 \quad (2.20)$$

due to the electroneutrality of the solution, yields

$$\nabla^2 \bar{\psi}_j(r) = \kappa^2 \bar{\psi}_j(r) \quad (2.21)$$

where

$$\kappa^2 = 4\pi\epsilon^2 \sum_{i=1}^S n_i z_i^2 / DkT \quad (2.22)$$

Solving Equation 2.21 gives

$$\bar{\psi}_j(r) = z_j \epsilon \exp[-\kappa(r-\bar{a})] / D\epsilon(1+\kappa\bar{a}) \quad (2.23)$$

The electrostatic contribution to the chemical potential on charging the j th ion having a radius equal to \bar{a} in the field of the other charged ions may be calculated by the equation

$$\begin{aligned} \Delta u_j(e) &= \left(\frac{\partial \Delta F(e)}{\partial n_j} \right)_{P,T,n_i} = \int_0^{z_j \epsilon} \bar{\psi}_j(e_j) de_j \\ &= z_j^2 \epsilon^2 / 2D\bar{a}(1+\kappa\bar{a}) \\ &= z_j^2 \epsilon^2 / 2D\bar{a} + (z_j^2 \epsilon^2 / 2D\bar{a}) \left(\frac{1}{1+\kappa\bar{a}} - 1 \right) \quad (2.24) \end{aligned}$$

Since the activity coefficient is a measure of the deviations of the solute from ideal behavior with concentration, the term

$$\sqrt{RT} \ln f_{\pm}$$

in Equation 2.8 is equated to the second term on the right

giving the concentration dependence of $\Delta u_j(\text{el})$ in Equation 2.24. For the case of a single electrolyte, the final expression for the activity coefficient becomes

$$\log f_{\pm} = - \beta_f \sqrt{c} / (1 + A' \sqrt{c}) \quad (2.25)$$

where

$$\beta_f = \frac{1}{2.303 v} \sum_{i=1}^2 \nu_i z_i^2 (DT)^{-3/2} (\pi N \epsilon^6 / 1000 k^3)^{1/2} \quad (2.26)$$

and

$$A' = \kappa a / \sqrt{c} \quad (2.27)$$

2. Critique of the Debye-Hückel theory

The fundamental approximation contained in the theory is given by Equation 2.16

$$U_{ji} = z_i \epsilon \bar{\psi}_j(r) \quad (2.16)$$

Since by definition,

$$U_{ji} = U_{ij} \quad (2.17)$$

then

$$z_i \epsilon \bar{\psi}_j(r) = z_j \epsilon \bar{\psi}_i(r) \quad (2.28)$$

Therefore,

$$\frac{\bar{\psi}_j(r)}{z_j} = \frac{\bar{\psi}_i(r)}{z_i} \quad (2.29)$$

Onsager (10,11) has pointed out that these relations would hold exactly if the mean distribution of charge in the neighborhood of a pair of ions, i and j , at a distance r from each other were always the sum of the charges induced by the two ions separately, a statement of linear superposition of fields. For high dilutions, lower valence ions and large ionic diameters (i.e., a low charge density), Equation 2.29 is nearly fulfilled.

Kirkwood's analysis suggests that if the potentials $\bar{\Psi}_j(r)$ and $\bar{\Psi}_i(r)$ are expressible as a power series in the charges, the lowest terms would conform with the Debye approximation (12). Though the charge cannot be reduced below $z_j e$ and $z_i e$, higher order terms could be presumably made insignificant by separating the ions to great distances as in very dilute solutions. It seems almost certain that the true laws must approach Debye's approximation in the limit of infinite dilution. An estimate of the effects of the higher order terms at finite concentrations is not known, however.

As stated previously, Debye and Hückel assumed the solvent to be a continuous, structureless medium (7). Accordingly, no change in the dielectric constant with concentration was considered. Certainly, any real solvent, particularly solvents which have molecules possessing a permanent dipole moment, would be expected to exhibit a

variation of dielectric constant with charge concentration. The variation would result from the ordered, rather than random, orientation of the dipoles of the solvent molecules in the vicinity of the charges. In a later paper, Hückel, by assuming that the dielectric constant varies linearly with concentration, deduced an additional contribution to the electrical work term which was roughly proportional to the square of the concentration (13). Fowler and Guggenheim have argued, however, that since Hückel did not allow the value of D to vary during the charging process (since it is a function of the ionic concentration), that Hückel's conclusion is not valid (9). They suggest that the electrical work would be proportional to the first power of the concentration and conclude that the limiting law is unaffected by variation of the dielectric constant with concentration.

The variation of D with temperature and pressure, however, must be recognized when deriving the other thermodynamic properties from the electrical chemical potential.

Several refinements have been developed in an attempt to avoid the approximation made when retaining only the first two terms in the expansion of the exponential part of the Boltzmann formula. Assuming $\nu_+ = \nu_-$ for the salt $C_{\nu_+}A_{\nu_-}$ (a symmetrical electrolyte) for simplicity, the Poisson-Boltzmann Equation 2.21 may be written

$$\nabla^2 \bar{\psi}_j(r) = \frac{8\pi\epsilon z_j n_j}{D} \sinh \frac{z_j e \bar{\psi}_j(r)}{kT} \quad (2.30)$$

Debye's approximation replaced the sinh function with

$$z_j \epsilon \bar{\psi}_j(r)/kT.$$

Müller solved Equation 2.30 directly without any approximation (14). It should be pointed out, however, that the use of this distribution function violates the theorem of the linear superposition of fields since the charge density, $\rho(r)$, is equal to

$$\rho(r) = 2z_j n_j \epsilon \sinh(z_j \epsilon \bar{\psi}_j(r)/kT) \quad (2.31)$$

and, hence, is not directly proportional to $\bar{\psi}_j$.

Gronwall, LaMer and Sandved (15) retained higher order terms in the expansion of the exponential term in the Boltzmann equation

$$\begin{aligned} \rho(r) = & \sum_{i=1}^S n_i z_i \epsilon \left[1 - z_i \epsilon \bar{\psi}_j(r)/kT + \frac{1}{2!} (z_i \epsilon \bar{\psi}_j(r)/kT)^2 \right. \\ & \left. - \frac{1}{3!} (z_i \epsilon \bar{\psi}_j(r)/kT)^3 + \dots \right] \quad (2.32) \end{aligned}$$

Again, retention of terms non-linear in $\bar{\psi}_j(r)$ is inconsistent with the assumption of the linear superposition of fields.

In spite of the inconsistency in the theory caused by these refinements, the use of the results of either Müller (14) or Gronwall, et al. (15) tends to yield more realistic ϕ parameters than the unrefined theory in fitting experimental data.

It may be noted, finally, that, for the special case of symmetrical valence electrolytes, the term second order in $\bar{\psi}_j(r)$ may be retained and not violate the theorem of the linear superposition of fields. This occurs because the summation of the second order terms

$$\sum_{i=1}^2 \frac{n_i z_i \epsilon}{2!} (z_i \epsilon \bar{\psi}_j(r)/kT)^2 = 0 \quad (2.33)$$

for symmetrical electrolytes. Coupling this fact with the recognition that for 1:1 electrolytes the charge density for a given concentration will be lower than that for electrolytes with other valences, suggests that the 1:1 type electrolytes as a class should give better agreement with the Debye-Hückel theory to higher concentrations. This conclusion is generally valid for all the thermodynamic properties.

The charging process given by Equation 2.24 was not actually that employed by Debye and Hückel in their derivation. The charging process of Debye and Hückel (7) is represented by the equation for the calculation of the electrical work

$$W(e1) = \Lambda A(e1) = \sum_{j=1}^s \int_{\lambda=0}^{\lambda=1} z_j \epsilon \bar{\psi}(\lambda z_j \epsilon) d\lambda \quad (2.34)$$

For this charging process, the charges of all of the ions are increased in the same ratio at the same time and K is changing. Fowler and Guggenheim (9) point out that the

integration should be carried out at constant pressure, not volume. Including the electrical work due to contraction of the solution during the charging process, yields

$$\Delta A(e1) = \sum_{j=1}^s \int_{\lambda=0}^{\lambda=1} z_j \epsilon \bar{\psi}_j(\lambda z_j \epsilon) d\lambda - P\Delta V \quad (2.35)$$

Then,

$$\Delta F(e1) = \Delta A(e1) + \Delta(PV) = \sum_{j=1}^s \int_{\lambda=0}^{\lambda=1} z_j \epsilon \bar{\psi}_j(\lambda z_j \epsilon) d\lambda \quad (2.36)$$

Substituting for the potential terms, integrating on λ and then taking the partial derivative with respect to n_j gives

$$\Delta u_j(e1) = (z_j^2 \epsilon^2 / 2D\bar{a}) + (z_j^2 \epsilon^2 / 2D\bar{a}) \left(\frac{1}{1 + \kappa_a^0} - 1 \right) \quad (2.24)$$

A term in $\kappa^3 v_j$ has been neglected where v_j is the molecular volume of the j th ion. In the concentration range over which the theory might be expected to apply, this is a valid approximation. Now there is also a volume term in κ since n_j was defined as the concentration of ions per unit volume. This volume unit has been reduced by the charging process and strictly should be replaced by an average volume intermediate between the volume unit for the ideal solution of discharged ions and that for the actual solution. Actually, the correction is negligible and the volume unit is considered unchanged.

The charging process of Güntelberg (16) used in this

derivation is given by Equation 2.24

$$\Delta u_j(e_1) = \left(\frac{\Delta F(e_1)}{\lambda_{n_j}} \right)_{T,P,n_i} = \int_0^{z_j e} \bar{\pi}_j(e_j) de_j \quad (2.24)$$

This differs from Debye's in that a single ion is being charged from 0 to $z_j e$ in the presence of the other totally charged ions.

The two charging processes give the same result as long as the approximations of Debye are used. However, when distribution functions such as that of Müller (14) or Gronwall, et al. (15) are used, the two methods give different results. Onsager has determined that the discrepancy arises from the fact that these distribution functions are not self consistent with the rest of the theory (11).

The $\overset{\circ}{a}$ parameter, defined as the average closest distance to which one ion may approach another ion can clearly be understood when the ions are considered as hard spheres. However, many ions are not spherical in shape and all ions are polarized or distorted when approached by another ion. Furthermore, ions will be solvated to a greater or lesser extent by the solvent medium. Under these circumstances, the physical significance of the $\overset{\circ}{a}$ parameter is less clearly defined. Nevertheless, the $\overset{\circ}{a}$ parameter does appear to be a qualitative indicator of the ion size for many systems. Fuoss and Krauss determined the $\overset{\circ}{a}$ parameters from the conductances of the tetraisoamylammonium halides, which form

large, essentially spherical ions, in benzene, which is presumably a non-solvating medium (17). They found a general increase in the $\overset{\circ}{a}$ parameter from fluoride to iodide, as would be expected. Solvents, however, also may affect the $\overset{\circ}{a}$ parameter by coordinating with the ions thereby increasing the distance of closest approach. In calculating the other thermodynamic properties from Equation 2.25 by differentiating with respect to temperature or pressure, the dependence of the $\overset{\circ}{a}$ parameter should be recognized. Since the $\overset{\circ}{a}$ parameter is present in the equation for the activity coefficient in the form $\kappa \overset{\circ}{a}$, it does not affect the limiting law, however, because κ goes to 0 at infinite dilution.

The total potential, $\bar{\psi}_j(r)$, due to the central ion and its ionic atmosphere at a distance r from the central ion is given by Equation 2.23

$$\bar{\psi}_j(r) = \frac{z_j e \exp[-\kappa(r-\overset{\circ}{a})]}{Dr(1+\kappa \overset{\circ}{a})} \quad (2.23)$$

If the j th ion is isolated with no surrounding charged atmosphere ($\kappa = 0$), the potential at a distance r becomes

$$\bar{\psi}_j^{\text{iso}}(r) = \frac{z_j e}{Dr} \quad (2.37)$$

From the theorem of the linear superposition of fields,

$$\bar{\psi}_j(r) = \bar{\psi}_j^{\text{iso}}(r) + \bar{\psi}_j^{\text{atm}}(r) \quad (2.38)$$

where $\bar{\psi}_j^{\text{atm}}(r)$ is the potential at a distance r from the central ion due to the surrounding atmosphere. Rearranging Equation 2.38 and substituting for $\bar{\psi}_j(r)$ and $\bar{\psi}_j^{\text{iso}}(r)$ from Equations 2.23 and 2.37 yields

$$\bar{\psi}_j^{\text{atm}}(r) = \frac{z_j \epsilon}{Dr} \left(\frac{\exp[-\kappa(r-a^{\circ})]}{1 + \kappa a^{\circ}} - 1 \right) \quad (2.39)$$

Evaluating this potential at $r = a^{\circ}$ gives

$$\begin{aligned} \bar{\psi}_j^{\text{atm}}(a^{\circ}) &= \frac{-z_j \epsilon \kappa}{D(1 + \kappa a^{\circ})} \\ &= \frac{-z_j \epsilon}{D(a^{\circ} + \frac{1}{\kappa})} \end{aligned} \quad (2.40)$$

Comparing with 2.37, the potential due to the atmosphere has the form of the potential at a distance $a^{\circ} + \frac{1}{\kappa}$ from an isolated ion of charge $-z_j \epsilon$. The quantity $1/\kappa$, called the mean thickness of the ionic atmosphere, is inversely proportional to the square root of ionic concentration. For dilute solutions, $1/\kappa$ is large and the interactions between the central ion and its atmosphere are long range in nature. For a 1 molar solution of a 1:1 electrolyte, however, $1/\kappa$ is approximately 3 \AA ; hence, the interactions are not long range. At these distances, the discrete nature of the ions and the solvent must surely be considered.

As has been shown, attempts to improve on the Debye-

Hückel theory by using more accurate forms of the Boltzmann distribution are fundamentally inconsistent. Bjerrum proposed an entirely different method of avoiding the error caused by the approximation of the distribution function (18). For two ions which approach each other sufficiently closely that the screening effect due to other ions may be neglected, the probability that an i ion will be a distance r from the central j ion is given by the equation

$$\text{Probability} = n_i \exp(-z_i z_j e^2 / DrkT) 4\pi r^2 dr \quad (2.41)$$

For ions of like sign, the function remains very low over the whole range of r . If the ions are of opposite sign, the function increases rapidly from a minimum at a distance

$$q = \frac{z_i z_j e^2}{2DkT} \quad (2.42)$$

Bjerrum defined an "ion pair" as any two ions which approach each other closer than this distance q . For electrolytes having an $\overset{\circ}{a}$ parameter greater than q , the approximations of Debye are considered valid since no ion pairs could be formed. For electrolytes having an $\overset{\circ}{a}$ parameter less than q , Bjerrum, in effect, replaced the $\overset{\circ}{a}$ parameter with the distance q . The free ions (those separated by a distance greater than q) are restricted to long range interactions and can be adequately treated by the Debye-Hückel theory. The ion pairs may be treated separately. Fuoss and Krauss have extended

this approach to the formation of triple ions and quadruples (a cluster of four ions) (19,20,21). In both theories, the "complex" is produced only by the action of Coulombic forces rather than by the formation of an electronic bond in the quantum mechanical sense. These theories have been particularly successful for electrolytes in solvents of low dielectric constant.

Stokes and Robinson added an extra term to the Debye-Hückel equation for the activity coefficient to reflect the solvation of the ions in the solution (22). The term includes the parameter, h , the number of moles of solvent combined with a mole of solute. The authors then proceeded to derive an equation relating this solvation (or hydration if the solvent is water) number to the g parameter and reduced their expression for the activity coefficient to one parameter. Though a multitude of ion-solvent effects are being accounted for by this single parameter, the authors obtained good agreement with experimental data for many 1:1 and 2:1 electrolytes at concentrations up to between 1 and 4 molal.

Glueckauf derived a similar parameter based on volume fraction statistics (23). Glueckauf's hydration numbers, unlike those of Robinson and Stokes, were nearly additive for separate ions. In both theories, however, the physical significance of the hydration number is somewhat unclear. According to the definition, h reflects the total number of water molecules coordinated to both the cation and the anion.

It is known that water tends to coordinate with ions by forming concentric spheres of molecules about the central ion. The character of these molecules gradually changes in going outward from the central ion from complexed water to solvent water (24). Then, \bar{h} must represent some average number for these molecules. Different properties of solutions might be expected to measure different averages of these water molecules. In fact, \bar{h} is found to vary with the property being determined, particularly in going from equilibrium thermodynamic properties to non-equilibrium transport properties.

Mayer has adapted his cluster theory of imperfect gases (25) to solutions of electrolytes (26). His model was essentially that of Debye's and his results reduce to the Debye-Hückel limiting law in sufficiently dilute concentrations, but this method avoids the self-consistency difficulties inherent in the Poisson-Boltzmann equation. Poirer has applied the theory to actual solutions and obtained fair results (27,28). However, since the model is essentially the same as that of Debye and Hückel, the theory cannot be expected to be valid in concentrated solutions.

In summary, the Debye-Hückel theory yields a limiting law for the behavior of the activity coefficient as a function of temperature, pressure and concentration for all valence type ions. With the single parameter, \bar{a}^0 , agreement with experiment up to several tenths molar in concentration

has been achieved for well behaved electrolytes. The many refinements to the theory represent attempts to extend the range of the theory to more concentrated solutions. After many years of efforts, Harned and Owen have concluded that "...the problem of concentrated solutions cannot be solved by an extension of the present theory..." (4, p. 547). Fuoss and Onsager contend that the approach to a theory of concentrated solutions "...must start with an adequate theory of fused salts..." (29, p. 680).

However, before a more complete theory can evolve, extensive, accurate data on electrolytes of all valence types in solution will be needed. Then, if the nature of the solvent, particularly water, short range ion-solvent interactions, and complex formation can be more completely understood, these may all be coupled together to yield a definitive theory valid over the entire concentration range of an electrolytic solution.

C. The Partial and Apparent Molal Volume

The molal volumes of solutions of nonelectrolytes show a nearly linear dependence on concentration (30). From the very early studies of electrolytic solutions, however, it was evident that the concentration dependence for these systems was considerably more complicated (31).

Masson, in 1929, discovered that the apparent molal volume of an electrolyte in dilute solution obeyed the

equation

$$\phi_V = \phi_V^0 + S_V \cdot c \quad (2.43)$$

where ϕ_V^0 and S_V were specific for every electrolyte (32).

This equation suggested that two factors needed to be considered: 1) the molal volume of an electrolyte at infinite dilution, and 2) the quantity S_V in the concentration term.

For a completely dissociated electrolyte, the ions may be expected to be acting independently and the molal volume at infinite dilution may be expected to be given by the expression

$$\phi_{V_{C\nu+A\nu-}}^0 = \nu_+ \phi_{V_C}^0 + \nu_- \phi_{V_A}^0 \quad (2.44)$$

where $\phi_{V_C}^0$ and $\phi_{V_A}^0$ are the ionic molal volumes at infinite dilution of the cation and anion, respectively. Taking the case of a 1:1 electrolytes for simplicity, for two electrolytes with a common ion, the difference in ϕ_V^0 's may be expressed by the equations

$$\begin{aligned} \phi_{V_{CA}}^0 - \phi_{V_{C'A}}^0 &= \phi_{V_C}^0 + \phi_{V_A}^0 - \phi_{V_{C'}}^0 - \phi_{V_A}^0 \\ &= \phi_{V_C}^0 - \phi_{V_{C'}}^0 = M \end{aligned} \quad (2.45)$$

and

$$\begin{aligned} \phi_{V_{CA}}^0 - \phi_{V_{CA'}}^0 &= \phi_{V_C}^0 + \phi_{V_A}^0 - \phi_{V_C}^0 - \phi_{V_{A'}}^0 \\ &= \phi_{V_A}^0 - \phi_{V_{A'}}^0 = N \end{aligned} \quad (2.46)$$

M and N should be constant and independent of the common ion. By determining the molal volumes at infinite dilution for a whole series of electrolytes, the molal volumes of all the ions may be related by the differences. Since the experimental properties are measured on the total solute, thermodynamics does not permit a determination of the molal volume of an individual ion to be made. Many attempts have been made, however, to arrive at a value of ϕ_v^0 for some particular ion by making use of various models and other physical properties. These attempts will be briefly commented on later. Clearly, once the ionic molal volume of one ion has been determined, the values for all the other ions, under the same solvent, temperature, and pressure conditions as the reference ion, may be calculated from the additivity relationships of Equations 2.44, 2.45, and 2.46.

Redlich and Rosenfeld derived the limiting law for the apparent molal volume from the Debye-Hückel theory in 1931 (33,34). Their result was

$$\phi_v = \phi_v^0 + kw^{3/2}c^{1/2} \quad (2.47)$$

where

$$w = 0.5 \sum_{i=1}^s v_i z_i^2 \quad (2.48)$$

and

$$k = N^2 \epsilon^3 (8\pi/1000D^3RT)^{1/2} \left(\frac{\partial \ln D}{\partial P} - a/3 \right) \quad (2.49)$$

P is the pressure and α may be taken as the compressibility of the solvent for dilute solutions. Their derivation was essentially a combination of Equations 2.5, 2.9, and the limiting form of 2.25.

From this equation, it is clear that all of the electrolytes of a given valence type should approach infinite dilution with the same limiting slope. Furthermore, the limiting slopes of different valence type electrolytes are all related to the same constant k by the valence factor w .

In 1927, Geffcken (35) fitted partial molal volume data for a number of alkali halide aqueous solutions to an equation of the form

$$\bar{V}_2 = \bar{V}_2^0 + \phi_v c \quad (2.50)$$

This equation may be derived from the Debye-Hückel theory by use of Equations 2.9 and 2.25, neglecting the \bar{a} parameter. Scott (36), and LaMer and Gronwall (37) tabulated ϕ_v^0 's and S_v 's for a number of 1:1 electrolytes from the best data of several sources. For comparison, Equation 2.11 gave

$$\bar{V}_2^0 = \phi_v^0 \quad (2.11)$$

and, using Equation 2.6, the limiting slope for the apparent molal volume, S_v , is simply related to that for the partial molal volume, ϕ_v , by the expression

$$\phi_v = 1.5 S_v \quad (2.51)$$

The authors concluded that the apparent molal volumes at infinite dilution for various combinations of electrolytes did show the expected additivity relationships. The limiting slopes did not, however, appear to converge to a common value. This failure of the electrolytes to approach a common limiting slope was undoubtedly due to the fact that the extrapolations were made from concentrations of several tenths molar.

Geffcken and Price analyzed more dilute data on potassium and sodium chlorides and sodium bromide and concluded that there was a convergence to a common limiting slope at high dilutions (38).

The evaluation of the constant k given by Equation 2.49 has been complicated by the presence of the term $\partial \ln D / \partial P$. Difficulty in accurately determining this term led early investigators to attempt to evaluate the constant from careful apparent molal volume studies in very dilute solutions. Older data of Baxter and Wallace (31) gave $k = 1.7 \pm 0.2$ at 25°C . Interpretation of more accurate data of many other workers (38,39,40,41,42,43,44) by Redlich (45) yielded $k = 1.86 \pm .02$ (25°C). Confirmation of this value came from a calculation of k in a 1964 review article by Redlich and Meyer (46). They calculated k equal to 1.868 (25°C) from direct measurements by Owen and coworkers (47) of D and $\partial D / \partial P$ and by Kell and Whalley of the compressibility of water (48).

The validity of Equation 2.47 as a limiting law for binary electrolytic solutions has been verified for electrolytes of 1:1, 2:1, and 3:1 valence types (45,46,49). However, all electrolytes begin to show deviations from the simple limiting law at concentrations ranging from 1 molar for some 1:1 electrolytes down to 0.001 molar or less for 3:1 electrolytes. Since experimental difficulties often make it nearly impossible to obtain accurate data in the low concentration range where the deviations from the limiting law are negligible (particularly for 3:1 electrolytes), proper representation of the data at higher concentrations and use of an accurate extrapolation function are prerequisites to obtaining reliable apparent molal volumes at infinite dilution.

Redlich and Meyer recommend the use of the equation

$$\phi_v^0 = \phi_v^0 + 1.868 w^{3/2} c^{1/2} + hc \quad (2.52)$$

to represent the data (46). The authors assert that this equation gives a better fit than Masson's equation (32) for solutions up to moderate concentrations. Furthermore, they claim that the use of the Debye-Hückel limiting slope, rather than a third adjustable parameter, would give a more accurate extrapolation, particularly for less accurate data.

Owen and Brinkley, however, criticized the equation of Redlich and Meyer on the basis that it neglects the effect

of the $\overset{\circ}{a}$ parameter (50). They proceeded to derive an equation for the apparent molal volume which included the distance of closest approach, $\overset{\circ}{a}$. Their result was

$$\phi_v = \phi_v^{\circ} + \frac{2}{3} \mathcal{S}_v \tau (\kappa_a^{\circ}) c^{1/2} + \frac{1}{2} w_v \theta (\kappa_a^{\circ}) c + \frac{1}{2} K_v c \quad (2.53)$$

where

$$\tau(\kappa_a^{\circ}) = \frac{3}{\kappa_a^{\circ 3/2}} \left[\frac{1}{2} \kappa_a^{\circ 2} - \kappa_a^{\circ} + \ln(1 + \kappa_a^{\circ}) \right] \quad (2.54)$$

$$\theta(\kappa_a^{\circ}) = \frac{4}{3} \left(\frac{-\sigma}{\kappa_a^{\circ}} \right) \quad (2.55)$$

$$\sigma(\kappa_a^{\circ}) = \frac{3}{\kappa_a^{\circ 3/2}} \left[1 + \kappa_a^{\circ} - \frac{1}{1 + \kappa_a^{\circ}} - 2 \ln(1 + \kappa_a^{\circ}) \right] \quad (2.56)$$

$$\mathcal{S}_v = 2.303 \sqrt{RT} \mathcal{S}_f \frac{3}{2} \left(\frac{\partial \ln D}{\partial P} - \frac{\beta}{3} \right) \quad (2.57)$$

$$w_v = -2.303 \sqrt{RT} \mathcal{S}_f A' \frac{1}{2} \left(\frac{\partial \ln D}{\partial P} - \beta - 2 \frac{\partial \ln \overset{\circ}{a}}{\partial P} \right) \quad (2.58)$$

and

$$K_v = 2.303 \sqrt{RT} B \left(\frac{\partial \ln B}{\partial P} + \sigma \right) \quad (2.59)$$

The quantity B arose from an empirical linear term added to Equation 2.24 which became

$$\log f_{\pm} = \frac{-\mathcal{S}_f \sqrt{c}}{1 + A' \sqrt{c}} + Bc \quad (2.60)$$

Equation 2.53 may be rearranged to give

$$\phi_v - \frac{2}{3} \mathcal{S}_v \tau c^{1/2} = \phi_v^{\circ} + \frac{1}{2} w_v \theta c + \frac{1}{2} K_v c \quad (2.61)$$

This equation has been used as an extrapolation function by Wirth and Collier (51), and by Spedding, Pikal and Ayers (52) for some 1:1 and 3:1 electrolytes in aqueous solution. ϕ_V^0 , W_V , and K_V were determined from the data. The $\overset{\circ}{a}$ parameters were obtained from activity coefficient or conductance data.

If W_V is known, Equation 2.58 allows the calculation of the quantity $\partial \ln \overset{\circ}{a} / \partial P$. Wirth and Collier evaluated this quantity for HClO_4 , HCl , and NaClO_4 . Spedding, Pikal, and Ayers, however, argue that the values cannot be expected to be significant since other higher order terms such as association and dielectric saturation may also contribute in large measure to the parameter W_V . Spedding *et al.* (52) and Poirer (27) have argued that the $\overset{\circ}{a}$ parameter is relatively insensitive to a change in pressure. The $\overset{\circ}{a}$ parameter is considered to include the effect of water molecules coordinated to the ions. These water molecules may be expected to be under considerable pressure due to the strong ion-dipole forces. Therefore, the compressibility of these water molecules should be very small. A change in the hydration number of the ions with changing pressure would, of course, seriously effect the argument. Assuming that there is no change in the effective hydration number of the ions with pressure, the quantity $\partial \ln \overset{\circ}{a} / \partial P$ may be considered small and, therefore, neglected. This latter assumption, however, is

certainly open to question.

Owen and Brinkley (50) by rearranging Equation 2.53 and also assuming the \bar{a} parameter independent of pressure, arrived at a more convenient expression for extrapolation

$$\phi_v - \frac{2}{3} \bar{g}_v \Omega_v c^{1/2} = \phi_v^0 + \frac{1}{2} K_v c \quad (2.62)$$

where

$$\Omega_v = \left(\frac{1}{1 + \kappa \bar{a}} \frac{\partial \ln D}{\partial P} - \frac{\sigma \bar{a}}{3} \right) \left(\frac{\partial \ln D}{\partial P} - \frac{\bar{a}}{3} \right)^{-1} \quad (2.63)$$

Ω_v is less than one for non-zero concentrations and approaches unity as the concentration approaches infinite dilution yielding the limiting law given in Equation 2.47.

In view of the many approximations made in arriving at Equation 2.62 including those inherent in the basic Debye-Hückel theory, the equation cannot be expected to be valid over an extensive concentration range. However, the function Ω_v may be expected to account, to a first approximation at least, for the effect of the \bar{a} parameter on the slope at very dilute concentrations; an effect ignored by the equation of Redlich and Meyer (46). This argument is supported by comparison with the analogous equation for the partial molal volume

$$\bar{V}_2 = \bar{V}_2^0 + \frac{\bar{g}_v \sqrt{c}}{1 + \kappa \bar{a}} + \frac{W_v c}{(1 + \kappa \bar{a})^2} + K_v c \quad (2.64)$$

which may be derived by straightforward thermodynamics. The coefficients are the same as in the equation for the apparent molal volume. The term $\partial \ln \bar{v} / \partial P$ is contained in W_V and has not been assumed equal to zero. For $\kappa \bar{a} \ll 1$, the limiting term in Equation 2.62 approximately reduces to

$$\frac{2}{3} \frac{\bar{v}_V \sqrt{c}}{1 + \kappa \bar{a}} \quad (2.65)$$

That is, Ω_V function alters the limiting slope in approximately the same manner as the quantity $(1 + \kappa \bar{a})$.

Many attempts have been made to evaluate the partial molal volume of individual ions at infinite dilution. A critical review of these attempts has recently been published by Panckhurst (53) so only a brief summation will be given here. The methods may be conveniently classified according to the basic assumptions contained in each. The classifications are:

- 1) methods which do not assume ionic radii;
- 2) methods which assume ionic radii and assume \bar{V}_{ion}^0 is independent of the sign of the ionic charge;
- 3) methods which assume ionic radii and assume \bar{V}_{ion}^0 is dependent on the sign of the ionic charge; and,
- 4) a method which assumes zero electrostriction for ions having large negative charges.

For the methods which assume ionic radii, the Pauling radii (54) are commonly used. However, Panckhurst has also introduced another set of ionic radii called "experimental" radii by Blandamer and Symons (55). These were based on X-ray analysis of the structure of NaCl crystals by Witte and Wölfel (56) who found that the electron density becomes effectively zero along the line of centers at 1.17 \AA from Na^+ and 1.64 \AA from Cl^- . Using these values, Gourary and Adrian obtained other values from known internuclear distances in crystals with the NaCl structure (57).

A particular unique method for determining the partial molal volumes of ions is that of Zana and Yeager (58,59). Their method is based on a direct experimental method using an ultrasonic technique and, unlike all the other methods, does not rely entirely on an analysis of volume measurements. They determined a quantity which was related to the apparent molal masses of the solvated cations and anions. For ion j , this is defined

$$W_j = (M_j)_h - (V_j)_h S_o \quad (2.66)$$

where

W_j is the apparent molal mass of the ion j ;

$(M_j)_h$ is the molecular weight of the solvated ion;

$(V_j)_h$ is the molar volume of the solvated ion;

S_o is the density of the solvent.

$(M_j)_h$ is the sum of the molar mass of the j ion and the mass

of bound water per mole of ion.

$$(M_j)_h = M_j + (M_j)_w \quad (2.67)$$

Zana and Yeager defined the ionic partial molal volume of the j ion as

$$\bar{V}_j = (V_j)_h - (M_j)_w/S_o \quad (2.68)$$

Combining Equations 2.66 through 2.68 yields

$$W_j = M_j - \bar{V}_j S_o \quad (2.69)$$

From Equation 2.69, the experimental quantities $(W_+ - W_-)$, the transport numbers at infinite dilution and the partial molal volumes of the electrolytes at infinite dilution, the authors deduced the partial molal volumes of the ions comprising the electrolyte.

Panckhurst has noted some inconsistencies in the method, however (53). Equation 2.68 defines the ionic apparent molal volume which is only equal to the ionic partial molal volume at infinite dilution. Also, W_j 's at finite concentrations are used with transport numbers and partial molal volumes at infinite dilution. Since W_j is not independent of concentration, this is a serious inconsistency. Panckhurst points out that these objections could be overcome if W_j could be evaluated at sufficiently high dilutions that the ionic apparent molal volumes could be assumed additive and if the

transport numbers and partial molal volumes of the electrolytes are evaluated at the same concentration as W_j . \bar{V}_j^0 could then be obtained by extrapolation to infinite dilution. The uniqueness and potential value of this method lies in the fact that it experimentally separates the partial molal volume of an electrolyte into its individual ionic components. All other methods rely on theoretical approaches to accomplish this separation.

One of the most comprehensive theoretical approaches is that of Noyes (60). This method assumes that the partial molal volume at infinite dilution for an ion is composed of two components

$$\bar{V}^0 = \bar{V}_{\text{int}}^0 + \bar{V}_{\text{el}}^0 \quad (2.70)$$

where \bar{V}_{int}^0 is the intrinsic volume of the ion in solution and \bar{V}_{el}^0 is the contribution to the volume due to electrostriction. Drude and Nernst (61), as early as 1894, arrived at an expression for \bar{V}_{el}^0 given by the expression

$$\bar{V}_{\text{el}}^0 = \frac{z^2 \epsilon^2}{2Dr} \left(\frac{\partial \ln D}{\partial P} \right)_T = - \frac{Az^2}{r} \quad (2.71)$$

where $A = 4.175 \text{ cm}^3 \text{ \AA} \text{ mole}^{-1}$ at 25° C using the values of Owen et al. (47). This is, of course, the pressure derivative of the electrical free energy which was discussed much later by Born (62). Equation 2.71 might be expected to serve as a theoretical limiting law which will be approached for suffi-

ciently large ions such that the solvent may be regarded as a dielectric continuum. Noyes represented deviations from this law by higher order terms in $1/r$ such that

$$\bar{V}_{el}^0 = -4.175/r + C_2/r^2 + C_3/r^3 + \dots \quad (2.72)$$

for univalent ions. The constants C_2 , C_3 , etc., differed for cations and anions. Noyes (60) derived functions for cations and anions which were required to extrapolate to the same intercept (\bar{V}_{H+}^0). In order to get the functions to extrapolate to a common intercept, he had to express \bar{V}_{int}^0 as either

$$\bar{V}_{int}^0 = \frac{4}{3} \pi N (r + b)^3 \quad (2.73)$$

or

$$\bar{V}_{int}^0 = \frac{4}{3} \pi N r^3 + J r^2 \quad (2.74)$$

where b and J were empirical parameters, rather than the simpler

$$\bar{V}_{int}^0 = \frac{4}{3} \pi N r^3 \quad (2.75)$$

Glueckauf (63) proposed a similar method in which he used the form given by Equation 2.74. He introduced the principle that the actual radius of the ion in solution ($r + b$) is the distance from the central ion to the nearest point on which the electrical charge of the ion can act with a force. He identifies this distance as the distance from the ion

center to the dipole center of the first layer of water molecules.

Of course, in a treatment such as that of Noyes, the calculation of the partial molal volume is very sensitive to a choice of ionic radii. Panckhurst has evaluated $\bar{V}_{H^+}^0$ from Noyes theory using the radii of Pauling and the "experimental" radii of Blandamer and Symons. The results are -0.9 and +4 cm³/mole, respectively. Clearly, accurate information about internuclear distances in solutions and the orientation of water molecules about the ions in solutions is necessary for a more knowledgeable choice of radii. Then, the separation of the partial molal volume of an electrolyte into its ionic components on a theoretical basis such as Noyes' might be approached with more confidence.

III. EXPERIMENTAL

A. Preparation of Materials

The rare earth salt solutions used in this research were prepared by dissolving the rare earth oxides with the appropriate C.P. acid. The rare earth oxides were obtained from the rare earth separation group of the Ames Laboratory of the Atomic Energy Commission. The oxides were analyzed by emission spectrographic analysis. The highest concentration of impurities due to other rare earths was 0.05 percent. Total impurities due to common metals were less than 0.05 percent and consisted mostly of Ca and Fe. Precise determination of some elements was impossible due to interference but their concentrations were estimated to be below 0.05 percent.

All solutions measured were made by weighing appropriate amounts of conductivity water and concentrated stock solutions prepared in the following manner. An approximately 3.0 molal stock solution was prepared by successively adding about 50 mls of the appropriate concentrated acid and an equivalent amount of oxide to 400 mls of hot conductivity water. The conductivity water used here and in all subsequent dilutions had a conductivity of 1×10^{-6} mhos or less. The final amounts of acid and oxide added allowed for a slight excess of oxide. The solution was filtered through a sintered glass filter and allowed to cool.

A 25 ml aliquot was titrated with a 0.1 N solution of

the acid on a Sargent Model D Recording Titrator in order to determine the equivalence pH of the R^{+3} hydrolysis. The main stock solution was then adjusted to this equivalence pH by adding sufficient amount of the acid. The solution was heated gently for a few hours to insure completeness of reaction, cooled and the pH adjusted again. This step was repeated until a stable pH was achieved. The solution was then stored in a tightly sealed Pyrex flask.

Each stock solution was analyzed by two of three methods:

- 1) an oxide precipitation, 2) a sulfate precipitation, and
- 3) an EDTA gravimetric titration.

For the oxide method, samples of a stock solution were weighed into crucibles previously brought to constant weight in a 900° C furnace. Oxalic acid, in 10 percent excess, was added to precipitate the rare earth ion. The oxalate precipitates were dried for 48 hours under heating lamps. The crucibles were then returned to the 900° C furnace to convert the oxalate to the oxide and bring the crucibles and oxide back to constant weight.

The sulfate method was similar to the oxide method except the rare earth ion was precipitated with 2M sulfuric acid. After drying under the heating lamps, the crucibles were heated with a Fisher burner to drive off excess sulfuric acid as SO_3 and H_2O . The furnace was maintained at 450° C. No conversion to oxide occurred.

In the EDTA method, a weighed amount of rare earth salt solution was diluted to about 100 mls with a sodium acetate-acetic acid buffer (pH 5) solution and titrated with EDTA using xylenol orange as an indicator. The buret containing the EDTA was weighed before and after the titration. The EDTA was previously standardized against a $\text{Zn}(\text{NO}_3)_2$ or $\text{Gd}(\text{NO}_3)_3$ solution prepared by weight using electrolytic Zn or high purity Gd metal prepared by the Metallurgy Group at the Ames Laboratory of the Atomic Energy Commission.

In all of the methods, the solution weights were corrected to weigh in vacuo. The precision of each analysis, done in triplicate, was ± 0.05 percent or less. The independent methods generally agreed to ± 0.1 percent or less. The mean value of the independent results was taken to be the concentration of the stock solution.

Two secondary stock solutions of about 0.6 and 0.2 molal were prepared by weighing appropriate amounts of the primary stock and conductivity water into Pyrex flasks. In this manner, the relative concentration error of the secondary stock solutions and the measured solutions was less than ± 0.02 percent.

B. Methods for Determining the Specific Gravity

1. History

There are two basic methods used in determining the density or specific gravity of solutions: 1) measuring the

mass of a known volume (pycnometry) or equivalently, measuring the volume of a known mass (dilatometry), or 2) matching the mean density of a float to that of a solution (4).

Careful pycnometry or dilatometry yields specific gravities with an uncertainty of $\pm 1 \times 10^{-5}$ or 10^{-6} . From the equation for the apparent molal volume,

$$\phi_v = \frac{1000}{d} (1 - S) + \frac{M_2}{d_{H_2O}} \quad (2.12)$$

an uncertainty of $\pm 1 \times 10^{-6}$ in S at $C = 0.01$ molar results in an uncertainty of ± 0.1 ml/mole in ϕ_v . For work at higher dilutions, determining the specific gravity to better than $\pm 1 \times 10^{-6}$ is clearly necessary to yield a meaningful ϕ_v .

A specialized dilatometer method has been described which is capable of accuracy of $\pm 2 \times 10^{-7}$ (64). In this method, the volume change occurring when a small amount of concentrated solution is mixed with a large amount of solvent is measured. The apparent molal volume of the initial concentrated solution may be determined by conventional pycnometry. The apparent molal volume of the final dilute solution is given by the expression

$$\phi_{v_{\text{final}}} = \phi_{v_{\text{initial}}} + \Delta V/n_2 \quad (3.1)$$

ΔV is the change in volume on mixing and n_2 is the number of moles of solute present.

Several float methods have been described which are also capable of high accuracy (65,66,67,68). These methods do not, however, require the additional pycnometer data and provide an independent check on the pycnometer data not possible with the dilatometer method described above. Therefore, a magnetic float method was selected for this research and is described in the following section.

2. The magnetic float method

The magnetic float apparatus employed in this research was patterned after the apparatus described by Lamb and Lee (66) and modified by others (1,3,69,70). This method consists of determining the current in a solenoid which is just sufficient to balance a float of known weight in a solution through the interaction of the field of the solenoid with a permanent magnet in the float. The float was designed so that its density was slightly less than that of conductivity water at 25^o C. The direction of the current in the solenoid was such that the field of the solenoid exerted a downward force on the float. A calibration factor, ψ , related the force exerted by the current in the solenoid to mg, the equivalent mass times the acceleration due to gravity. Additional mass could be added to the float by placing platinum weights in a recessed area at the top of the float.

At equilibrium, the forces acting downward and upward on the float are equal.

$$\text{Force}_{\text{down}} = \text{Force}_{\text{up}}$$

$$(Wt + \#I^{\circ} + wt_{\text{soln}}) g = Vd_{\text{soln}}g \quad (3.2)$$

Wt is the mass corrected to vacuum of the float; I° is the current at balance, hereafter called the equilibrium current; # is the calibration factor relating the current to mass; w_{soln} is the mass corrected to the effective mass in solution of any platinum weights added to the float; V is the volume of the float; g is the acceleration due to gravity; and d_{soln} is the density of the solution. A similar equation may be written for the float in pure water:

$$(Wt + I_{\circ}^{\circ}) g = Vd_{\text{H}_2\text{O}}g \quad (3.3)$$

I_{\circ}° is the equilibrium current in pure water. No platinum weights were necessary in pure water. Because the volume of the float cannot be determined to sufficient accuracy, it is eliminated by dividing Equation 3.3 by 3.4 to yield

$$S = \frac{d_{\text{soln}}}{d_{\text{H}_2\text{O}}} \frac{Wt + \#I^{\circ} + wt_{\text{soln}}}{Wt + \#I_{\circ}^{\circ}} \quad (3.4)$$

The mass in solution of the Pt weight may be calculated by the equation

$$wt_{\text{soln}} = wt_{\text{vac}} \left(1 - \frac{d_{\text{soln}}}{d_{\text{pt}}}\right) \quad (3.5)$$

where w_{vac} is the mass in vacuum of the platinum weights and d_{pt} is the density of platinum. In practice, a d_{soln} may

be chosen and then refined by a reiterative process between Equations 3.4 and 3.5.

C. Apparatus

1. The solution cell

The solution cell in Figure 1 built by M. J. Pikal (3) was a cylinder constructed of Pyrex tubing approximately 50 cm in height and 10 cm in diameter. An inner 55/50 standard taper mounted on the top of the cell provided access to the interior (Figure 1, A). A cap for this opening was provided by an outer 55/50 standard taper which had been closed off just above the taper. A 6 cm portion of Pyrex tubing terminated with an inner 14/35 ground glass joint served as a holder, B, for the thermometer. A matching taper was attached with Apiezon wax to the stem of a Leeds and Northrup platinum resistance thermometer, C, for installation in the cell. The thermometer was used with a Model G-2 Leeds and Northrup Mueller Bridge to measure the solution temperature in the cell to $\pm 0.001^\circ \text{C}$. An outer 24/40 standard taper was attached to the top of the cell to receive a matching ground glass bearing with a stirring rod, D. Power to the stirring rod was provided by a variable speed electric motor which was attached to the stirring rod by a flexible piece of rubber tubing after the stirrer was lowered into the solution. A fourth opening in the top of the cell consisted of an outer 7/25 standard taper which could be capped by a

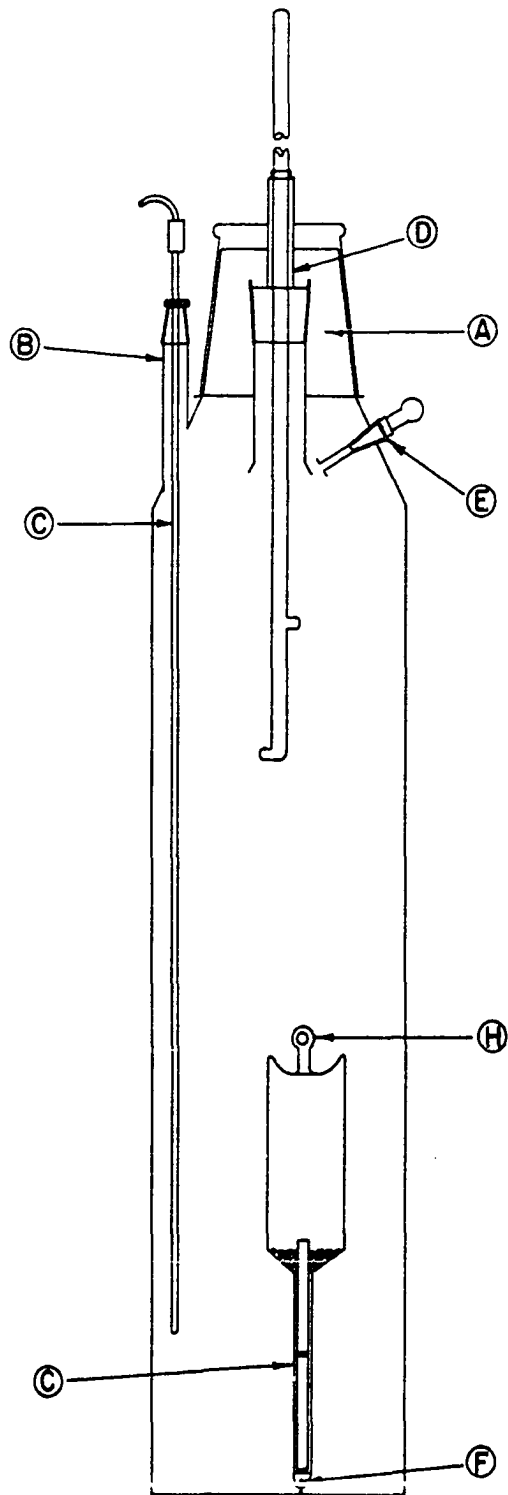


Figure 1. The solution cell and magnetic float

matching inner taper closed above the joint, E. Addition of a concentrated stock solution to the cell was made using a 60-ml weight burette with an inner 7/25 standard taper with a 2-1/2 cm delivery tip. The weight burette was designed so that the delivery tip just touched the stirring rod when the burette was seated in the receiving taper. In this position, the solution could be allowed to drain down the stirring rod into the bulk solution without splashing on the sides of the cell.

2. The float

A schematic diagram of a specific gravity float is also shown in Figure 1. Two floats, approximately 100 ml and 75 ml in volume respectively, were used in this research. The 75-ml float was made of 3-1/2 cm o.d. thick wall Pyrex tubing 8 cm in length tapered to a 9-cm portion of 1-cm o.d. tubing. The 1-cm tubing was closed at the bottom to form a solid glass bead into which a small piece of tungsten wire was sealed (Figure 1, F). The tungsten wire was ground to a point to serve as the contact point with the bottom of the cell. Two 1-1/2 inch magnetic stirring bars with the teflon removed were placed end to end in the lower section of the float to serve as the permanent magnet, G. Lead shot was added as ballast and Apiezon wax was melted into the spaces between the shot and magnet and allowed to harden to seal everything in place. The top of the float was molded

inward to form a recessed area and closed. A glass eyelet was attached in the center of the recessed area, H. A 3 foot glass rod terminating in a Pt hook was used to lift the float in and out of the cell. The 100-ml float was made of similar materials and differed only in dimensions.

3. The constant temperature bath

The constant temperature bath constructed by B. O. Ayers is shown in Figure 2 with the solution cell containing the float mounted in its holder. Since the apparatus has been fully described by Ayers (1), only a brief description will be given here.

The main component of the bath was a 30-gallon stainless steel drum (Figure 2,A) fitted on opposite sides with 4 inch x 7 inch windows of Plexiglas. The drum was secured in a wooden box, B, filled with Zonolite insulation. Plywood tunnels on opposite sides of the box exposed the windows in the drum.

Temperature control was maintained by a mercury thermostat, C, connected to an electronic relay controlling a 250 watt immersion heater, D. Cooling water from an auxiliary bath maintained at about 22° C was pumped through copper coils, E, by a centrifugal pump. Stirring in the main bath was provided by a tubular turbine stirrer, F, which was mounted to a separate stand to avoid transmitting vibration to the cell.

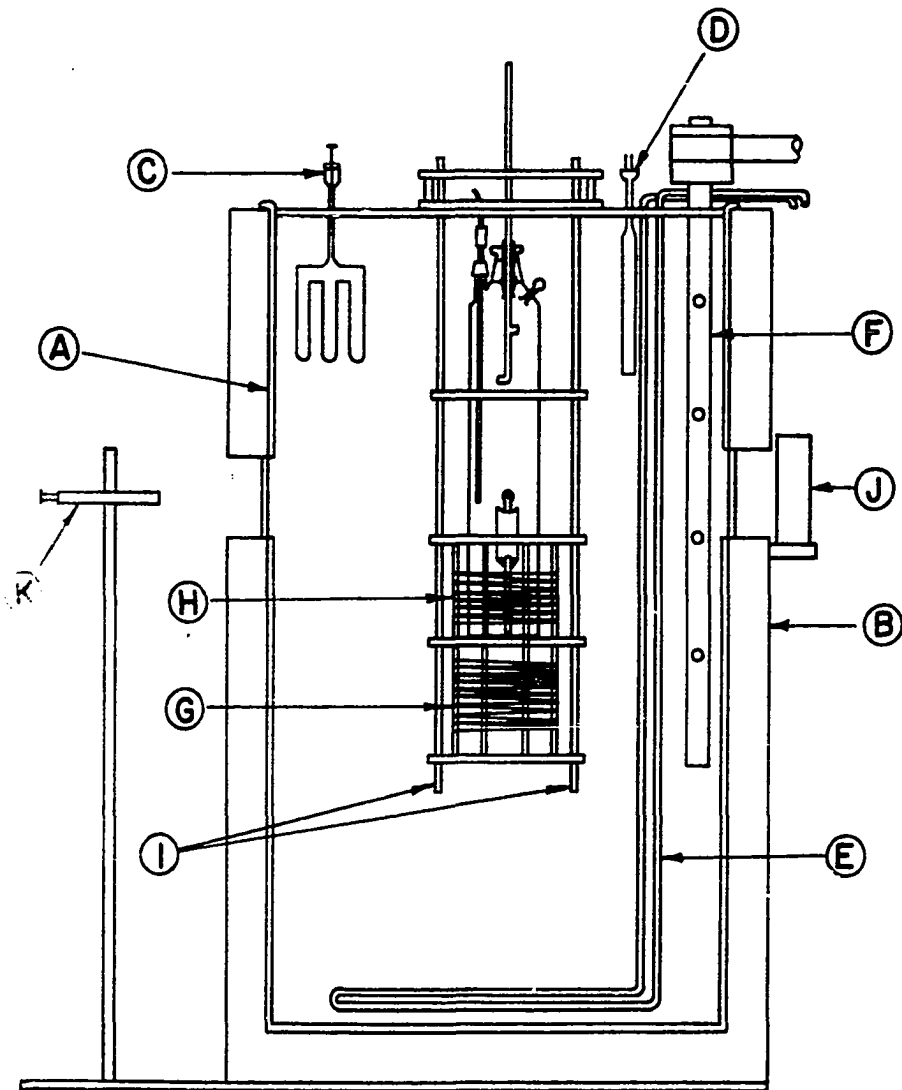


Figure 2. Apparatus for the determination of the specific gravities of solutions

The main solenoid, G, consisted of 27 turns of number 24 insulated copper wire wound on an octagonal frame approximately 6-1/2 inches across by 6 inches high. The auxiliary solenoid, H, of 30 turns was also wound on the frame just above the main solenoid. The solenoid frame and a hinged mounting bracket were attached to two 5/8 inch brass rods 34 inches in length, I, which were, in turn, attached to a triangular frame. This triangular frame had three adjustable legs which rested on a matching triangular frame mounted to the housing of the bath.

A fluorescent light, J, in front of one window provided illumination in the bath. The position and motion of the float in the cell were observed through the other window by a telescope, K, with an ocular scale.

4. The platinum weights

Platinum weights, to be added to the float, were made from annealed platinum wire. Weights in approximate denominations of 5, 10, 25, 50, 100, 500, 1000, and 2000 milligrams were constructed and coded so that each weight be identified. With this system, a particular combination of weights used on the float for a determination could be weighed together after the determination.

An Ainsworth type FDJ microbalance with keyboard milligram weights and an optical lever was employed to weigh the Pt weights.

5. The electrical circuits

The rather simple electrical circuits required for the apparatus are shown in Figure 3.

In the main solenoid circuit, three Willard DD-3-3 type 6 volt storage batteries were used as a constant voltage source (Figure 3, A). The potential across a 1 ohm standard resistor, B, in series with the solenoid was determined by a Rubicon Type B potentiometer, C, in effect, making the potentiometer an ammeter.

The auxiliary solenoid was used to provide a small extra downward force on the float while the solution currents and motions of the float dissipated. The electrical current in the auxiliary solenoid could first be decreased to about 2 milliamperes by opening switch D before opening the circuit with switch E. Switch E could be reversed to allow some control of the float movement during the initial step of pulling the float to the bottom of the cell.

D. Procedure

1. Pressure calibration

Using $4.57 \times 10^{-11} \text{ cm}^2/\text{dyne}$ for the compressibility of water at 25° C , 1 atmosphere (71) and assuming the specific gravity float to be incompressible, a change in atmospheric pressure of 10 millimeters causes a change in the density of water of $6 \times 10^{-7} \text{ gms/ml}^3$ which is outside the experimental errors of the method. Since daily changes in atmo-

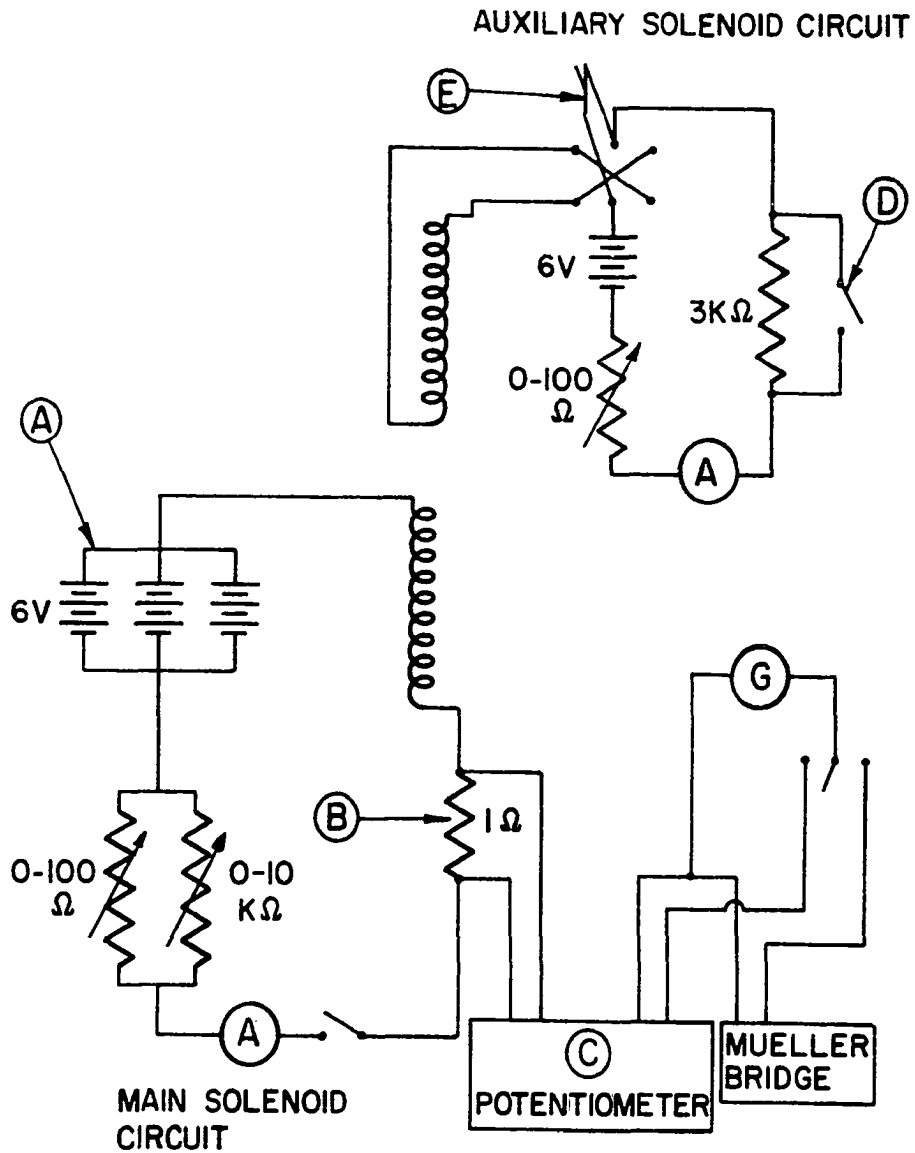


Figure 3. The electrical circuit diagram for the specific gravity apparatus

spheric pressure well in excess of 10 millimeters are common, it was necessary to apply a correction for this effect.

Since the floats also compressed slightly with increase in barometric pressure, a calibration factor to correct both for the compression of the water and the float was determined experimentally. The calibration factor was obtained by measuring the equilibrium current for the float in pure water while the cell was pressurized at levels between 710 mm and 770 mm. The factor was 0.020 ± 0.005 milliamperes per millimeter of mercury (equivalent to 0.0013 ± 0.0003 milligrams per millimeter of mercury for the 75 ml float. The 100 ml float used in this research required no pressure corrections. The compressibility of the float was evidently identical to that of the water within the sensitivity of the calibration.

2. Specific gravity determination

Prior to a specific gravity run, the solution cell was filled with alcoholic potassium hydroxide cleaning solution and the float was lowered into the cell for a cleaning period of at least two hours. The alcoholic potassium hydroxide was then replaced with 1N hydrochloric for a similar period. The process was finally repeated with conductivity water.

After the final rinse, the cell and float were dried with filtered air passed through Anhydrone. The float was placed in the balance room, allowed to reach equilibrium and then weighed.

Approximately 1500 grams of conductivity water were weighed into the assembled solution cell. A funnel with a long stem sufficient to reach nearly to the bottom of the cell was used to eliminate splashing on the sides of the cell.

The cell was then placed in the bath and the float lowered into the cell. The system was allowed to equilibrate overnight.

The mass calibration factor, ϕ , was determined at the beginning of each run by first determining the equilibrium current for the float alone, then adding an approximately 5 milligram weight to the float and determining a new equilibrium current. This process was repeated until three or four weights had been added to the float. Typical values of ϕ for the two floats used were 0.1350 ± 0.0005 mg/ma and 0.06600 ± 0.0001 mg/ma, respectively.

In determining an equilibrium current, the float was gently pulled down to the bottom of the cell by use of the auxiliary solenoid. The current in the main solenoid was adjusted to a value which was about 1 milliamperes in excess of the suspected equilibrium current. Switch D (Figure 3) was opened to decrease the auxiliary current to about 2 milliamperes. After waiting for a period of 3 to 5 minutes, the auxiliary solenoid was switched off and the float was closely observed through the telescope for a time interval

of 3 to 6 minutes. If no motion was observed the auxiliary solenoid was turned back on, the current in the main solenoid was recorded and then decreased by 0.1 milliamperes and the sequence repeated. When the float finally rose, the current at that time was averaged with the previous value and that value and the barometric pressure were recorded. The float was then bobbed rapidly in and out of the solution to dislodge any bubbles which may have formed and another equilibrium current determined. In this manner, a typical equilibrium current of about 400 milliamperes could be determined to ± 0.1 milliampere.

At the beginning of the second day of the run, the equilibrium current of pure water, I_0^0 , was determined. A predetermined amount of a stock solution at the proper concentration was weighed into the cell. With the float held against the inner wall of the cell by means of a large bar magnet lowered into the water bath on the outside of the cell, the solution was stirred rapidly for 10 to 20 minutes. Platinum weights were added to the float until a rough determination showed the new equilibrium current to be within ± 20 milliamperes of I_0^0 . After temperature equilibrium was regained, the equilibrium current for the solution, I^0 , was determined, and the denominations and codes of the Pt weights used were recorded. The solution was stirred once again and the determination of I^0 repeated.

Four or five concentrations were determined during each run. I_0^0 and the equilibrium currents for the first two concentrations were determined in the same day to minimize any error introduced by drifting of I_0^0 , which is most acute for the higher dilutions. The platinum weights were rinsed in dilute nitric acid and conductivity water, heated to a red heat in a Bunsen burner flame and placed in the balance room to be subsequently weighed. The equilibrium currents were corrected to the average of the barometric pressure readings taken during the determination of I_0^0 when the corrections were applicable.

E. Results

The specific gravities of the chlorides of Eu, Tm and Lu, the nitrates of Pr, Sm, Eu, Gd, Tb, Dy, Ho, Tm, and Lu, and the perchlorates of La, Nd, Gd and Lu were determined at 25° C from 0.0015 molal to between 0.1 and 0.2 molal by the above procedure.

The results are given in Table 1. The concentration is given in molality, m ; the specific gravity is S ; and ϕ_v is the experimental apparent molal volume in milliliters per mole calculated from Equation 2.12. The data for each salt was fitted to a polynomial of the form

$$\phi_v = a_0 + a_1 m^{1/2} + a_2 m + a_3 m^{3/2} \quad (3.6)$$

by the method of least squares. Δ is the difference between

Table 1. Specific gravities and apparent molal volumes of aqueous rare earth salt solutions at 25° C

m	$m^{1/2}$	S	ϕ_v	Δ
EuCl₃				
0.0015141	0.038911	1.0003716	12.93	+ .06
0.0039532	0.062874	1.0009678	13.53	- .04
0.0085577	0.092508	1.0020900	14.11	- .05
0.013941	0.11807	1.0033995	14.46	+ .04
0.025005	0.15813	1.0060789	15.17	- .02
0.038930	0.19731	1.0094441	15.63	+ .07
0.060947	0.24687	1.014735	16.36	- .05
0.083770	0.28943	1.020209	16.79	+ .01
0.13022	0.36086	1.031280	17.61	- .03
0.14364	0.37900	1.034475	17.76	+ .02
TmCl₃				
0.0014559	0.038156	1.0003859	10.26	- .11
0.0037803	0.061484	1.0010007	10.60	+ .14
0.0083995	0.091649	1.0022159	11.49	- .08
0.013888	0.11785	1.0036579	11.90	+ .03
0.025338	0.15918	1.0066538	12.64	- .02
0.040879	0.20219	1.010709	13.21	+ .02
0.060504	0.24598	1.015810	13.82	- .03
0.091887	0.30313	1.023940	14.45	.00
0.12948	0.35983	1.033628	15.11	+ .03
0.16997	0.41227	1.043976	15.91	- .02

Table 1. (Continued)

m	$m^{1/2}$	S	ϕ_v	Δ
		LuCl_3		
0.0014693	0.038331	1.0004005	8.77	+ .02
0.0042900	0.065498	1.0011666	9.41	- .04
0.0081541	0.090300	1.0022141	9.80	+ .05
0.014181	0.11908	1.0038420	10.39	- .03
0.025942	0.16107	1.0070117	11.00	+ .04
0.039228	0.19806	1.010578	11.59	- .03
0.059456	0.24384	1.015995	12.14	+ .02
0.079110	0.28127	1.021238	12.64	- .04
0.13040	0.36111	1.034871	13.48	+ .03
0.17026	0.41263	1.045392	14.13	- .01
		$\text{Pr}(\text{NO}_3)_3$		
0.0015717	0.039645	1.0004409	46.51	- .07
0.0027462	0.052404	1.0007696	46.78	+ .05
0.0059755	0.077301	1.0016703	47.46	+ .09
0.0084704	0.092035	1.0023624	48.05	- .09
0.014593	0.12080	1.0040586	48.75	- .01
0.019795	0.14069	1.0054949	49.21	+ .04
0.021672	0.14721	1.0060098	49.46	- .05
0.046237	0.21502	1.012739	50.92	+ .06
0.084937	0.29483	1.017814	51.82	- .04
0.10753	0.32792	1.029297	53.07	.00

Table 1. (Continued)

m	$m^{1/2}$	S	ϕ_V	Λ
		$\text{Sm}(\text{NO}_3)_3$		
0.0015944	0.039930	1.0004616	46.96	- .08
0.0027899	0.052820	1.0008068	47.27	+ .01
0.0073060	0.085475	1.0021060	48.14	+ .12
0.013998	0.11831	1.0040184	49.24	- .04
0.024594	0.15682	1.0070299	50.32	- .11
0.040055	0.20014	1.011406	51.18	+ .05
0.061299	0.24759	1.017376	52.15	+ .03
0.094529	0.30746	1.026656	53.12	- .01
		$\text{Eu}(\text{NO}_3)_3$		
0.0013786	0.037130	1.0004003	47.72	- .05
0.0039554	0.062892	1.0011457	48.40	+ .01
0.0077379	0.087965	1.0022362	49.01	+ .07
0.013964	0.11817	1.0040225	49.85	- .04
0.025543	0.15982	1.0073317	50.71	+ .01
0.037858	0.19457	1.010833	51.42	- .03
0.059586	0.24410	1.016983	52.23	+ .03
0.080662	0.28401	1.022909	52.91	- .04
0.13292	0.36458	1.037506	53.94	+ .05
0.16994	0.41224	1.047733	54.65	- .02

Table 1. (Continued)

m	$m^{1/2}$	S	ϕ_v	λ
$Gd(NO_3)_3$				
0.0015843	0.039203	1.0004680	47.98	- .05
0.0031253	0.055904	1.0009222	48.28	+ .09
0.0091300	0.095551	1.0026832	49.38	- .04
0.014844	0.12184	1.0043523	49.99	- .07
0.025460	0.15956	1.0074454	50.60	+ .05
0.042439	0.20601	1.012363	51.46	- .03
0.058521	0.24191	1.017010	51.88	+ .08
0.10245	0.32008	1.029587	53.06	- .10
0.12903	0.35921	1.037171	53.36	+ .05
$Tb(NO_3)_3$				
0.0015444	0.039299	1.0004586	48.11	.00
0.0029613	0.054418	1.0008780	48.55	- .04
0.0062717	0.079194	1.0018558	49.09	+ .01
0.0081931	0.090516	1.0024225	49.29	+ .07
0.014699	0.12124	1.0043339	50.03	- .05
0.019633	0.14012	1.0057815	50.32	.00
0.026018	0.16130	1.0076501	50.67	+ .01
0.039951	0.19988	1.011713	51.31	- .05
0.054039	0.23246	1.015812	51.67	+ .04
0.063217	0.25143	1.018472	51.94	+ .01
0.095308	0.30872	1.027731	52.68	- .01

Table 1. (Continued)

m	$m^{1/2}$	S	ϕ_v	Λ
$Dy(NO_3)_3$				
0.0014162	0.037632	1.0004265	47.47	+ .06
0.0038275	0.061867	1.0011497	48.22	- .03
0.0072204	0.084973	1.0021644	48.79	- .04
0.012222	0.11055	1.0036568	49.28	+ .01
0.021352	0.14612	1.0063713	49.95	.00
0.038440	0.19606	1.011434	50.64	+ .05
0.056246	0.23716	1.016682	51.22	.00
0.090170	0.30028	1.026628	51.97	- .04
0.12472	0.35311	1.036695	52.52	+ .02
$Ho(NO_3)_3$				
0.0016234	0.040291	1.0004940	46.76	- .01
0.0043423	0.065896	1.0013194	47.17	+ .02
0.0084317	0.091824	1.0025571	47.69	- .05
0.013695	0.11703	1.0041480	48.00	+ .06
0.027136	0.16471	1.0081896	48.89	- .05
0.041536	0.20380	1.012505	49.41	+ .02
0.060891	0.24676	1.018279	49.98	+ .01
0.087175	0.29525	1.026088	50.52	.00
$Pr(NO_3)_3$				
0.0015486	0.039352	1.0004803	44.91	- .01
0.0069909	0.083612	1.0021614	45.81	+ .01
0.012184	0.11038	1.0037602	46.29	+ .02

Table 1. (Continued)

m	$m^{1/2}$	S	ϕ_v	Δ
$\text{Tm}(\text{NO}_3)_3$ (continued)				
0.020774	0.14413	1.0063956	46.92	- .04
0.032708	0.19927	1.012184	47.67	+ .03
0.054500	0.23367	1.016714	48.17	- .02
0.089976	0.29996	1.027432	48.87	+ .04
0.13119	0.34524	1.036220	49.43	- .04
0.17911	0.41244	1.051455	50.05	+ .01
$\text{Lu}(\text{NO}_3)_3$				
0.020774	0.048240	1.0007388	43.60	- .15
0.032708	0.064864	1.0013352	43.70	+ .12
0.054500	0.091188	1.0026334	44.30	+ .05
0.089976	0.11794	1.0043963	44.84	.00
0.13119	0.15760	1.0078306	45.48	+ .01
0.17911	0.18774	1.011090	45.97	- .03
0.039550	0.19887	1.012435	46.14	- .04
0.062377	0.24975	1.019554	46.73	+ .02
0.080979	0.28457	1.025327	47.16	.00
0.091039	0.30173	1.028434	47.45	- .08
0.11224	0.33502	1.034992	47.70	+ .04
0.13031	0.36098	1.040550	48.00	+ .03
0.15394	0.39235	1.047803	48.29	+ .10
0.17039	0.41278	1.052793	48.72	- .10

Table 1. (Continued)

m	$m^{1/2}$	S	ϕ_V	Δ
$\text{La}(\text{ClO}_4)_3$				
0.0016705	0.040872	1.0005733	94.29	- .01
0.0041338	0.064295	1.0014167	94.69	+ .05
0.0080654	0.089808	1.0027584	95.27	- .08
0.014392	0.11997	1.0049138	95.65	+ .01
0.025316	0.15911	1.0086229	96.15	+ .05
0.037431	0.19347	1.012715	96.62	- .03
0.049250	0.22192	1.016699	96.87	+ .03
0.078819	0.28075	1.026598	97.51	- .05
0.11997	0.34637	1.040259	98.03	+ .03
0.16892	0.41100	1.056296	98.74	- .01
$\text{Nd}(\text{ClO}_4)_3$				
0.0014998	0.038727	1.0005298	89.56	+ .06
0.0038779	0.062273	1.0013675	90.09	- .08
0.0086602	0.093060	1.0030496	90.44	+ .05
0.013802	0.11748	1.0048520	90.87	- .03
0.025725	0.16039	1.0090205	91.38	+ .03
0.036773	0.19176	1.012866	91.81	- .02
0.059142	0.24319	1.020618	92.34	+ .01
0.078678	0.28050	1.027349	92.73	.00
0.12946	0.35981	1.044695	93.46	- .01
0.16902	0.41112	1.058064	93.90	.00

Table 1. (Continued)

m	$m^{1/2}$	S	ϕ_V	Δ
$Gd(ClO_4)_3$				
0.0013634	0.036924	1.0004953	92.54	+ .16
0.0038374	0.061947	1.0013908	93.31	- .14
0.0084896	0.092139	1.0030725	93.67	.00
0.014425	0.12010	1.0052119	94.08	.00
0.025633	0.16010	1.0092409	94.50	+ .08
0.036856	0.19198	1.013256	94.96	- .04
0.058958	0.24281	1.021136	95.38	+ .02
0.077909	0.27912	1.027855	95.69	.00
0.12895	0.35910	1.045791	96.38	- .04
0.16923	0.41138	1.059795	96.78	+ .02
$Lu(ClO_4)_3$				
0.0015190	0.038986	1.0005872	87.18	- .03
0.0040230	0.063427	1.0015526	87.51	+ .05
0.0085205	0.092307	1.0032825	88.04	- .04
0.014424	0.12010	1.0055490	88.38	+ .01
0.025887	0.16089	1.0099340	88.95	- .04
0.038626	0.19653	1.014793	89.30	+ .02
0.061208	0.24740	1.023359	89.85	- .01
0.079598	0.28213	1.030307	90.11	+ .05
0.12812	0.35794	1.048471	90.87	- .05
0.17039	0.41278	1.064148	91.27	+ .02

the calculated and the experimental value. The partial molal volume may be easily calculated from the parameters of Equation 3.6 by the expression

$$\bar{V}_2 = a_0 (\bar{V}_2^0) + \frac{3}{2} a_{1m}^{1/2} + 2 a_{2m} + \frac{5}{2} a_{2m}^{3/2} \quad (3.7)$$

The specific gravity was calculated from Equations 3.4 and 3.5. The density of platinum was taken as 21.428 grams per cubic centimeter (72). The density of water used was 0.997075 grams per milliliter (73).

Table 2 lists the parameters for Equation 3.6 with the root mean square deviation. The data of Pikal and Ayers is also included (1, 3). The points were weighted using the inverse of the square of the probable error in ϕ_v .

Table 3 shows the parameters and the root mean square deviation for the data fitted to the Owen-Brinkley extrapolation given by Equation 2.62. For the nitrates Pr through Gd, Equation 2.62 did not satisfactorily represent the data. An additional term, $Dc'^{3/2}$, was used for these salts with the exception of Nd. The a^0 parameters used in the Owen-Brinkley function, obtained from conductivity or activity coefficient data, are also listed with their sources.

The additivity relationships of the partial molal volumes at infinite dilution are illustrated by Table 4. The values of some common electrolytes have been included for comparison. The ϕ_v^0 's used were, with the exception of

Table 2. Parameters for calculating $\bar{\phi}_v$ and \bar{V}_2 from Equations 3.6 and 3.7

Salt	a_0	a_1	a_2	a_3	Rmsd.
LaCl ₃ ^a	14.38	27.83	-42.02	33.97	.08
PrCl ₃ ^b	10.96	26.58	-42.55	39.22	.04
NdCl ₃ ^a	10.48	21.15	-19.28	11.63	.03
SmCl ₃ ^b	11.42	20.56	-21.81	14.90	.02
EuCl ₃ ^b	12.08	24.81	-40.83	39.67	.04
GdCl ₃ ^b	13.30	21.72	-25.94	18.92	.04
TbCl ₃ ^b	13.51	21.02	-23.02	16.70	.07
DyCl ₃ ^b	12.82	22.90	-29.97	24.97	.04
HoCl ₃ ^b	11.83	24.38	-35.72	32.58	.03
ErCl ₃ ^b	10.96	25.33	-38.86	35.01	.04
TmCl ₃	9.03	31.85	-71.69	84.52	.06
YbCl ₃ ^a	9.22	26.64	-45.10	40.81	.11
LuCl ₃	7.88	25.22	-41.56	41.27	.03
La(NO ₃) ₃ ^a	49.08	32.19	-53.01	52.21	.11
Pr(NO ₃) ₃	45.20	32.44	-26.53	2.66	.06
Nd(NO ₃) ₃ ^a	44.74	40.42	-54.02	39.39	.12
Sm(NO ₃) ₃	45.60	32.80	-16.09	-36.65	.07
Eu(NO ₃) ₃	46.49	33.65	-51.98	44.20	.04

^aSource: Avers (1).^bSource: Pikal (3).

Table 2. (Continued)

Salt	a_0	a_1	a_2	a_3	Rmsd.
$\text{Gd}(\text{NO}_3)_3$	46.73	32.24	-56.24	50.71	.07
$\text{Tb}(\text{NO}_3)_3$	46.96	32.07	-68.78	80.51	.03
$\text{Dy}(\text{NO}_3)_3$	46.35	34.42	-80.82	93.60	.04
$\text{Ho}(\text{NO}_3)_3$	46.05	17.10	5.92	-42.72	.04
$\text{Er}(\text{NO}_3)_3^a$	45.59	20.28	-19.95	13.05	.03
$\text{Tm}(\text{NO}_3)_3$	43.98	24.92	-37.65	31.42	.03
$\text{Yb}(\text{NO}_3)_3^a$	43.60	22.31	-25.72	17.62	.03
$\text{Lu}(\text{NO}_3)_3$	42.28	26.31	-44.57	43.73	.07
$\text{La}(\text{ClO}_4)_3$	93.37	24.31	-50.53	56.14	.04
$\text{Nd}(\text{ClO}_4)_3$	88.91	19.32	-26.63	22.38	.04
$\text{Gd}(\text{ClO}_4)_3$	91.91	23.13	-48.95	52.49	.07
$\text{Lu}(\text{ClO}_4)_3$	86.43	19.64	-30.69	28.19	.03

Table 3. Parameters for Owen-Brinkley extrapolation function

Salt	ϕ_V^0	1/2 K_V	D'	Rmsd.	\bar{a} (Å)
EuCl ₃	12.09	7.71		.06	5.6 (74)
TmCl ₃	9.44	10.47		.12	5.8 (75)
LuCl ₃	7.95	9.32		.07	6.0 ^a
Pr(NO ₃) ₃	45.46	64.67	-117.67	.07	4.5 ^a
Sm(NO ₃) ₃	45.86	79.06	-169.22	.08	4.4 (76)
Eu(NO ₃) ₃	46.87	35.11	- 53.20	.08	4.4 ^a
Gd(NO ₃) ₃	47.00	29.50	- 54.35	.08	4.4 (77)
Tb(NO ₃) ₃	47.30	9.17		.09	4.6 ^a
Dy(NO ₃) ₃	46.84	7.61		.11	4.8 ^a
Ho(NO ₃) ₃	45.66	7.04		.06	5.1 (76)
Tm(NO ₃) ₃	44.06	8.22		.08	5.8 ^a
Lu(NO ₃) ₃	42.45	9.95		.10	6.1 ^a
La(ClO ₄) ₃	93.36	7.00		.05	7.0 (77)
Nd(ClO ₄) ₃	88.55	4.37		.06	6.0 (77)
Gd(ClO ₄) ₃	91.77	3.27		.07	6.4 (77)
Lu(ClO ₄) ₃	86.18	6.30		.04	7.4 ^a

^aEstimated from values for nearest neighbors.

Table 4. The additivity relationships of ϕ_v°

Cation	$\phi_v^{\circ}R(NO_3)_3 - \phi_v^{\circ}RCl_3$	$\phi_v^{\circ}R(ClO_4)_3 - \phi_v^{\circ}RCl_3$
La ⁺³	34.9	78.9
Pr ⁺³	34.5	
Nd ⁺³	34.6	78.4
Sm ⁺³	34.7	
Eu ⁺³	34.8	
Gd ⁺³	33.9	78.7
Tb ⁺³	34.1	
Dy ⁺³	34.2	
Ho ⁺³	33.9	
Er ⁺³	34.7	
Tm ⁺³	34.6	
Yb ⁺³	34.1	
Lu ⁺³	34.5	78.2
Average:	34.4 \pm 0.3	78.6 \pm 0.3
3(HClO ₄ -HCl)		78.8 (50, 51)
3(NaClO ₄ -NaCl)		78.9 (50, 51)
3(KNO ₃ -KCl)	34.7	(50, 78)
3(NH ₄ NO ₃ -NH ₄ Cl)	34.2	(79, 80)

$\text{Nd}(\text{NO}_3)_3$, those obtained from the Owen-Brinkley extrapolation listed in Table 3 and a similar extrapolation by Pikal (3). The ϕ_v^0 for $\text{Nd}(\text{NO}_3)_3$ was determined from a fit of the data to Equation 3.6 by Pikal (3).

Figure 4 shows the apparent molal volume, ϕ_v , versus molarity to the one half, $c^{1/2}$, of $\text{Lu}(\text{ClO}_4)_3$. The experimental points are circled for identification. The smooth curve is from an equation of the form of 3.6. The straight line is the limiting slope given by the Debye-Hückel equation. The concentration dependence for this salt is typical of the behavior of all the perchlorates and chlorides, except TmCl_3 , studied and also the nitrates from Ho to Lu (including those studied by Ayers and Pikal (1,3)). The apparent molal volumes show a negative deviation from the Debye-Hückel limiting slope. The molarity concentration scale was used since that is the form required by the Owen-Brinkley function. The molality scale was used in Equation 3.6 since it allows the use of the simple Equation 3.7 for calculating \bar{V}_2 . The equation for \bar{V}_2 resulting from expressing ϕ_v as a polynomial in $c^{1/2}$ is more complicated and, hence, less useful for calculating \bar{V}_2 . Actually, for the rather low concentrations studied in this research, the two scales do not differ greatly.

Figure 5 shows the Owen-Brinkley extrapolation function for $\text{Lu}(\text{ClO}_4)_3$. The function fits the data well with just

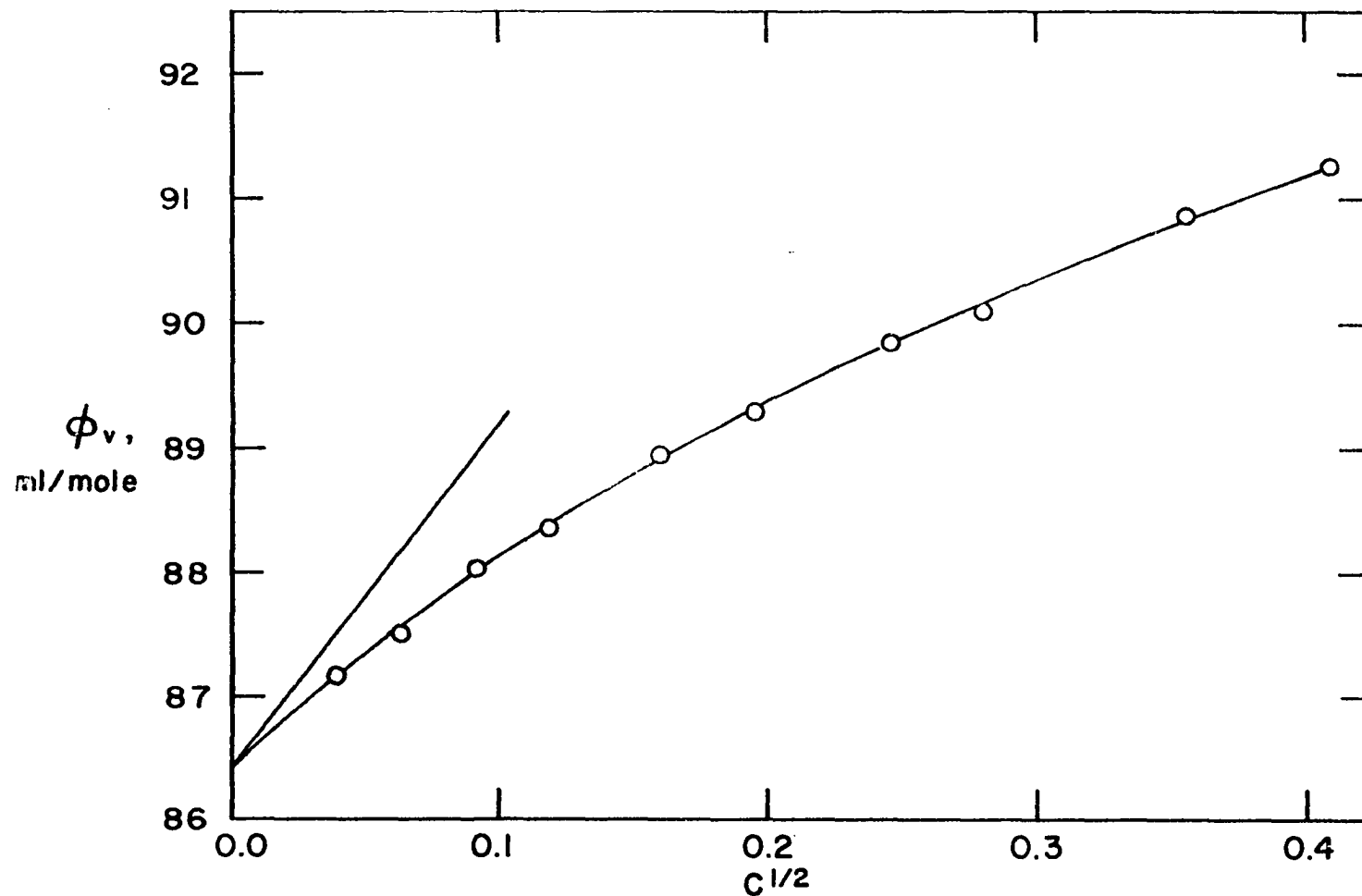


Figure 4. Apparent molal volume of $\text{Lu}(\text{ClO}_4)_3$ at 25°C

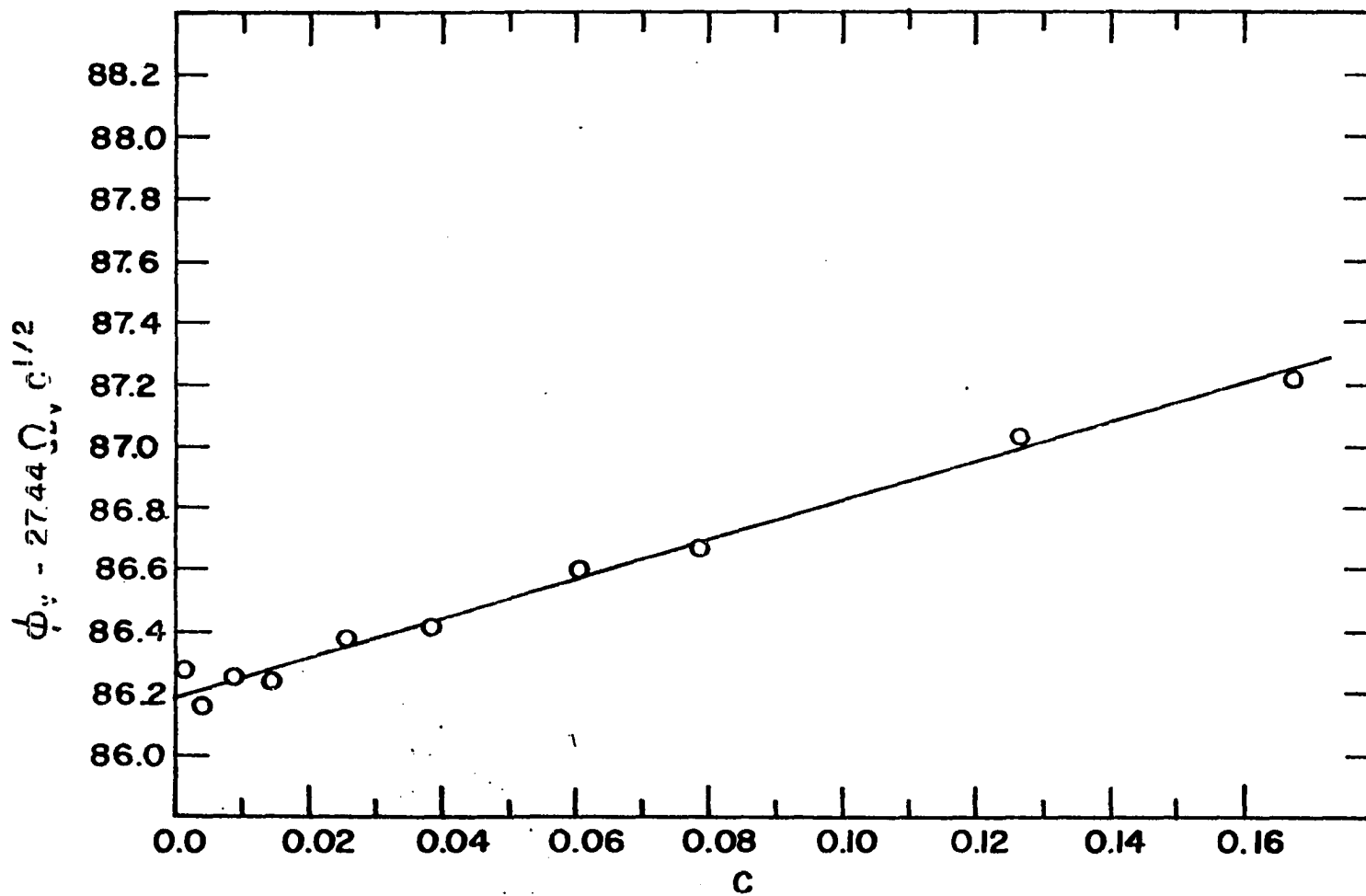


Figure 5. Owen-Brinkley extrapolation of ϕ_v for $\text{Lu}(\text{ClO}_4)_3$

two adjustable parameters. This is generally true for all the chlorides, perchlorates and nitrates mentioned before.

Figure 6 gives the concentration dependence of ϕ_v for $\text{Eu}(\text{NO}_3)_3$. Again, the straight line is the Debye-Hückel limiting slope. The apparent molal volume exhibits a positive deviation from the limiting slope. This behavior is present for all the nitrates from La to Dy, and for TmCl_3 . Figure 7 shows the data of $\text{Eu}(\text{NO}_3)_3$ when treated with the two parameter Owen-Brinkley function. Clearly, this function does not adequately represent the data. This is also the case for $\text{Nd}(\text{NO}_3)_3$, $\text{Pr}(\text{NO}_3)_3$, $\text{Sm}(\text{NO}_3)_3$, and $\text{Gd}(\text{NO}_3)_3$. TmCl_3 , and Tb and Dy nitrate, however, did fit the Owen-Brinkley function fairly well with two adjustable parameters.

Figure 8 is a graph of the apparent molal volumes at infinite dilution of the rare earth nitrates versus ionic radius. The ionic radii of Pauling were used (54). Because of the additivity nature of ϕ_v^0 , a similar graph results when the chlorides or perchlorates are plotted.

F. Experimental Errors

The experimental equipment and procedure employed in this research were essentially identical to that employed by M. J. Pikal (3). An extensive error analysis has been made by Pikal so only a brief analysis will be given here.

The specific gravities of the solutions were calculated from Equation 3.4

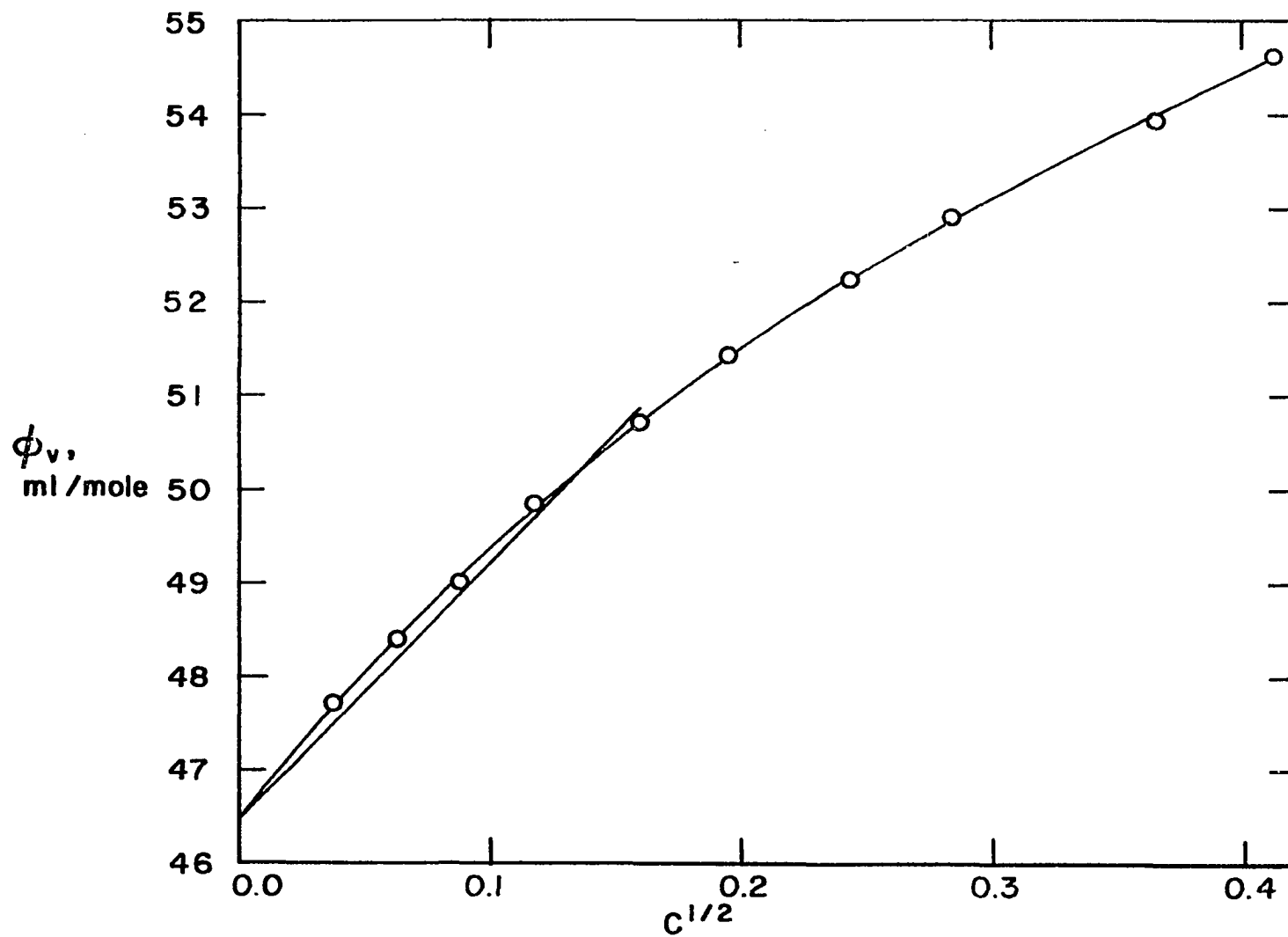


Figure 6. Apparent molal volume of $\text{Eu}(\text{NO}_3)_3$ at 25° C

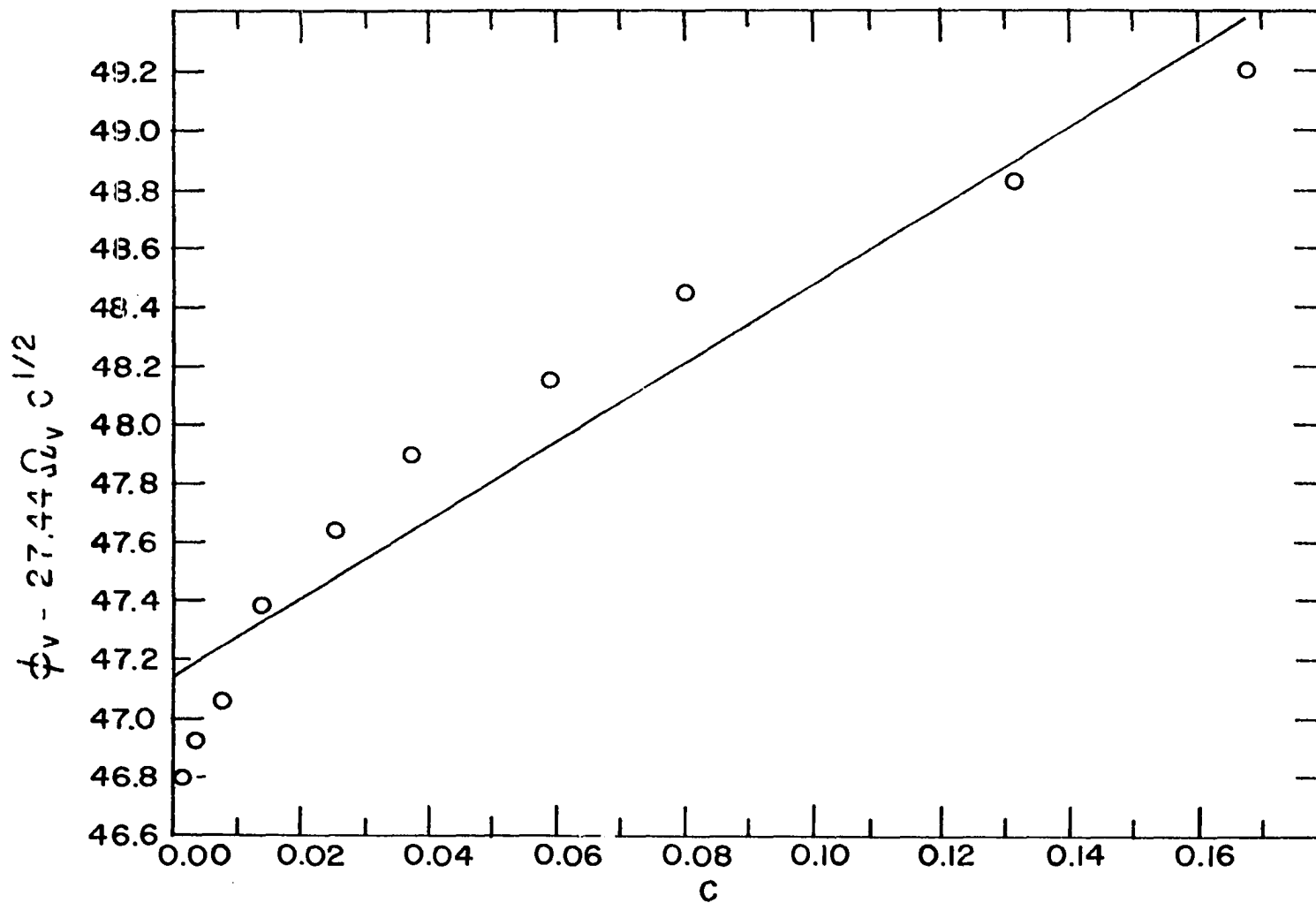


Figure 7. Owen-Brinkley extrapolation of ϕ_v for $\text{Eu}(\text{NO}_3)_3$

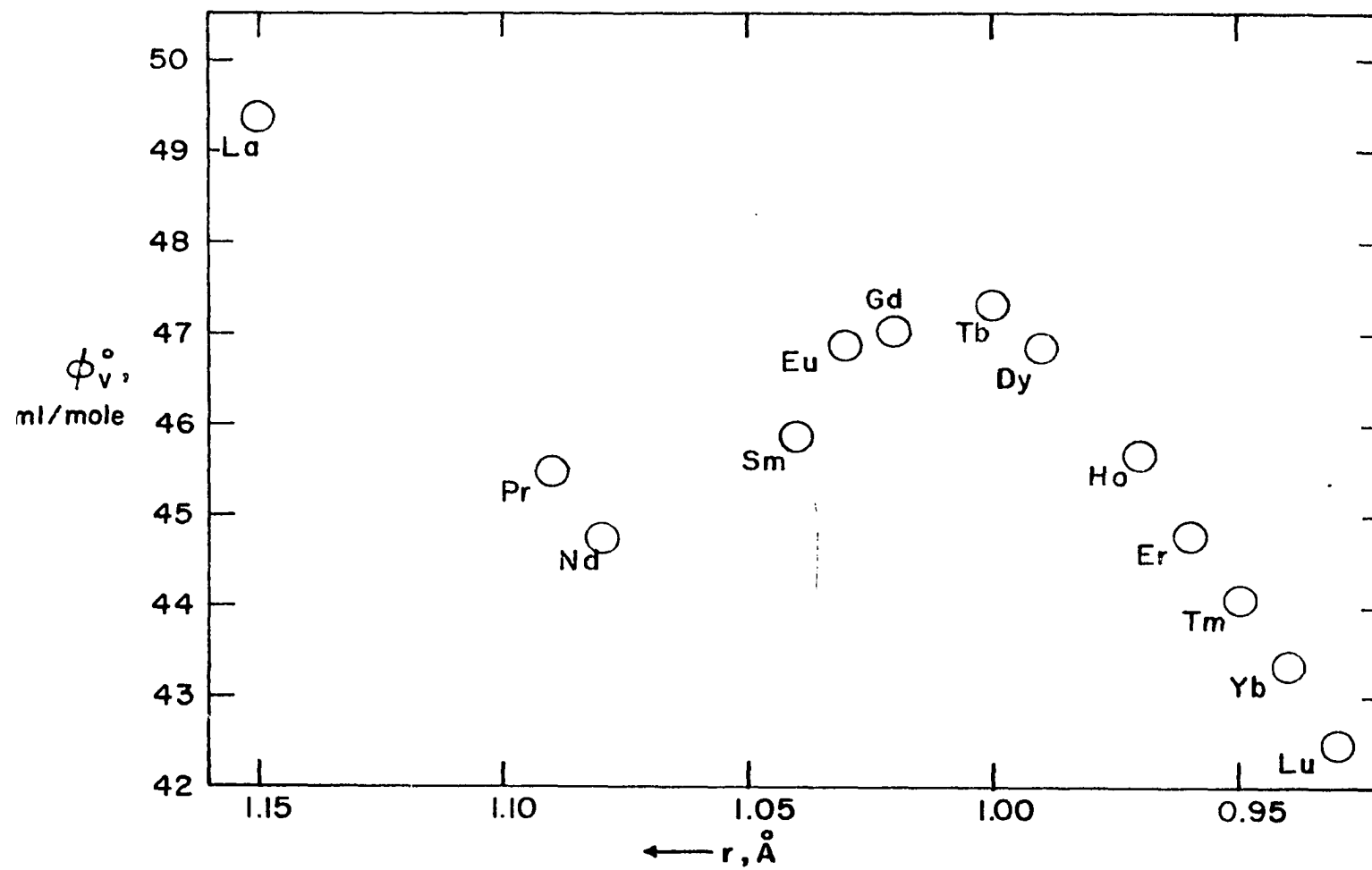


Figure 8. Apparent molal volumes at infinite dilution of the rare earth nitrates

$$S = \frac{Wt + \psi I^{\circ} + wt_{\text{soln}}}{Wt + \psi I^{\circ}_0} \quad (3.4)$$

The law of propagation of precision indices (81) yields the following equation for the square of the probable error in S:

$$\begin{aligned} P^2(S) = & \left(\frac{\partial S}{\partial Wt}\right)^2 P^2(Wt) + \left(\frac{\partial S}{\partial wt_{\text{soln}}}\right)^2 P^2(wt_{\text{soln}}) \\ & + \left(\frac{\partial S}{\partial \psi}\right)^2 P^2(\psi) + \left(\frac{\partial S}{\partial I^{\circ}}\right)^2 P^2(I^{\circ}) + \left(\frac{\partial S}{\partial I^{\circ}_0}\right)^2 P^2(I^{\circ}_0) \end{aligned} \quad (3.8)$$

where $P(X)$ is the probable error in the mean value of quantity X . The quantities used for the various components of Equation 3.8 are tabulated in Table 5.

Table 5. Estimate of the components of the probable error comprising Equation 3.8

Variable, X	$(\partial S/\partial X)$	$P(X)$
Wt^a	$2 \times 10^{-3} \text{ c (g)}^{-1}$	$\pm 5 \times 10^{-4} \text{ (g)}$
wt_{soln}	$1 \times 10^{-2} \text{ (g)}^{-1}$	$\pm \sqrt{5} \times 10^{-4} \text{ c (g)}$
ψ	$2 \times 10^{-1} \text{ (ma/g)}$	$\pm 5 \times 10^{-7} \text{ (g/ma)}$
I°	$1 \times 10^{-6} \text{ (ma)}^{-1}$	$\pm 1 \times 10^{-1} \text{ (ma)}$
I°_0	$1 \times 10^{-6} \text{ (ma)}^{-1}$	$\pm 1 \times 10^{-1} \text{ (ma)}$

^ac is the molar concentration.

Since the term $P(w_{\text{soln}})$ is itself a calculated quantity given by Equation 3.5, it was derived by applying the law of propagation of precision indices to that equation. Combination of terms in Table 5 yields

$$P(S) = (6 \times 10^{-12} \cdot c^2 + 3 \times 10^{-14})^{1/2} \quad (3.9)$$

The apparent molal volumes were calculated by Equation 2.12

$$\phi_v = \frac{1000}{c} (1 - S) + \frac{M_2}{d_{\text{H}_2\text{O}}} \quad (2.12)$$

The probable error in ϕ_v , then, is given by the expression

$$P(\phi_v) = \left[\left(\frac{1000(1-S)}{c^2} \right)^2 P^2(c) + \left(\frac{1000}{c} \right)^2 P^2(S) \right]^{1/2} \quad (3.10)$$

Pikal noted that the quantity $1000(1-S)/c$ was nearly constant with c (3). For this work, the value was approximately 300. The probable error in the concentrations of the stock solutions was estimated to be ± 0.1 percent. An additional error of about ± 0.02 percent was introduced during the dilution process in arriving at the final dilute solutions. Combining Equations 3.9 and 3.10 and introducing the error values discussed above yields

$$P(\phi_v) \cong \left[(0.36)^2 + \frac{3 \times 10^{-8}}{c^2} \right]^{1/2} \quad (3.11)$$

Values of $P(\phi_v)$ at even concentrations of molarity, c , are listed in Table 6.

Table 6. Probable error in the apparent molal volume

c	P(ϕ_v)	c	P(ϕ_v)
0.001	0.40	0.010	0.36
0.002	0.37	0.100	0.36
0.004	0.36	0.200	0.36

It should be noted that the relative concentration error for the points for a particular salt is only ± 0.02 percent and, therefore, the relative error in ϕ_v for a salt is given by the equation

$$P(\phi_v)_{\text{relative}} \cong \left[(0.06)^2 + \frac{3 \times 10^{-8}}{c} \right]^{1/2} \quad (3.12)$$

It can be seen that the major error due to an error in the concentration of the stock solution causes a displacement of the whole ϕ_v curve upward or downward on the ϕ_v axis. This would influence the absolute value of ϕ_v^0 but not the variation of ϕ_v with concentration. The errors in S and in the concentration resulting from dilution of the stock will predominantly influence the concentration behavior and not ϕ_v^0 if a suitable extrapolation function for ϕ_v^0 is used. The Owen-Brinkley extrapolation function was expected to limit the extrapolation error in ϕ_v^0 to ± 0.1 ml/mole. With the

error from the uncertainty in the concentration of the stock solution, this yields a probable error in ϕ_v^0 of ± 0.4 ml/mole. Since the additivity relationships may be expected to be valid, the uncertainty listed in Table 4 for the additivity relationships should be a measure of the error in ϕ_v^0 . That uncertainty is ± 0.3 ml/mole and yields a probable error in ϕ_v^0 of ± 0.2 ml/mole. It is felt that the higher error calculated from the error analysis arises from an overestimation of the error in the concentration. This error may actually be closer to ± 0.05 percent. The contribution to the probable error in ϕ_v^0 based on this error would then be 0.21 ml/mole rather than 0.36 ml/mole. Therefore, a probable error in ϕ_v^0 of ± 0.2 ml/mole is believed to be the best estimate.

IV. CONCLUSIONS

The rare earth salts studied to date may be grouped into two classes according to the type of concentration dependence of their apparent molal volumes. In the first class are included all of the chlorides and perchlorates studied and the nitrates from Tb to Lu. When the effect of the $\overset{\circ}{a}$ parameter on the apparent molal volume is considered, these salts are found to conform to the Debye-Hückel theory in the dilute concentration range. The second class includes the nitrates from La to Gd. These salts do not conform to the simple theory even when the effect of the $\overset{\circ}{a}$ parameter is included. It may be noted that in the classes mentioned above, the data of Pikal and Ayers are also included (3,1).

As was mentioned before, the Owen-Brinkley function given by the equation

$$\phi_v - 27.44 \Omega_v c^{1/2} = \phi_v^{\circ} + \frac{1}{2} K_v c \quad (2.62)$$

includes the effect of the $\overset{\circ}{a}$ parameter on the apparent molal volume. Ω_v , a function of the $\overset{\circ}{a}$ parameter and the square root of the molarity given by Equation 2.63, is less than 1 at finite concentrations and approaches unity as the concentration approaches infinite dilution. Salts which deviate negatively from the limiting law would be expected to be well represented by this function. Salts which show a positive deviation from the limiting law cannot be made to fit the

function unless unreasonably small values of the a^0 parameter are used.

The data was first fitted to Equation 2.62. The a^0 parameter, the mean distance of closest approach, was obtained from activity coefficient or conductivity data or, if not available, interpolated from the values for neighboring ions in the rare earth series. ϕ_v^0 and $\frac{1}{2} K_v$ were determined by the least squares method. As shown in Figures 5 and 7, some salts were well represented by the function while others were not. The standard deviations given in Tables 2 and 3 indicate that many of the salts could be equally well represented by the 2 parameter Owen-Brinkley equation as by the 4 parameter empirical polynomial. For the "light" rare earth nitrates, however, this was not the case. The data for these salts were then fitted to an extended Owen-Brinkley equation of the form

$$\phi_v - 27.44 \Omega_v c^{1/2} = \phi_v^0 + \frac{1}{2} K_v c + Dc^{3/2} \quad (4.1)$$

Two criteria were used to decide whether or not the additional term should be used:

1. The additional term should result in a significant (> 50 percent) decrease in the standard deviation. Furthermore, the resulting standard deviation should be comparable to that for the empirical polynomial fit.

2. No large cycling with concentration of the experi-

mental points about the curve was allowed.

Based on these criteria, the nitrates from La to Gd, except Nd, were well represented by Equation 4.1. The standard deviation for the $\text{La}(\text{NO}_3)_3$ data of Ayers, 0.17, was higher than for the other salts shown in Table 3. However, it compares favorably with the deviation from the empirical polynomial fit, 0.11, and no large cycling was evident. Though the standard deviation did decrease by about 50 percent for $\text{Nd}(\text{NO}_3)_3$ with the use of the higher order term, the resulting deviation was still greater than twice that for the empirical polynomial. Furthermore, large cycling of the data was still occurring. Addition of yet higher order terms for $\text{Nd}(\text{NO}_3)_3$, up to 5 parameters, was necessary to produce a fit comparable to the 4 parameter empirical polynomial. Consequently, the use of the Owen-Brinkley extrapolation function for $\text{Nd}(\text{NO}_3)_3$ could not be justified.

It may also be noted that the a_1 coefficient of Equation 3.6, the power series in $m^{1/2}$, is also an indicator of whether or not a salt may be represented by the simpler Owen-Brinkley equation. The a_1 coefficient is the coefficient of the $m^{1/2}$ term and, hence, might be called the "experimental" limiting slope. From a comparison of the a_1 coefficients in Table 2 for all the salts studied to date, it may be generally said that a salt having an a_1 coefficient near or below the limiting slope of 27.44 will be well represented by

the two parameter Owen-Brinkley equation in the dilute concentration range and may be put in the first class of salts. Further, salts having an a_1 higher than the limiting slope will require the higher term in the Owen-Brinkley function. This generalization, however, is not upheld in the cases of TmCl_3 and Tb and Dy nitrate. These salts have a_1 coefficients in excess of the limiting law and yet are represented by the simple Owen-Brinkley equation within experimental error. The discrepancy, of course, is due to the fact that the uncertainty in a_1 is large. Pikal found that his data could be essentially equally well represented by a third, fourth or fifth degree polynomial (3). From the variation of a_1 for these fits, he estimated the error in a_1 to be at least 25 percent. If the Gaussian criterion (81) is used to determine the appropriate fit, a third degree polynomial is generally indicated for the data. The method of least squares also allows an evaluation of the error in the coefficients determined (81, 82). An average error of ± 8 percent was evaluated for a_1 .

On the basis of the behavior of $\text{Nd}(\text{NO}_3)_3$, Ayers suggested that the positive deviation from the limiting law might be caused by formation of a neodymium nitrate complex (1). The formation of the mono-nitrate complex would effect the apparent molal volume in two ways. First, some 3:1 charge type electrolyte would be replaced by a 2:1 electrolyte. The

limiting slope of the apparent molal volume for a 2:1 electrolyte, however, is only 9.7. Second, the molal volume at infinite dilution for the 2:1 electrolyte would be greater than for the 3:1, uncomplexed form. The formation of the complex would be accomplished by a nitrate ion displacing a water molecule from the first or second coordination sphere of the rare earth ion. Owing to the relatively open structure of solvent water, this displacement would result in a positive volume change. This positive volume might be expected to be enhanced by a general "loosening" of the remaining coordinated water molecules due to a reduction in the effective charge of the central species. Due to these factors, an estimation of the apparent molal volume at infinite dilution for the complex is difficult to make.

The possibility that the nitrate ion might be acting as a bidentate ligand, replacing two water molecules on formation of a complex, must also be considered. Karraker has reported that, with tri-n-butyl phosphate, nitrate ion acts as a bidentate ligand with La^{+3} , Ce^{+3} , Gd^{+3} , Tb^{+3} and Dy^{+3} and implies similar coordination with Pr^{+3} , Nd^{+3} , Sm^{+3} and Eu^{+3} (83). However, under the same conditions with Er^{+3} and Yb^{+3} , only monodentate nitrate was found.

There is also disagreement concerning whether the complex is inner sphere or outer sphere. Choppin and Strazik from the determination of the ΔH and ΔS of the reaction for

several rare earth complexes concluded that the complex is outer sphere (84). Abrahamer and Marcus from density, N.M.R. and molar absorptivity studies on $\text{Er}(\text{NO}_3)_3$ concluded that the complex was predominantly inner sphere with some outer sphere complexing also occurring (85). Until the mechanism of the complex formation is more definitely understood, no theoretical estimate of the ϕ_v^0 for the complex can be made. $\Delta\phi_v^0$, the difference between the ionic molal volumes at infinite dilution for the complexed and free ion, could be experimentally determined by studying the pressure dependence of the equilibrium constant extrapolated to infinite dilution. To date, however, no such studies have been made for aqueous rare earth nitrate systems.

The solution may be considered as composed of two electrolytes which vary in their relative amounts with the total concentration. The apparent molal volume of the solution is the mole fraction weighted average of the apparent molal volumes of the two electrolytes. The dominant effect is a rapid increase in the apparent molal volume with concentration due to increasing concentration of the complex with its higher ϕ_v^0 . As the concentration decreases to infinite dilution, the equilibrium is shifted toward the free rare earth ion. The Owen-Brinkley function, therefore, may still be expected to be valid as an extrapolation function.

It was found that the function could be used to fit the data when the amount of complexing was not too great. It

was previously mentioned that the α parameters for the nitrates were determined from conductance data. The conductance data was fitted to the appropriate extrapolation function by adjusting the α^0 parameter. Small deviations in the conductance due to small amounts of complexing result in a lowering of the α^0 parameter. A comparison of the α^0 parameters listed in Table 3 indicates that the "light" rare earth nitrates are complexing to a larger extent than the "heavy" rare earths. The use of the depressed α^0 parameter in the Owen-Brinkley function, then, serves to compensate partially for complexing which is occurring. The addition of the third parameter in the $c^{3/2}$ term enables the function to fit the data well if the amount of complexing is not too great. The failure of the function to fit $\text{Nd}(\text{NO}_3)_3$ may be due to the fact that Nd^{+3} is complexing to a considerably greater extent than the others. But, on the other hand, a simultaneous shift in another equilibrium, that between Nd^{+3} ions of different coordination number, might also be occurring. This equilibrium will be discussed in more detail later.

If the assumption that positive deviations of the apparent molal volumes are caused by complex formation is correct, the data indicate that the rare earth nitrates from La to Gd are complexing to a greater extent than those from Tb to Lu. Furthermore, Nd shows the most amount of complex

formation. This agrees with the trend shown by the $\overset{\circ}{a}$ parameters though the $\overset{\circ}{a}$ parameters indicate that Tb and Dy should show a degree of complexing intermediate between the two groups. The sensitivity of the apparent molal volume to complexing, however, is not sufficient to indicate this. Krumholtz has determined the stability constants for some of the rare earth nitrates at 25^o C and an ionic strength of 1.0 (86). The stability constants determined for La, Pr, Nd, Eu and Tb were in the range 1.1 to 2.04. The stability constants for Tm, Yb and Lu were all 0.6.

A similar analysis of the concentration behavior of the apparent molal volumes of the rare earth chlorides and perchlorates studied to date indicate that no complexing comparable to that of the "light" rare earth nitrates is occurring. It is generally considered that the perchlorate ion does not form complexes and, for this reason, NaClO₄ and HClO₄ is generally chosen as the ionic medium when studying the complexing of other ions. Some evidence has been found for the formation of a second sphere perchlorate complex with Cr⁺³ at high concentrations (87). A similar outer sphere complex of ClO₄⁻ with Ce⁺³ has been postulated on the basis of uv spectral data (88). Nevertheless, the assumption that the amount of any perchlorate complex present in the solutions studied in this research may be considered negligible should be valid.

The stability constants for the rare earth chlorides have been found to be in the range 0.05 to 0.40 at an ionic strength of 1.0 and 22° C (89). The stability constants would not be expected to differ greatly at 25° C from those at 22° C. Therefore, it may be concluded that the rare earth chlorides, as a series, complex less at an ionic strength of 1.0 than the "heavy" rare earth nitrates which were found to be complexing the least among the nitrate series. This is in agreement with the conclusions drawn from the apparent molal volume data. A comparison of the stability constants at an ionic strength of 1.0 with the ϕ_v data which is at predominantly higher dilutions is not, of course, strictly valid. However, the change in the stability constants with ionic strength might be expected to be roughly parallel for the nitrates and chlorides. The trends, therefore, may be expected to be maintained at higher dilutions. A more quantitative analysis of the data is not possible until a clearer understanding of the mechanism of the complex formation is gained and a knowledge of the stability constants at lower concentrations and the pressure dependence of these constants are available.

The apparent molal volumes at infinite dilution for the chlorides and nitrates when plotted against rare earth ionic radius follow the trends found by Ayers and expanded by Pikal for the chlorides (1,3). The basic characteristics are a

fairly smooth decrease in ϕ_v^0 with decreasing ionic radius of the rare earth ion for the rare earths from La to Nd and from Tb to Lu. For the rare earths from Nd to Tb, there is an increase in ϕ_v^0 with decreasing ionic radius. The incomplete data for the rare earth perchlorate series indicates that the same trend is prevailing.

At infinite dilution, the assumption is made that the salt is completely ionized and no ion-ion interactions are occurring. If the data for an electrolyte is taken at sufficiently dilute concentrations that the number of ion-ion interactions are rapidly decreasing and if the extrapolation of the data to infinite dilution adequately represents the decrease in the remaining amount of ion-ion interactions, the ϕ_v^0 obtained will obey the additivity relationships given by the equation

$$\phi_{v_{C\nu+A\nu-}}^0 = \nu_+ \phi_{v_C}^0 + \nu_- \phi_{v_A}^0 \quad (2.44)$$

The data in Table 4 indicate that these conditions are being met and the additivity relationships are being obtained. For a particular rare earth anion series, then, the contribution to ϕ_v^0 made by the anions should be constant across the series. The trends found in ϕ_v^0 for a rare earth series should be independent of the nature of the anion and depend only on the nature of the rare earth ions and their interactions with the solvent. The additivity relationships show that this con-

dition is well satisfied.

The difficulties of separating the molal volume at infinite dilution of an electrolyte into its ionic components have already been discussed. The different methods yield a range in $\phi_{\text{VH}^+}^{\circ}$ from -7.24 to +3.9 ml/mole (90,53). For lack of a better value for a reference ion, the value of Panckhurst of -0.9 ml/mole for H^+ will be used (53). This value was calculated by the method of Noyes using the ionic radii of Pauling (60,54). The ionic molal volumes at infinite dilution for the trivalent rare earths may then be calculated. The results are given in Table 7 in ml/mole. The values for an ion are an average of the values obtained from the apparent molal volumes at infinite dilution of the chloride and nitrate salts. The values of ϕ_{V}° for the anions used were: $\phi_{\text{VCl}^-}^{\circ} = 19.0$ ml/mole and $\phi_{\text{VNO}_3^-}^{\circ} = 30.3$ ml/mole. These were taken from the tabulation by Stokes and Robinson (90) and corrected to $\phi_{\text{VH}^+}^{\circ} = -0.9$ ml/mole. The values of $\bar{V}_{2\text{R}+3}^{\circ}$ in Table 7 have an average uncertainty of ± 0.3 ml/mole arising from the uncertainty in ϕ_{V}° of the rare earth salts and in the ionic molal volumes of the anions. There is also a systematic error arising from the uncertainty in $\phi_{\text{VH}^+}^{\circ}$. This is estimated by Panckhurst to be ± 1.0 ml/mole (53). The values for cerium and promethium, included for completeness, were obtained by estimating values for ϕ_{V}° for the nitrates and chlorides from Figure 5 and from an analogous

Table 7. The ionic molal volumes at infinite dilution of the trivalent rare earth ions at 25° C

R^{+3}	$\bar{V}_{2R^{+3}}^{\circ}$	\bar{V}_{int}°	$\Delta\bar{V}^{\circ}$
La	-42.0	+3.8	-45.8
Ce	(-44.5)	(+3.4)	(-47.9)
Pr	-45.7	+3.3	-49.0
Nd	-46.5	+3.2	-49.7
Pm	(-47.3)	(+3.0)	(-50.3)
Sm	-45.4	+2.8	-48.2
Eu	-44.5	+2.7	-47.2
Gd	-43.9	+2.7	-46.6
Tb	-43.7	+2.5	-46.2
Dy	-44.2	+2.4	-46.6
Ho	-45.3	+2.3	-47.6
Er	-46.0	+2.2	-48.2
Tm	-47.2	+2.2	-49.4
Yb	-47.6	+2.1	-49.7
Lu	-48.8	+2.0	-50.8

graph for the chlorides and assumes they will fall on the smoothed curves. Consequently, these values should be treated as only rough estimates. It should be emphasized that sign of \bar{V}_{2R+3}° is minus indicating that a decrease in the volume on the addition of R^{+3} is occurring.

The \bar{V}_{int}° is the contribution to the ionic molal volume due to the size of the ion and was calculated from the equation

$$\bar{V}_{int}^{\circ} = \frac{4}{3} N \pi r^3 = 2.52 r^3 \quad (2.73)$$

where r is the ionic radius of Pauling in Angstroms (54). However, it is generally believed that the radius of an ion in solution is greater than its ionic crystal radius (60,63). These values, then, are probably slightly low.

$\Delta\bar{V}^{\circ}$ is the negative contribution to the ionic molal volume due to the interaction of the ions with the solvent. It was calculated by the equation

$$\Delta\bar{V}^{\circ} = \bar{V}_{2R+3}^{\circ} - \bar{V}_{int}^{\circ} \quad (4.2)$$

Since \bar{V}_{int}° is probably low due to the use of the ionic crystal radius rather than the ionic solution radius, $\Delta\bar{V}^{\circ}$ will be low in magnitude.

The effects of ion-solvent interactions may be artificially classified into two groups: 1) an electrostriction effect and 2) a coordination effect. The electrostriction

effect basically is the attraction of the polar solvent molecules by the electric field of the ions leading to a compression of the solvent about the ions. This compression is limited, however, by the tendency of the solvent molecules to seek specific geometric arrangements about the ions, the coordination effect.

From Equation 2.73, it is apparent that \bar{V}_{int}° will decrease with decreasing ionic radius across the whole series as is shown in Table 7. The electrostriction contribution to the $\Delta\bar{V}^{\circ}$ term is assumed to be given by Equation 2.71

$$\bar{V}_{el}^{\circ} = - \frac{Az^2}{r} \quad (2.71)$$

This equation also predicts a continuous decrease in \bar{V}_{el}° with decreasing ionic radius. These two terms together qualitatively, at least, predict the decrease in ϕ_{VR+3}° with decreasing ionic radius in agreement with the trends found from La to Nd and from Tb to Lu. The increase in ϕ_{VR+3}° from Nd to Tb, present in the $\Delta\bar{V}^{\circ}$ term listed in Table 7, apparently is due to a change in the limiting of the electrostriction effect caused by a change in the coordination of solvent molecules about the rare earth ions. This is the explanation suggested by Spedding with Ayers (1) and later modified by Saeger and Spedding (2).

They suggested that the rare earth ions in aqueous solution may exist in an equilibrium between two coordination

forms. For the larger ions from La to Nd, the species with the higher coordination number is preferred. For the smaller ions from Tb to Lu, the form with the lower coordination number predominates. For the ions after Nd to up to Tb, the equilibrium is shifting rapidly with decreasing ionic radius from the higher to the lower coordination form.

There is considerable evidence to support a change in coordination across the rare earth series (91,92,93,94,95). The values of the coordination numbers and where the change occurs, however, are still a matter of some debate. This data suggests that the change is occurring from Nd to Tb. It is not possible, however, to determine the absolute coordination numbers unambiguously.

Pikal (3), by assuming geometric models for the 8 and 9 coordinated Tb ion, was able to calculate the difference in volume between the two coordination forms. He then drew a line through the points for La, Pr, and Nd, assumed to have a coordination number of 9, on a graph of the chlorides analogous to Figure 5 and extend the line to the radius for Tb. From this, he obtained a value for ϕ_v° for the hypothetical 9 coordinated Tb ion. The difference between this value and the actual ϕ_v° for Tb, assumed to have a coordination of 8, compared favorably with that obtained from the models. The calculation is quite sensitive to the choice of models, however, and only proves that the change in coordination from

8 to 9 is compatible with the ϕ_v^0 data.

Hoard et al. (96) have determined the X-ray structure of some hydrated salts of the La(EDTA) ion. They found La to be coordinated with one EDTA molecule and three water molecules. They suggested that Lu would be coordinated to one EDTA molecule and two water molecules. If the EDTA molecule can be assumed to be a sexidentate ligand, this yields coordination numbers for La and Lu of 9 and 8, respectively. The transition from 9 to 8 is thought to occur around Eu and Gd.

Forsberg and Moeller (97) studied the complexing of $\text{Ln}(\text{en})_4^{+3}$ and $\text{Ln}(\text{en})_3^{+3}$ with NO_3^- , Cl^- , Br^- and ClO_4^- where (en) is the ligand ethylenediamine. They found that the number of anions complexing depended on the number of ethylenediamine ligands present, the size of the rare earth ion and the size of the anion. Coordination numbers of 9 and 8 were found. Furthermore, the point at which the coordination number changed from 9 to 8 occurred at successively larger rare earth ions when the ligand was varied from NO_3^- to Cl^- to Br^- . In agreement with the previous discussion, ClO_4^- was not found to form a complex.

Karraker, from a study of hypersensitive and normal absorption bands in Nd^{+3} aqueous solutions, concluded that Nd ion undergoes a change in coordination from 9 to 8 as the concentration of Nd^{+3} increases (98). This is compatible with the idea that an equilibrium exists between the ions

in solution.

It may also be noted that, for the rare earth perchlorate and chloride series, which show nearly parallel concentration behavior across each series over the concentration range studied, the trend in ϕ_v with rare earth ionic radius is maintained over the whole concentration range. Due to the substantial complexing occurring in the nitrates at low concentrations, however, large deviations from the trend are occurring at concentrations of a few thousandths molal. A shift in the equilibrium with rare earth concentration from the higher to the lower coordination form might be expected for the ions from Pr or Nd to Gd as reported by Karraker (98) for Nd. The data of Spedding et al.¹ for concentrated solutions suggest that a shift of this type might be occurring. However, the data in this study indicate that no appreciable shift in the equilibrium has yet occurred in the dilute concentration range up to 0.17 molal.

¹Spedding, F. H., H. O. Weber, V. W. Saeger, K. A. Gray, P. K. Boneau, M. A. Brown, C. W. Dekock, and J. Baker, Ames, Iowa, Private communication, 1969.

V. SUMMARY

The apparent molal volumes of the rare earth perchlorates, chlorides and nitrates studied to date have been found to approach the Debye-Hückel limiting law in dilute solutions. Furthermore, all of these salts, with the exception of $\text{Nd}(\text{NO}_3)_3$, were found to conform in dilute solution to the Debye-Hückel theory in the form of the Owen-Brinkley equation when the effect of the $\overset{\circ}{a}$ parameter was included. For the rare earth nitrates from La to Gd, which are known to complex to a greater extent than the other salts, an additional term in the Owen-Brinkley equation was necessary to compensate for the effect of the complex formation.

When the apparent molal volumes at infinite dilution of a rare earth series are plotted against rare earth ionic radius, ϕ_v° decreases from La to Nd and from Tb to Lu but increases from Nd to Tb with decreasing ionic radius. The variation was found to be independent of the anion indicating that no ion-ion interactions such as complexing are occurring at infinite dilution, as expected, and that the Owen-Brinkley equation is correctly extrapolating the data. An analysis of the components contributing to ϕ_v° determined that the trend was present in the term representing the ion-solvent interactions of the rare earth ions. This is in agreement with the suggestion of Spedding and co-workers that a change in coordination of water molecules about the rare earth ions

is occurring in the area from Nd to Tb (52). Furthermore, for the rare earth perchlorate and chloride series, which show a nearly parallel concentration behavior over the concentration range studied, the trend in ϕ_v with rare earth ionic radius is maintained over the whole concentration range investigated. Due to the complexing effect in the nitrates, however, large deviations from the trend are occurring at concentrations of a few thousandths molal.

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