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APPARENT AND PARTIAL MOLAL VOLUMES OF SOME RARE EARTH SALTS IN AQUEOUS SOLUTIONS

by

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I. INTRODUCTION

Since its introduction in 1923, the interionic attraction theory of Debye and Hückel (1) has been applied to the study of nearly all the properties of electrolytic solutions. In general, the theory is found to explain the behavior of solutions most adequately in a very dilute concentration range. The deviations of actual solution behavior from the proper limiting laws are found to increase with increasing concentration and complexity of valence type, and to be greater for non-equilibrium than for thermodynamic processes. Certain of these discrepancies are probably due to oversimplifications in the basic assumptions of the theory, and others to the approximations introduced to simplify the mathematical treatment.

Various attempts have been made to extend the theory to account for such variables as the change of dielectric constant with concentration, the formation of complex-ion-aggregates, hydration, and deviations from Boltzmann distribution of the ions. These extended forms, which will be discussed in a later section of this thesis, have resulted mainly in equations containing additional parameters, which can be adjusted for better agreement with experimental data, but which have little theoretical significance.

In addition, applications of the theory to the study of many solution properties involve various partial differential coefficients which are difficult to evaluate. While this difficulty is not due to inherent faults in the basic theory, it has limited the applications to a considerable extent, particularly in the application of extended forms of the theory to those properties involving partial differentiation of the basic equations.

A voluminous literature has evolved on the applications of the interionic attraction theory. Properties of strong 1-1 electrolytes have been extensively studied in aqueous solutions and as mixtures of electrolytes in aqueous solutions. Considerable study has also been made of these electrolytes in nonaqueous solutions and in systems of mixed solvents. The volume of information on the properties of polyvalent electrolytes is not nearly so extensive, and was, until very recently, largely confined to the study of 1-2 and 2-1 types of electrolytes. This literature, up to 1949, is thoroughly reviewed in the monograph of Harned and Owen (2).

The study of solutions of more complex electrolytes is desirable for two principal reasons. First, the Debye-Hückel equation in its extended form is found to be a function of the magnitudes of the ionic charges and the size of the ions.

Secondly, the more highly charged ions allow greater possibility of complex-ion formation and of stronger interaction between the ions and polar solvents. Gronwall, LaMer, and Sandved (3) and LaMer, Gronwall, and Grieff (4) have studied the expanded form of the Debye-Hückel equation and found that, for electrolytes of higher valence types, considerable deviations from the limiting laws are to be expected. The problem of ionic association has been studied by Bjerrum (5) and Fuoss and Kraus (6).

The scarcity of data on the properties of more complex electrolytes is due, in large measure, to undesirable properties exhibited by most solutes of these types. In particular, these electrolytes show a general tendency to hydrolyze to a considerable extent, thus leading to greater difficulty in the interpretation of results. Also, the number of strong electrolytes among the common salts of this type is very limited.

There is, however, a group of polyvalent electrolytes exhibiting many of the desired properties. This group consists of the salts of the rare earth metals and strong acids. These salts hydrolyze to a slight degree, but not to the extent generally exhibited by other salts of similar valence types. Furthermore, there are a number of other attractive properties exhibited by this series of elements.

From lanthanum through lutecium there is the possibility of a series of 14 salts having a common anion. Combinations of these metals with the anions of the halogen acids, nitric acid, perchloric acid, and sulfuric acid make available several extensive series of strong electrolytes of the 3-1 and 3-2 valence types. Moreover, the stepwise addition of the 4f electrons to an inner shell in the rare earth elements leads to two additional interesting properties. These are the variation in the magnetic susceptibilities of the ions and the lanthanide contraction or the decrease in atomic radii with increasing atomic number. There are thus available several groups of rare earth salts in which the physical properties of the cations vary regularly through the series. It should hence be possible to study the properties of solutions of various electrolytes as functions of the physical and chemical properties of the rare earth ions.

Use of these salts in the study of solutions has been limited, until very recently, by the unavailability of the pure salts. Due to the extremely slight differences in chemical properties from element to element, the individual elements cannot be readily separated by ordinary chemical procedures. The classical methods for the separation of the rare earths involve laborious and lengthy processes such as recrystallizations. By these methods and by taking advantage of the different oxidation states of some of the elements, small quantities of a number of the rare earths have been obtained in a reasonably pure form. However, only a few of the rare earth salts were available by these means, and these in relatively small amounts.

Large quantities of rare earth salts, of a high degree of purity, have become available only since the development of ion exchange methods of separation. The methods developed at Iowa State College (7,8,9,10,11,12,13,14,15) have made the rare earth oxides available in kilogram-quantities and of spectrographic purity.

Prior to the development of ion exchange methods of separation, data on solutions of rare earth salts were limited largely to salts of lanthanum, cerium, praseodymium, and neodymium (16,17,18). Since the pure salts have become more available, study of their physico-chemical properties in aqueous solutions has been extended to include a large number of rare earth salts and a variety of properties (19,20,21,22,23,24,25).

The purpose of this research is to extend the study of such solutions to include the apparent and partial molal volumes of some rare earth salts in aqueous solutions. The present study is directed particularly to the lower concentration range, up to about 0.3 molar, in which the more common experimental methods are of little value. The ultimate purpose of this research is to study the applicability of the proper limiting laws to unsymmetrical 3-1 electrolytes, and to accumulate accurate data for the apparent and partial molal volumes, the interpretation of which may reveal pertinent information concerning the mechanics of solutions. In particular, it is expected that such data may prove useful in the interpretation of ionic association and of solute-solvent interaction.

II. THEORY

A. Thermodynamic Review

The application of the interionic attraction theory to the thermodynamic properties of solutions requires the use of certain fundamental principles of thermodynamics. The necessary thermodynamic background will be reviewed in this section.

The first and second laws of thermodynamics may be combined into the following generalized formula:

$$dE = TdS - PdV + \sum_i \mu_i dn_i + (\partial E/\partial X)_{S,V,n_j}\, dX \qquad (1)$$

where

E is the internal energy,

T is the absolute temperature,

S is the entropy,

P is the pressure,

V is the volume,

$\mu_i = (\partial E/\partial n_i)_{S,V,n_j,X}$ is the chemical potential,

n_i and n_j are the numbers of moles of components i and j, and

X is any other variable on which the internal energy depends.

Since it is often preferable to use other independent variables, certain new thermodynamic functions may be defined as follows:

$$\text{Heat Content} = H = E + PV \tag{2}$$

$$\text{Free Energy} = F = H - TS = E + PV - TS \tag{3}$$

$$\text{Work Function} = A = E - TS\ . \tag{4}$$

Since the free energy, heat content, and work function are functions of the thermodynamic state, changes in the values of these functions may be written as total differential equations. Evaluation of the partial differential coefficients in these equations through use of equations 1, 2, 3, and 4 gives:

$$dH = TdS + VdP + \sum_i \mu_i dn_i + (\partial H/\partial X)_{S,P,N}\, dX \tag{5}$$

$$dF = -SdT + VdP + \sum_i \mu_i dn_i + (\partial F/\partial X)_{T,P,N}\, dX \tag{6}$$

$$dA = -SdT - PdV + \sum_i \mu_i dn_i + (\partial A/\partial X)_{T,V,N}\, dX\ . \tag{7}$$

From equations 1, 5, 6, and 7, it is seen that the chemical potential is equal to

$$\mu_i = (\partial E/\partial n_i)_{S,V,n_j,X} = (\partial H/\partial n_i)_{S,P,n_j,X}$$

$$= (\partial F/\partial n_i)_{T,P,n_j,X} = (\partial A/\partial n_i)_{T,V,n_j,X} \quad . \qquad (8)$$

The chemical potential is an important quantity in thermodynamics, being, as its name implies, a measure of the reactive capacity of the *ith* component in any given process. The fundamental significance of the chemical potential was first recognized by J. Willard Gibbs who was able to show that, for a system of *i* components in *p* phases, the condition for equilibrium at constant temperature and pressure is

$$\begin{array}{l} \mu_1^{\prime} = \mu_1^{\prime\prime} = \cdots\cdots\cdots\cdots \mu_1^{P} \\ \mu_2^{\prime} = \mu_2^{\prime\prime} = \cdots\cdots\cdots\cdots \mu_2^{P} \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ \mu_i^{\prime} = \mu_i^{\prime\prime} = \cdots\cdots\cdots\cdots \mu_i^{P} \quad . \end{array} \qquad (9)$$

In chemical thermodynamics, it is often more convenient to use two less general functions first defined by Lewis (26, 27). These functions are the fugacity, *f*, and the activity, *a*. The fugacity and activity may be partially defined by the following equations:

$$\mu = \mu^{*} + RT \ln \rho \qquad (10)$$

$$\mu = \mu^{\circ} + RT \ln a \qquad (11)$$

where μ^{*} and μ° are the chemical potentials in the reference and standard states, respectively.

The number of moles of the individual ionic species in a solution cannot be varied independently due to the requirement of electrical neutrality. Although the individual ions are of fundamental importance in solution behavior, it is impossible thermodynamically, to evaluate free energies, activities, etc., of the individual ionic species. It is advantageous, however, to define certain ionic activity products or ratios.

If an electrolyte $C_{\nu_+} A_{\nu_-}$ dissociates according to the following reaction:

$$C_{\nu_+} A_{\nu_-} \longrightarrow \nu_+ C_+ + \nu_- A_- \qquad (12)$$

where

C represents the cation,

A represents the anion,

ν_+ is the number of cations formed on dissociation, and

ν_- is the number of anions formed on dissociation, then the activity may be defined as

$$a = a_+^{\nu_+} \quad a_-^{\nu_-} = a_\pm^{\nu}; \quad \nu = \nu_+ + \nu_- \ . \qquad (13)$$

Substitution into equation 11 gives

$$\mu = \mu^\circ + RT \ln (a_+^{\nu_+} \quad a_-^{\nu_-}) = \mu^\circ + \nu RT \ln a_\pm \ , (14)$$

where $\underline{a_\pm}$ is the mean ionic activity.

To complete the definition of activity, it is necessary to specify the standard state. The choice of standard state is arbitrary and is generally chosen for convenience in the particular system under study. In many instances, the standard state corresponds to a purely hypothetical state. In these cases a measure of clarity may be gained by defining the activity in terms of a reference state, that is, the state in which the activity coefficient is equal to unity. It should be emphasized that the reference state and the standard state are not independent but are related through the activity and activity coefficient.

The definitions of activity and activity coefficient depend on the concentration units used. Since Raoult's law and Henry's law are expressed in terms of mole fractions, an activity coefficient defined in terms of the mole fraction is of theoretical interest. The rational activity coefficient is defined as

$$f_\pm \equiv a_{N\pm}/N_\pm = (f_+^{\nu_+} \quad f_-^{\nu_-})^{1/\nu} \quad ;$$
$$f_\pm \longrightarrow 1 \text{ as } N_\pm \longrightarrow 0 \quad , \tag{15}$$

where all the quantities except the mean ionic mole fraction, $N_\pm$, have been previously defined. The mean ionic mole fraction is defined by

$$N_\pm \equiv (N_+^{\nu_+} \quad N_-^{\nu_-})^{1/\nu} \tag{16}$$

where N is the mole fraction of the particular component whose activity is to be defined.

The concentrations of solutions are more generally expressed in terms of molality, m or molarity, c, and corresponding activity coefficients may be defined as

$$\gamma_\pm = a_{m\pm}/m_\pm = (\gamma_+^{\nu_+} \quad \gamma_-^{\nu_-})^{1/\nu} \quad ;$$
$$\gamma_\pm \longrightarrow 1 \text{ as } m_\pm \longrightarrow 0 \tag{17}$$

$$y_\pm \equiv a_{c\pm}/c_\pm = (y_+^{\nu_+} \quad y_-^{\nu_-})^{1/\nu} \quad ;$$
$$y_\pm \longrightarrow 1 \text{ as } c_\pm \longrightarrow 0 \quad . \tag{18}$$

In equations 17 and 18

$\gamma_\pm$ is the practical activity coefficient,

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

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

$c_\pm$ is the mean ionic molarity.

The mean ionic molality is defined by

$$m_\pm \equiv (m_+^{\nu_+} \; m_-^{\nu_-})^{1/\nu} = m(\nu_+^{\nu_+} \; \nu_-^{\nu_-})^{1/\nu} \quad , \qquad (19)$$

and the mean ionic molarity by

$$c_\pm \equiv (c_+^{\nu_+} \; c_-^{\nu_-})^{1/\nu} = c(\nu_+^{\nu_+} \; \nu_-^{\nu_-})^{1/\nu} \quad . \qquad (20)$$

Since the chemical potential, μ, is independent of the units in which the concentration is expressed, equation 14 may be written as

$$\begin{aligned} \mu &= \mu_N^o + \nu \, RT \ln f_\pm N_\pm = \mu_m^o + \nu RT \ln \gamma_\pm m_\pm \\ &= \mu_c^o + \nu \, RT \ln y_\pm c_\pm \end{aligned} \qquad (21)$$

where the superscript refers to the reference state and the subscript to the concentration units used. Furthermore, since,

$$N_\pm = \frac{m_\pm M_1}{\nu m M_1 + 1000} = \frac{c_\pm M_1}{\nu c M_1 + 1000(\rho - c M_2)} \qquad (22)$$

at all concentrations, and

$$N_{\pm} = \frac{m_{\pm} M_1}{1000} = \frac{c_{\pm} M_1}{1000 \rho_0} \qquad (23)$$

at infinite dilution,

$$\begin{aligned} \mu_N^o &= \mu_m^o + RT \ln 1000/M_1 \\ &= \mu_c^o + RT \ln 1000 \rho_0/M_1 \end{aligned} \qquad (24)$$

where

$\underline{M_1}$ is the molecular weight of the solvent,

$\underline{M_2}$ is the molecular weight of the solute,

$\underline{\rho_0}$ is the density of the solvent, and

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

Equations 21 and 24 may be combined to give

$$\begin{aligned} \ln f_{\pm} &= \ln \gamma_{\pm} + \ln (m_{\pm}/N_{\pm})(M_1/1000) \\ &= \ln y_{\pm} + \ln (c_{\pm}/N_{\pm})(M_1/1000 \rho_0) \end{aligned} \qquad (25)$$

as the relation between the activity coefficients in infinitely dilute solutions.

Combination of equations 22 and 25 results in the following general relationships between the activity coefficients:

$$\ln f_{\pm} = \ln \gamma_{\pm} + \ln (1 + m \nu M_1/1000) \qquad (26)$$

$$\ln f_{\pm} = \ln y_{\pm} + \ln\left[(\rho/\rho_0) - c(\nu M_1 - M_2)/1000\, \rho_0\right] \qquad (27)$$

$$\ln \gamma_{\pm} = \ln y_{\pm} + \ln\left[(\rho/\rho_0) - cM_2/1000\, \rho_0\right] \ . \qquad (28)$$

The rational activity coefficient, $f_{\pm}$, will be used to derive most relationships used in this thesis, but this may be converted through use of the interconversion equations 26, 27, and 28.

If G is any extensive thermodynamic variable, that is, if G is a function of the number of moles of the component present, the corresponding partial molal quantity $\overline{G_i}$ is defined as

$$\overline{G_i} = (\partial G/\partial n_i)_{T,P,n_j} \ . \qquad (29)$$

In this expression, n_i refers to the number of moles of the variable component i, n_j to all the other components which are held constant, while T and P are the absolute temperature and pressure, also held constant.

It should be noted that, while G is an extensive property, the partial molal quantity G_i is an intensive property.

For a multicomponent system, multiplication of the number of moles of each component by a constant, k, results in an increase of the property G in the ratio of k, i.e.,

$$G(kn_1, kn_2, \ldots\ldots kn_i) = kG(n_1, n_2, \ldots\ldots n_i) \quad . \quad (30)$$

This is the condition for a homogeneous function of the first degree, to which application of Euler's theorem gives

$$n_1(\partial G/\partial n_1)_{T,P,n_j,X} + n_2(\partial G/\partial n_2)_{T,P,n_j,X} + \ldots\ldots n_i(\partial G/\partial n_i)_{T,P,n_j,X} = G \quad . \quad (31)$$

The partial differential coefficients of equation 31 are defined as partial molal properties by equation 29. As a result

$$n_1\overline{G}_1 + n_2\overline{G}_2 + \ldots\ldots n_i\overline{G}_i = G \quad . \quad (32)$$

Differentiation of equation 32 gives

$$n_1\, d\overline{G}_1 + \overline{G}_1\, dn_1 + n_2\, d\overline{G}_2 + \overline{G}_2\, dn_2 + \ldots\ldots n_i\, d\overline{G}_i + \overline{G}_i\, dn_i = dG \quad . \quad (33)$$

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

$$dG = (\partial G/\partial n_1)_{T,P,n_i,X}\, dn_1 + (\partial G/\partial n_2)_{T,P,n_j,X}\, dn_2 + \ldots\ldots(G/ n_i)_{T,P,n_j,X}\, dn_i \tag{34}$$

$$= \overline{G}_1\, dn_1 + \overline{G}_2\, dn_2 + \ldots\ldots \overline{G}_i\, dn_i \quad . \tag{35}$$

Combination of equations 33 and 35 gives

$$n_1\, d\overline{G}_1 + n_2\, d\overline{G}_2 + \ldots\ldots n_i\, d\overline{G}_i = 0 \quad , \tag{36}$$

a familiar form of the Gibbs-Duhem equation.

For a two component system, such as those studied in this thesis,

$$n_1\, d\overline{G}_1 = -n_2\, d\overline{G}_2 \tag{37}$$

and

$$n_1\, \overline{G}_1 + n_2\, \overline{G}_2 = G \quad . \tag{38}$$

It is thus necessary to determine G_1 experimentally for only one component of a two component system since the value for the second component can then be obtained from equation 37 by analytical or graphical integration.

There are many other thermodynamic relationships involving partial molal quantities. For example, the partial molal free energy is related to the chemical potential through equation 8 and hence, through equations 10 and 11, to the fugacity and the activity. In particular, if the partial molal property is the partial molal volume, $\overline{V_1}$, we have from equation 6

$$(\partial F/\partial P)_{T,n_j,X} = V \quad \text{or} \quad \Big(\partial(F-F^\circ/\partial P\Big)_{T,n_j,X} = V - V^\circ . \qquad (39)$$

Differentiation of equation 39 with respect to n_1 gives

$$\Big(\partial(\overline{F}_1 - \overline{F}_1^\circ)/\partial P\Big)_{T,n_j,X} = \overline{V}_1 - \overline{V}_1^\circ \quad . \qquad (40)$$

This expression will be used to relate the partial molal volume to the Debye-Hückel equations.

The apparent molal quantities, defined as

$$\phi_G = (G - n_1 \overline{G}_1^\circ)/n_2 \quad , \qquad (41)$$

are related to the partial molal quantities by

$$\overline{G} = (\partial G/\partial n_2)_{T,P,n_j} = n_2(\partial \phi_G/\partial n_2)_{T,P,n_j} + \phi_G . \quad (42)$$

The apparent molal quantities have the advantage, as will be shown in a later section of this thesis, of being more easily determined experimentally. Partial molal quantities may then be obtained from the apparent molal quantities by analytical or graphical methods.

B. Interionic Attraction Theory

The development of the interionic attraction theory to its present state of usefulness was based upon a relatively simple physical model and effected through the use of elementary principles of electrostatics, hydrodynamics, and statistical mechanics. However, the essential concepts of ionizable solutes and of mutual interactions between the ions did not spring full grown to the aid of scientists, but were born in an orderly fashion as a consequence of systematic investigations and scientific intuition.

In the latter decades of the nineteenth century, physical chemistry was rapidly developing into an important branch of science with a great amount of interest centered on the freezing points, boiling points, osmotic pressures, vapor pressures, and electrical properties of solutions.

These properties were found to obey certain limiting laws. Such relations as

$$\pi V = nRT \, , \qquad (43)$$

where

π is the osmotic pressure,

V is the total volume of the solution,

n is the number of moles of solute,

R is the gas constant,

T is the absolute temperature,

and

$$\Delta T_e = K_e X_2 \, , \qquad (44)$$

where

ΔT_e is the elevation of the boiling point,

K_e is a constant, characteristic of the solvent, and

X_2 is the mole fraction of the solute,

were found to represent the behavior, with a reasonable degree of accuracy, of a large number of solutes in extremely dilute solutions. Concurrently, it was found that for many solutes the deviations of these properties from the limiting laws were much greater than experimental error.

An important advance in the theory of solutions was made by van't Hoff (28) who discovered that solutions exhibiting abnormal colligative properties were also good conductors of electricity. In an attempt to give quantitative expression of such behavior, van't Hoff introduced a parameter, the van't Hoff i factor, into equation 43. This factor was intended as a correction for all deviations regardless of the source and had no particular theoretical significance.

The same initial volume of the Zeitschrift fur physikalische Chemie (February, 1887) which contained the papers of van't Hoff, contained also, the first publication by S. Arrhenius (29) of his theory of ionic dissociation. Arrhenius postulated that when an electrolyte is dissolved in water, it dissociates, to a varying degree, into positive and negative ions in the following manner:

$$C_{\nu_+} A_{\nu_-} \longrightarrow \nu_+ C_+ + \nu_- A . \qquad (45)$$

If α is the degree of dissociation, a solution containing n molecules of solute in a specified volume will contain a total of $n(1 - \alpha + \nu\alpha)$ particles. This total is made up of $n(1 - \alpha)$ undissociated molecules and $\nu\alpha n$ ions.

Arrhenius further demonstrated, that if the theory of van't Hoff concerning osmotic pressure were valid, the following relationship should hold:

$$i = \frac{n(1 - \alpha + \nu\alpha)}{n} = 1 - \alpha + \nu\alpha \quad . \qquad (46)$$

The value of i can presumably be calculated from data for any colligative property. Arrhenius used the ratio of the observed to calculated freezing point depressions for the calculation of α. In addition, Arrhenius assumed the degree of dissociation, α, to be equal to the ratio Λ/Λ_0, where Λ is the equivalent conductance at concentration c and Λ_0 is the equivalent conductance at infinite dilution.

More numerous and more precise data on the behavior of electrolytes clearly indicated that the Arrhenius theory was not wholly adequate to explain the behavior of all electrolytes, even in moderate dilution. The behavior of weak electrolytes, such as most organic acids and bases, was found to support the theory, whereas solutions of strong electrolytes, i.e., strong acids, strong bases, and many salts did not yield results compatible with the theory.

Although the Arrhenius theory fell into considerable disrepute following its failure to predict the behavior of strong electrolytes, it provided a tremendous impetus to the study of solutions. The two principal assumptions of the Arrhenius theory were that ions exist in solution and that the ions behave independently of each other, acting as ideal solutes along with the undissociated molecules. The second of these assumptions has now been superseded by the concept of the total ionization of strong electrolytes, the deviations from ideal behavior being attributed to interactions between the ions. The first assumption was an important advance in the study of electrolytes and provided the foundation of all modern theories.

J. J. van Laar (30) was the first to clearly point out that ions cannot be expected to behave as ideal solutes, due to the strong electrostatic forces acting between them. This viewpoint was accepted and emphasized by Sutherland (31) and N. Bjerrum (32) who postulated that the electrostatic attraction was sufficient to account for all the behavior of solutions of strong electrolytes. Hertz (33) and Ghosh (34, 35,36) attempted unsuccessfully to formulate mathematical expression of the interionic attraction. In 1912, Milner (37) was successful in his analysis of the problem but his mathematical treatment was tedious and the results not wholly adequate.

In 1923, Debye and Hückel (1) introduced the concept of the "ionic atmosphere" and through use of Poisson's equation effected a solution of Milner's equation leading to exact relations for the behavior of electrolytes in very dilute solutions.

In the following treatment of the Debye-Hückel theory, any development pertaining to non-equilibrium processes will be ignored except that necessary for application of the theory to equilibrium processes. A completely generalized treatment of the theory may be found in the treatise of Harned and Owen (2).

The fundamental assumptions of the Debye-Hückel theory are:

1. Strong electrolytes are completely ionized in solution.
2. All deviations from ideal behavior may be explained on the basis of coulombic attractions between the ions.
3. The solvent is a uniform medium with a uniform dielectric constant.
4. The time average charge distributions obey Boltzmann statistics.
5. The Poisson-Boltzmann equation may be solved by use of an exponential expansion, which converges sufficiently rapidly so that higher terms may be neglected.

Assume an electrolytic solution contains n_1, n_2, n_3, ... n_s ions per cubic centimeter of the species indicated by the subscripts with charges e_1, e_2, e_3, ... e_s respectively.

Since Coulomb forces, $e_i e_j/Dr^2$, act between all pairs of ions separated by a distance r in a medium of dielectric constant D, the motion of the ions will not be independent. As a result, the presence of one ion will influence the distribution of all other ions and each ion will be surrounded by an ionic atmosphere containing, on an average, a slight excess of charges of the opposite sign. For a quantitative description of such a system, an analytical expression for the ionic distribution is required.

If it is assumed that, under the influences of the interionic attraction and thermal motion, the ions follow a Boltzmann distribution, the distribution factor will be given by

$$n_{ji} = n_i \, e^{-e_i \psi/kT} \quad , \qquad (47)$$

where ψ is the electrostatic potential, k is the Boltzmann constant, T is the absolute temperature, n_i is the concentration of i ions, and n_{ji} is the time average concentration of i ions in the vicinity of a j ion.

The charge density, ρ, for an electrolytic solution is equal to

$$\rho = \sum_{i=1}^{s} n_{ji} e_i = \sum_{i=1}^{s} n_i e^{-e_i \psi/kT} e_i \quad , \quad (48)$$

where the summation is over all the kinds of ions in the solution. An exponential expansion, and the neglect of higher order terms gives

$$\rho \simeq \sum_{i=1}^{s} n_i e_i \left(1 - \frac{e_i \psi}{kT}\right) = \sum_{i=1}^{s} \left(n_i e_i - n_i e_i \frac{e_i \psi}{kT}\right) . \quad (49)$$

This approximation is valid only when ψe_i is small compared to *kT*. This condition is approximately fulfilled at very low concentrations for electrolytes of simple valence types.

The condition of electrical neutrality requires that

$$\sum_{i=1}^{s} n_i e_i = 0 \quad , \qquad (50)$$

and the charge density becomes

$$\rho = -\sum_{i=1}^{s} n_i e_i \frac{e_i \psi}{kT} . \qquad (51)$$

In a medium of dielectric constant, D, the potential, ψ, and charge density, ρ, are related through Poisson's equation

$$\nabla \cdot \nabla \psi = -\frac{4\pi\rho}{D} . \qquad (52)$$

The Laplacian operator, $\nabla \cdot \nabla$, may be expressed in any convenient space coordinates.

In the absence of external fields and of concentration and velocity gradients, the ionic atmospheres are spherically symmetrical, and the potential, ψ, is a function of r only. Under these conditions, equation 52 becomes

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial \psi}{\partial r}\right) = -\frac{4\pi\rho}{D} = \frac{4\pi}{D}\sum_{i=1}^{s} n_i e_i \frac{e_i \psi}{kT} . \qquad (53)$$

Replacing e_i^2 by $Z_i^2 \epsilon_i^2$ where Z_i is the valence of the ion and ϵ_i is the electronic charge, and defining the quantity κ by

$$\kappa^2 = \frac{4\pi e^2}{DkT} \sum_{i=1}^{s} n_i z_i^2 \tag{54}$$

gives

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial \psi}{\partial r}\right) = \kappa^2 \psi \ . \tag{55}$$

Integration of equation 55 gives

$$\psi = \frac{Ae^{-\kappa r}}{r} + \frac{A'e^{\kappa r}}{r} \quad , \tag{56}$$

where *A* and *A'* are integration constants which must be evaluated from boundary conditions.

Since ψ must equal zero for an infinite value of *r*, *A'* must be zero and the value of the potential becomes

$$\psi = \frac{Ae^{-\kappa r}}{r} \ . \tag{57}$$

A second boundary condition requires that the electric field must be continuous. Thus when *r* is equal to the minimum distance of closest approach, a_i, the field of the ion and its atmosphere, $(\partial \psi/\partial r)$, must be equal to $(-Z_1 \epsilon/Dr^2)$, the field due to the ion alone. From equation 57

$$\frac{\partial \psi}{\partial r} = -\frac{A}{r^2} e^{-\kappa r} (1 + \kappa r), \tag{58}$$

and in order to satisfy the boundary condition

$$\left(\frac{\partial \psi}{\partial r}\right)_{r=a_1} = -\frac{A}{a_1^2} e^{-\kappa a_1}(1 + \kappa a_1) = -\frac{Z_1 \epsilon}{Da_1^2} . \tag{59}$$

Thus

$$A = \frac{Z_1 \epsilon}{D} \frac{e^{\kappa a_1}}{1 + \kappa a_1} . \tag{60}$$

Substitution of equation 60 into equation 57 gives, for $r = a_1$,

$$\psi = \frac{Z_1 \epsilon}{Da_1} \frac{1}{1 + \kappa a_1} , \tag{61}$$

which may also be written as

$$\psi = \frac{Z_1 \epsilon}{Da_1} - \frac{Z_1 \epsilon}{D} \frac{\kappa}{1 + \kappa a_1} . \tag{62}$$

The term $(Z_i \epsilon / Da_i)$ gives the potential due to the charge on the central ion alone, and is independent of the concentration. The second term on the right hand side of equation 62 is the potential, ψ', due to the ionic atmosphere and is a function of the concentration.

The quantity $1/k$ has the dimensions of length. This quantity, called the Debye length, is a measure of the distance from the central ion at which the maximum of potential occurs. This distance is a function of the concentration.

The electrical contribution to the work content is given by

$$W_{(el)} = \Delta A_{(el)} = \sum_{i=1}^{s} \int_0^{Z_i} \psi' de. \qquad (63)$$

From equations 8 and 63, it follows that

$$\Delta \mu_{i(el)} = \left(\frac{\partial \Delta A(el)}{\partial n_i}\right)_{V,T} = \int_0^{Z_i} \psi' de. \qquad (64)$$

Integration of equation 64, which corresponds to charging the ion (38,39) by increments de in the presence of a potential ψ', due to an existing ion atmosphere, gives

$$\Delta \mu_{i(el)} = \frac{-z_i^2 \epsilon^2}{2D} \frac{\kappa}{1 + \kappa a_i} \quad . \qquad (65)$$

The chemical potential of the <u>ith</u> constituent is defined as

$$\Delta \mu_i = \mu_i^o + RT \ln f_i + RT \ln N_i \qquad (66)$$

in which $\underline{f_i}$ is the activity coefficient and $\underline{N_i}$ is the mole fraction. This can be divided into two parts such that

$$\Delta \mu_i = \Delta \mu_{i(ideal)} + \Delta \mu_{i(el)} \quad , \qquad (67)$$

where

$$\Delta \mu_{i(ideal)} = RT \ln N_i \quad , \qquad (68)$$

and

$$\Delta \mu_{i(el)} = RT \ln f_i \quad . \qquad (69)$$

Equation 68 is an expression for the chemical potential of an ideal solution, which presumably would apply to a solution of electrolytes were it not for the ionic charges. For a single ion, equations 65 and 69 give

$$\Delta\mu_{i(el)} = kT \ln f_i = -\frac{Z_i \epsilon^2}{2D} \frac{\kappa}{1 + \kappa a_i} \qquad (70)$$

or

$$\ln f_i = \frac{-Z_i \epsilon^2}{2DkT} \frac{\kappa}{1 + \kappa a_i} \quad . \qquad (71)$$

The definition of κ, equation 54, contains the quantity $\sum n_i Z_i^2$. This quantity is related to the molar concentration, c_i, of ion species i by

$$\sum_{i=1}^{s} n_i Z_i^2 = \frac{N}{1000} \sum_{i=1}^{s} c_i Z_i^2 \qquad (72)$$

in which N is Avagadro's number.

The ional strength, Γ, is defined as

$$\Gamma \equiv \sum_{i=1}^{s} c_i Z_i^2 = 2\,\omega \ , \qquad (73)$$

where $\underline{\omega}$ is the ionic strength defined by Lewis and Randall (40) as

$$\omega = \tfrac{1}{2} \sum_{i=1}^{s} c_i z_i^2 \quad . \tag{74}$$

The combination of equations 54, 71, 72, and 73 gives

$$\ln f_i = \frac{-z_i^2 \epsilon^2}{DkT} \left(\frac{\pi n \epsilon^2}{1000\ DkT} \right)^{\frac{1}{2}} \sqrt{\Gamma} \quad \frac{1}{1 + \left(\frac{4 \pi N \epsilon^2}{1000\ DkT} \right)^{\frac{1}{2}} \sqrt{\Gamma}} \quad . \tag{75}$$

Taking the logarithm of equation 15 gives

$$\ln f_{\pm} = \frac{1}{\nu} \sum_{i=1}^{s} \nu_i \ln f_i \quad . \tag{76}$$

Hence,

$$\ln f_{\pm} = \frac{-\$'_f \sqrt{\Gamma}}{1 + A\sqrt{\Gamma}} \quad , \tag{77}$$

where

$$\mathcal{S}_f' = \frac{1}{\nu} \sum_{i=1}^{s} \nu_i \; z_i^2 \left(\frac{\pi N \epsilon^6}{1000(DkT)^3} \right)^{1/2} \tag{78}$$

and

$$A = \left(\frac{4\pi N \epsilon^2}{1000 \;\; DkT} \right)^{1/2} \; a^{o} \;\; . \tag{79}$$

Converting to common logarithms and substituting values for the physical constants gives

$$\log f_{\pm} = \frac{-\mathcal{S}_f \sqrt{\Gamma}}{1 + A\sqrt{\Gamma}} \quad , \tag{80}$$

where

$$\mathcal{S}_f = \frac{1.283 \times 10^6}{(DT)^{3/2}} \; \frac{1}{\nu} \sum_{i=1}^{s} \nu_i z_i^2 \;\; . \tag{81}$$

Equation 80 is the most generally useful form of the Debye-Hückel limiting law.

A number of attempts have been made to extend the Debye-Hückel theory to give better agreement with experimental data for solutions at higher concentrations and for electrolytes of more complex valence types.

Gronwall, La Mer, and Sandved (3) and La Mer, Gronwall, and Grieff (4) have studied forms of the fundamental Debye-Hückel equation in which higher terms of the exponential expansion are retained. The results of these studies indicate that for symmetrical electrolytes of high valence types, for electrolytes whose $\underline{a}^{o}$ values are low, and for solvents of low dielectric constant, departure from the limiting law should be found. The predicted departure from the limiting law is much larger for unsymmetrical valence type electrolytes, even in a solvent of high dielectric constant.

Ionic association or the formation of ion pairs was studied by N. Bjerrum (5). By assuming the ions to be rigid unpolarizable spheres in a medium of uniform macroscopic dielectric constant and by ignoring non-polar quantum bonds and ion-solvent interaction, Bjerrum arrived at

$$P = \frac{Nc_i}{1000}\left[\exp\left(\frac{-Z_i Z_j \epsilon^{2}}{DrkT}\right)\right] 4\pi r^2 dr \qquad (82)$$

as the probability distribution function. In equation 82 P is the probability and r is the distance measured from the center of the j ion.

If the i and j ions are of opposite charge, the probability as given by equation 82 exhibits a minimum at

$$r_{(min)} = q = \frac{\epsilon^2 |z_i z_j|}{2DkT} \quad . \qquad (83)$$

Bjerrum assumed that two ions at a distance $r < q$ are associated. For 1-1 electrolytes in water at 18° C. the minimum occurs at 3.52 angstroms. According to this hypothesis, 1-1 electrolytes for which the mean distance of closest approach, a^o, is less that 3.5 angstroms will form ion pairs while for similar electrolytes with values of a^o greater than 3.5, the Debye-Hückel theory should hold.

The theory of ionic association has been extended by Fuoss and Kraus (41,42,43) to include the formation of triple and quadruple ions.

The effect of concentration on the dielectric constant of the solvent was considered by Hückel (44). By assuming the dielectric constant of the medium to vary linearly with the ion concentration, Hückel obtained the expression

$$\log f_{\pm} = \frac{-\mathcal{S}_f\sqrt{\Gamma}}{1 + A\sqrt{\Gamma}} + B\,\Gamma \quad , \qquad (84)$$

in which B is a parameter to be determined from experimental data.

A quadratic term in c has been added to an extended form of the Debye-Hückel equation. This term is based on a suggestion by Onsager (45) that repulsive force terms might be expressed by a van der Waals co-volume correction. This idea was further developed by Van Rysselberghe and Eisenberg (46, 47).

G. Scatchard (48,49) made an extensive theoretical study of concentrated solutions of electrolytes with particular interest in the alkali halides. Scatchard's equation for the activity coefficient contains two parameters and requires knowledge of the molal volume, dielectric constant, valence, effective salting out radius for each ion, the effective collision diameter of a pair of ions, and the molecule-molecule interaction coefficient.

Although most of the extended forms of the Debye-Hückel theory, discussed in this section, are based in part on theoretical considerations, the better agreement with experimental results is due largely to the presence in the equations of a larger number of adjustable parameters.

Two recent advances in the theory of electrolytic solutions appear capable of providing more accurate descriptions of concentrated solutions. In both instances the physical models differ slightly from the Debye-Hückel model and other distribution factors are substituted for the Boltzmann factor.

A Fermi-Dirac form of ion distribution function has been deduced by Dutta and Bagchi (50,51,52,53,54). In deriving this distribution function, the available configuration space was divided into elementary cells of a size determined by the volume of exclusion of the ions. The assumption that only one particle can occupy a cell, and application of standard methods of statistical mechanics gave the distribution functions:

$$n_+ = \frac{N}{A_+ e^{Z_+ \epsilon \psi / kT} + 1} \quad ; \quad n_- = \frac{N}{A_- e^{Z_- \epsilon \psi / kT} + 1} \quad .(85)$$

In equations 85, $\underline{N}$ is the total number of ions per unit volume, $\underline{n_+}$ and $\underline{n_-}$ are the number of positive and negative ions per unit volume, $\underline{Z_+}$ and $\underline{Z_-}$ are the valences of the positive and negative ions, $\underline{\psi}$ is the potential at any point around a central ion, and $\underline{A_+}$ and $\underline{A_-}$ are constants. The constants were evaluated from consideration of the ionic concentration at an infinite distance from the central ion, i.e., where ψ approaches zero, and found to be

$$A_{+} = \frac{Z_{+}}{Z_{-}} \quad ; \quad A_{-} = \frac{Z_{-}}{Z_{+}} \;. \qquad (86)$$

Bagchi (54) applied this distribution function to the calculation of activity coefficients for strong electrolytes. For 1-1 electrolytes the values agree very well with experimental values up to a concentration of about 4 molar. For polyvalent electrolytes, the agreement is not as satisfactory even in dilute solutions.

The second recent modification in the distribution function for ions in solution is that due to Eigen and Wicke (55, 56, 57, 58a, 58b) who have shown that it is possible to extend the Debye-Hückel theory to higher concentrations by replacing the Boltzmann factor by another distribution function in which hydration and volume effects are taken into consideration. For strongly hydrated ions, this new distribution function has the form

$$\frac{n_r}{n_\pm} \cdot \frac{N_\pm - n_\pm}{N_\pm - n_r} = e^{\mp(Z \epsilon \psi(r)/kT)} \quad , \qquad (87)$$

where

n_r is the number of ions per cubic centimeter at a distance r from the central ion,

$n_\pm$ is the average number of ions per cubic centimeter at a distance $r = \infty$ from the central ion,

$N_\pm$ is the number of possible ion-sites per cubic centimeter, and

$\psi(r)$ is the electrostatic potential at a distance r from the central ion.

The number of possible ion-sites $N_\pm$ is given by

$$N_\pm = (N_+^{\nu_+} \; N_-^{\nu_-})^{1/\nu} \quad , \tag{88}$$

where

$$N_+ = \frac{1}{v_+} \; ; \quad N_- = \frac{1}{v_-} \quad . \tag{89}$$

The quantities v_+ and v_- are the volumes of the hydrated ions.

The distribution function, equation 87, corresponds to an equilibrium between the ions and vacant ion-sites of the form

$$\text{Ion}_{(r)} + \text{Ion site}_{(\infty)} \rightleftharpoons \text{Ion}_{(\infty)} + \text{Ion site}_{(r)} \tag{90}$$

for which the free energy of exchange is equal to $Z \epsilon \psi(r)$. The concentration of ion-sites at a distance r from the central ion is equal to $(N_{\pm} - n_r)$ and the concentration at infinity is equal to $(N_{\pm} - n_{\infty})$. Application of the law of mass action leads to equation 87.

Eigen and Wicke have applied this distribution function to the mean ionic activity coefficients of halogen acids, lithium halides, magnesium chloride and other electrolytes and have obtained excellent agreement.

C. Partial and Apparent Molal Volumes

1. Introduction and theory

Partial molal volumes are related to the mean ionic activity coefficients through fundamental thermodynamic relationships.

Equation 40, namely

$$\left(\frac{\partial(\overline{F}_2 - \overline{F}_2^o)}{\partial P}\right)_{T,n_j,X} = \overline{V}_2 - \overline{V}_2^o \quad , \qquad (40)$$

combined with equations 6, 14, and 15 gives

$$\overline{V}_2 - \overline{V}_2^o = \nu RT \frac{\partial \ln f_{\pm}}{\partial P} \quad . \qquad (91)$$

Substituting from equation 77 and performing the indicated differentiation gives

$$\overline{V}_2 - \overline{V}_2^{\circ} = \frac{\mathcal{S}_v \sqrt{\Gamma}}{1 + A\sqrt{\Gamma}} + \frac{W_v \sqrt{\Gamma}}{(1 + A\sqrt{\Gamma}\,)^2} \;, \qquad (92)$$

where

$$\mathcal{S}_v = 2.303\, \nu RT\, \mathcal{S}_f \cdot \tfrac{1}{2}\left(\frac{3\,\partial \ln D}{\partial P} - \beta\right) \quad , \qquad (93)$$

$$W_v = 2.303\, \nu RT\, \mathcal{S}_f\, A\left(\frac{\partial \ln D}{\partial P} - \frac{2\,\partial \ln a^{\circ}}{\partial P} - \beta\right) , \qquad (94)$$

and

$$\beta = (\partial \ln \Gamma/\partial P)_T \;. \qquad (95)$$

In order to apply equation 92, it is necessary to have data for the partial differential coefficients. Where these data are not available the equation is generally used in the form

$$\overline{V}_2 - \overline{V}_2^{\circ} = \frac{\mathcal{S}_v \sqrt{\Gamma}}{1 + A\sqrt{\Gamma}} \quad , \qquad (96)$$

or in the extreme limiting form

$$\overline{V}_2 - \overline{V}_2^0 = \mathscr{S}_v\sqrt{\Gamma} = S_v\sqrt{c} \quad , \tag{97}$$

where

$$S_v = \mathscr{S}_v\,(\sum_i \nu\, z_i^2)^{\frac{1}{2}} \quad . \tag{98}$$

Numerical values for the coefficient of compressibility $\underline{\beta = \partial \ln \Gamma / \partial P}$ and for $\underline{\partial \ln D / \partial P}$ are known for water at 25° C. Although these coefficients apply, in a strict sense, to the properties of the solutions, substitution of the values for water probably does not introduce serious errors for solutions at moderate concentrations.

The apparent molal volume,

$$\phi_v = \frac{V - n_1\overline{V}_1^0}{n_2} \quad , \tag{99}$$

may be expressed as a function of the concentration and the various parameters of the Debye-Hückel equation. From equation 99, on differentiation,

$$\frac{\partial(n_2\phi_v)}{\partial n_2} = \overline{V}_2 \quad , \tag{100}$$

hence

$$\phi_v = \frac{1}{n_2} \int_0^{n_2} \overline{V}_2 \, dn_2 \quad . \qquad (101)$$

Substituting for $\overline{V}_2$ from equation 97 gives

$$\phi_v = \frac{1}{n_2} \int_0^{n_2} (\overline{V}_2^o + S_v\sqrt{c}) \, dn_2 = \frac{1}{m} \int_0^{m} (\overline{V}_2^o + S_v\sqrt{c}) \, dm. \quad (102)$$

For extremely dilute solutions, for which $c \simeq m$,

$$\phi_v = \frac{1}{c} \int_0^{c} (\overline{V}_2^o + S_v\sqrt{c}) \, dc \quad , \qquad (103)$$

which on integration gives

$$\phi_v = \phi_v^o + (2/3)\, S_v\sqrt{c} = \phi_v^o + S_\phi \sqrt{c} \quad , \qquad (104)$$

where $\phi_v^o = \overline{V}_2^o$ and $S_\phi = 2/3\ S_v$, as the limiting expression for the apparent molal volume. This equation was first derived by Redlich and Rosenfeld (59) although an empirical relation of the same form had been observed by Masson (60) at an earlier date.

It is interesting to note that the slope of the limiting law for the apparent molal volume is equal to 2/3 that of the limiting law for the partial molal volume.

2. Methods for calculation of partial molal volumes

There are a number of graphical methods for the calculation of partial molal volumes.

The most obvious method, suggested by the defining equation for the partial molal volume, consists of determining the slope of V vs. n_2 curves. If V is the total volume of a solution containing n_2 moles of solute and a constant number of moles, n_1, of solvent, the slope of the curve at any concentration n_2 gives the partial molal volume, $\bar{V}_2 = (\partial V/\partial n_2)_{T,P,n_1}$, of component 2. This method is not capable of giving results of high precision due to the difficulty of accurately determining the slope of the curve at any given point.

A second graphical method, the chord-area method (61) is capable of giving more accurate values of partial molal volumes from data on total volumes as a function of molality. This method requires the calculation and tabulation of values of n_2, V, ΔV, Δn_2, and $\Delta V/\Delta n_2$. Values of $\overline{V}_2$ may be obtained from a smooth curve drawn through the chords of a plot of $\Delta V/\Delta n_2$ vs. n_2.

The graphical method of intercepts (62) yields values of $\overline{V}_2$ and $\overline{V}_1$ from one graphical plot. The molal volume, $v = V/(n_1 + n_2)$, of the solution is plotted against the mole fraction, $N = n_2/(n_1 + n_2)$. If, for any value of the mole fraction, N_2, a tangent is drawn to the curve, the intercept at $N_2 = 1$ gives $\overline{V}_2$ and the intercept at $N_1 = 1$ gives $\overline{V}_1$ for a solution of composition N_2. This method suffers from the common defect of most graphical methods, the difficulty of accurately drawing the tangent to a curve at a given point.

An analytical method may be used for the calculation of partial molal volumes whenever the total volume of the solution can be expressed as an algebraic function of the composition. If

$$V = a + bn_2 + cn_2^2 + dn_2^r \quad , \qquad (105)$$

where a, b, c, and d, are empirically determined parameters, differentiation gives

$$\overline{V}_2 = \left(\frac{\partial V}{\partial n_2}\right)_{T,P,n_j} = b + 2cn_2 + rdn_2^{r-1} \quad . \qquad (106)$$

This method is capable of giving accurate results provided the experimental data are accurate and sufficiently numerous to permit precise evaluation of the parameters by least-square methods.

The apparent molal volume is a convenient function for use in the calculation of partial molal volumes. Furthermore, apparent molal volumes are easily calculable from experimentally determined density data. For use in the calculation of partial molal volumes, apparent molal volumes are usually expressed as a function of a power series in the concentration of the form

$$\phi_v = a + bm^{1/2} + cm + \dots\dots km^r \qquad (107)$$

with empirically determined constants a, b, c, ... k. Application of equation 100 then gives

$$\bar{V}_2 = m\left(\frac{\partial \phi_v}{\partial m}\right)_{T,P,n_j} + \phi_v$$

$$= a + (3/2)bm^{1/2} + 2cm + \dots\dots\left[(r/2) - 1\right]km^r. \qquad (108)$$

Accurate measurement of the volume of a liquid and particularly of a small change in volume is very difficult to achieve. However, since

$$V = W/\rho \tag{109}$$

it is possible to determine the volume, V, from measurements of the density, ρ, and the weight, W, of the liquid.

Apparent molal volumes may be readily obtained from measurements of density or specific gravity. If the quantities $V = (n_1M_1 + n_2M_2)/\rho$, $\bar{V}_1^0 = M_1/\rho_0$, and $n_2 = n_1M_1m/1000$ are substituted into equation 99, the apparent molal volume is given by

$$\phi_v = \frac{1000}{m\rho}\left(1 - \frac{\rho}{\rho_0}\right) + \frac{M_2}{\rho} \quad , \tag{110}$$

where M_2 is the molecular weight of the solute, ρ_0 is the density of the solvent, and ρ is the density of the solution of molal concentration m.

Since the molal concentration, m, and the molar concentration, c, are related by

$$\frac{1}{c} = \frac{1}{m\rho} + \frac{M_2}{1000\,\rho} \quad , \tag{111}$$

the apparent molal volume may also be expressed as

$$\phi_v = \frac{1000}{c}\left(1 - \frac{\rho}{\rho_0}\right) + \frac{M_2}{\rho_0} \quad . \tag{112}$$

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

3. Determination of density or specific gravity of solutions

Differentiation of equation 112 with respect to the specific gravity, $S = \rho/\rho_0$, gives

$$d\phi_v = -\frac{1000}{c}\,dS \quad . \qquad (113)$$

The uncertainty in ϕ_v due to error in the measurement of the specific gravity, S, is thus seen to be a function of the concentration, c, with the relative uncertainty increasing with decreasing concentration. For a concentration of 0.001 molar, an error of $\pm 1 \times 10^{-6}$ in S results in an uncertainty of ∓ 1.0 cubic centimeter in ϕ_v. But the values of ϕ_v for solutions of extreme dilution are of particular importance. The limiting law for apparent molal volumes, equation 104, may be expected to hold only for very dilute solutions and the limiting value of the apparent molal volume, ϕ_v^0, must be obtained by extrapolation to infinite dilution. It is therefore imperative that the specific gravity be measured by a sensitive and accurate method.

A large number of methods have been developed for the determination of the specific gravities of liquids. These methods vary in accuracy from the most simple type of pycnometer or specific gravity bottle with a precision of about ±0.001 to dilatometric and magnetically controlled float methods with an accuracy of about $\pm 1 \times 10^{-7}$. The various methods are reviewed by Bauer in Physical Methods of Organic Chemistry (63). The advantages and disadvantages of each method are given as well as the accuracy to be expected from each method under optimum experimental conditions.

The method adopted for the present study is that of the magnetically controlled float originally developed by Lamb and Lee (64) and subsequently improved by Geffcken, Beckmann, and Kruis (65) and by MacInnes, Dayhoff, and Ray (66). This method, which will be described more completely in the experimental section of this thesis, has the advantage of being as sensitive in the dilute concentration range as in solutions of high concentration.

4. Recent developments in partial and apparent molal volumes

Volume changes which accompany the dissolution of matter and chemical reactions in a liquid phase have long been known and have been the subject of much study. Both partial and apparent molal volumes had been extensively studied before the advent of the Debye-Hückel theory and various interesting interpretations had been offered. However, it was only in 1929 that D. O. Masson (60) discovered the apparent molal volume of strong electrolytes to be a linear function of the square root of the molar concentration, i.e.,

$$\phi_v = a + bc^{\frac{1}{2}} , \qquad (114)$$

where a and b are characteristic constants for each salt. Wade (67), in 1899, narrowly missed obtaining this equation, expressing the results of his measurements in the form

$$\phi_v = \text{Const.} + \frac{n^{d-1}}{f(2^{d-1})} , \qquad (115)$$

where n is the concentration in gram-equivalents and d and f are constants characteristic of each salt. In this case, however, the quantity d, as determined by Wade, is almost constant for all strong electrolytes, having a value of about 1.5 for strontium chloride, calcium chloride, lithium chloride, and hydrochloric acid, and values of 1.64 for potassium chloride and 1.70 for sodium chloride. It is of interest to note that Wade obtained a value of d equal to 2.0 for cane sugar thus anticipating the discovery that $\underline{\phi_v}$ for non-electrolytes varies linearly with $\underline{c}$ rather than with $\underline{c^{\frac{1}{2}}}$ (68).

A. F. Scott (69) applied the Masson equation to the data of Baxter and Wallace (70) for solutions of 15 alkali halides and found excellent agreement. Scott found additivity relationships for $\underline{b}$, such as

$$\begin{gathered} b_{MCl} - b_{MBr} = \text{constant} \\ \text{and} \\ b_{LiX} - b_{NaX} = \text{constant} \end{gathered} \qquad (116)$$

to hold to within about ±0.07 cubic centimeters.

La Mer and Gronwall (71) also used the data of Baxter and Wallace to develop empirical equations for the partial molal volumes of the alkali halides. They also found additivity relationships to hold for partial molal volumes at infinite dilution.

The data of Baxter and Wallace were obtained from relatively concentrated solutions as were those of Geffcken (72, 73), Köhner (74), Huttig (75), Höleman and Köhner (76), and Shibata and Höleman (77). In every case, except for the lithium halides, Masson's equation represents the data extremely well over the concentration range measured and for temperatures from 0° to 70° C. The constant *b* is specific for each salt and is a function of the temperature.

In 1931, Redlich and Rosenfeld (59) derived an expression for the apparent molal volume, ϕ_v, from the Debye-Hückel theory. This equation,

$$\phi_v = \phi_v^o + \frac{2}{3} \mathcal{S}_v \sqrt{c} = \phi_v^o + \mathcal{S}_\phi \sqrt{c} \quad , \qquad (117)$$

where

$$\mathcal{S}_v = \frac{1.477 \times 10^6 RT}{(DT)^{3/2}} \left(\frac{\partial \ln D}{\partial P} - \beta \right) \left(\sum_{i=1}^{s} \nu_i z_i^2 \right)^{3/2} , \qquad (118)$$

indicates that for a given temperature, pressure, and solvent the limiting slope should be the same for all strong electrolytes of the same valence type.

At the time this equation was derived, the accepted values for the fundamental physical constants and the best available data for $(\partial \ln D/\partial P)$ and β gave a value of 1.86 for S_ϕ for 1-1 electrolytes in water at 25° C.

In order to test the limiting slope, S_ϕ, it is necessary to have accurate data for solutions at high dilution. Geffcken, Beckmann, and Kruis (65) developed a differential float method for the determination of relative densities with a very high precision. The effect of variations in temperature was minimized by the use of duplicate float systems for the simultaneous measurement of the densities of the solution and of pure solvent.

The data obtained by these authors and by Geffcken and Price (78) appeared to verify a limiting slope of about 1.9 for 1-1 electrolytes in aqueous solutions at 25°C. The function $\underline{\phi_v - 1.9\sqrt{c}}$ was found to be reasonably constant.

Additional data by Redlich and Bigeleisen (79,80) and Redlich and Neilsen (81) appeared to substantiate a value of about 1.9 for the limiting slope.

However, there are some strong 1-1 electrolytes which did not appear to give this slope even in very dilute solutions. The limiting slopes for solutions of ammonium chloride (82), ammonium nitrate (78), and hydrochloric acid (73,83) appeared to be closer to 1.6.

According to equation 118, the slope of equation 104 for 1-2 and 2-1 type electrolytes should be equal to

$$\left(\sum_{i=1}^{s} 1/2\,\nu_i z_i^2\right)^{3/2} = (3)^{3/2} \qquad (119)$$

times the slope for 1-1 electrolytes. The slope for 1-2 and 2-1 type electrolytes should thus be equal to about 9.9.

Data obtained from moderately concentrated solutions of most electrolytes of these types were found to have slopes which were specific for each salt (78,84,85,86,87,88), while accurate data for strontium chloride (89) appeared to conform to equation 104 with a slope of 9.9 in extremely dilute solutions.

There are only a few data in the literature for partial and apparent molal volumes of salts of more complex valence types. The apparent molal volumes of cupric sulfate (82) did not appear to approach the theoretical limiting slope while the limiting slope for nickel sulfate (90) appeared to be in excellent agreement.

Data for electrolytes of more complex valence types are too fragmentary and were measured at such high concentrations as to be of no value for testing the limiting law.

Within recent years, changes in the accepted values of the fundamental physical constants (91) and in certain empirical equations representing the pressure (92,93) and temperature (94) dependence of the dielectric constant have resulted in changes in the calculated values of the various limiting slopes. On the basis of these changes, Owen and Brinkley (95) have recalculated the slopes and have found that the theoretical value of S_ϕ for 1-1 electrolytes at 25° C should be about 2.5 rather than 1.9.

By utilizing the Debye-Hückel equation in the form

$$\log f_{\pm} = - \frac{S_f \, c^{1/2}}{1 + \kappa a^o} + Bc \quad , \qquad (120)$$

Owen and Brinkely (95) derived an extrapolation formula for the apparent molal volume, ϕ_v, of the form

$$\phi_v - \frac{2}{3} \, S_v \Omega_v c^{1/2} = \phi_v^o + \frac{1}{2} K_v c \quad . \qquad (121)$$

The function Ω_v is defined as

$$\Omega_v \equiv \left[\frac{1}{1 + \kappa a^o} \frac{\partial \ln D}{\partial P} - \frac{\sigma}{3} \beta \right] \left[\frac{\partial \ln D}{\partial P} - \frac{1}{3} \beta \right]^{-1} , \qquad (122)$$

where

$$\sigma = \frac{3}{\kappa^3 \, a^{o3}} \left[1 + \kappa a^o - \frac{1}{1 + \kappa a^o} - 2 \ln(1 + \kappa a^o) \right] . \qquad (123)$$

An extensive table of values for the function σ is given in the text of Harned and Owen (96). The empirically adjustable term, $\frac{1}{2}K_v c$, where K_v contains the derivative of B_c (equation 120), is approximately equal to

$$\frac{1}{m} \int_0^m K_v c \, dm \tag{124}$$

up to a concentration of about 1 molar.

Owen and Brinkley applied this extrapolation formula to the data of Kruis (89) for sodium chloride, of Geffcken and Price (78) for potassium chloride, and of Redlich and Bigeleisen (79) for hydrochloric acid. In all three cases the representation of the experimental data was excellent.

Wirth and Collier (97) found the extrapolation formula of Owen and Brinkley, equation 121, to represent the apparent molal volumes of sodium chloride to a concentration of 0.75 N, of potassium chloride to 1.0 N and of hydrochloric acid to 0.2 N. However the extrapolation equation in the form

$$\begin{aligned} \phi_v - \phi_v^o = {} & 2.303\, \nu RT\, S_f \left(\frac{1}{1 + \kappa a^o} \frac{\partial \ln D}{\partial P} - \frac{\beta}{3} \right) c^{1/2} + \\ & 2.303\, \nu RT\, S_f A' \frac{\partial \ln a^o}{\partial P} \theta c + \tfrac{1}{2} K_v c \quad , \end{aligned} \tag{125}$$

where

$$A' = \kappa a^o / c^{1/2} \tag{126}$$

and

$$\Theta = 1 - \frac{8}{5}\,\kappa a^{\circ} + \frac{12}{6}\,\kappa^{2} a^{\circ 2} - \ldots\ldots ; \quad \kappa a^{\circ} \leq 1, \qquad (127)$$

was found to represent the data over the entire concentration range when $\partial \ln a^{\circ}/\partial P$ was treated as an additional adjustable parameter. The values obtained for $\partial \ln a^{\circ}/\partial P$ appeared to be very reasonable.

The extrapolation formula of Owen and Brinkley, in its present form, is not applicable to electrolytes of more complex valence types. In the derivation of equation 121, no consideration was given to the extended terms of the Debye-Hückel theory. These terms must be investigated more fully before the formula is applied to electrolytes of higher valence types. In addition, more information is needed on the derivatives $\partial \ln a^{\circ}/\partial P$ and $\partial \ln D/\partial P$ and on the change in dielectric constant with concentration.

A number of semi-empirical relationships between apparent molal volumes and certain other physical properties, and a number of interesting interpretations of apparent molal volumes are discussed in a later section of this thesis.

III. EXPERIMENTAL

A. Method

As shown by equations 110 and 112, the apparent molal volumes of solutes are calculated from the experimentally determined specific gravities of the solutions.

The method used, in this research, for measuring specific gravities was the magnetically controlled float method originated by Lamb and Lee (64) and modified by Geffcken, Beckmann, and Kruis (65), and MacInnes, Dayhoff, and Ray (66).

This method consists of determining the current in a solenoid which is just sufficient to balance a float of known weight, in the solution, through the interaction of the field of the solenoid with a permanent magnet in the float. The interaction between the solenoid and the permanent magnet is empirically calibrated in terms of the weight equivalence, $\underline{\psi}$, of the current. The float is weighted so that it barely sinks in the solution and the magnetic field is applied in the opposing direction.

When the forces acting downward on the float are equal to those acting upward, we have

$$W + w = \rho V + I_0 \psi \quad , \qquad (128)$$

where W is the weight of the float; w is the weight of platinum added to the float, corrected to its weight in solution; ρ, is the density of the solution; V is the volume of the float; I_0 is the solenoid current necessary to balance the float, and ψ is the factor for converting the current into its weight equivalent. An analogous expression

$$W = \rho_0 V + I_0^0 \psi \quad , \tag{129}$$

holds for the same float at equilibrium in the pure solvent. In equation 129, ρ_0 is the density of the solvent, and I_0^0 is the solenoid current required to balance the float.

Solving equations 128 and 129 for ρ and ρ_0 and taking their ratio, gives

$$S = \frac{\rho}{\rho_0} = \frac{W + w - I_0 \psi}{W - I_0^0 \psi} \tag{130}$$

for the specific gravity of the solution.

The weight of platinum w, corrected for the buoyancy of the solution of density ρ, is related to the weight in vacuo, w', by

$$w = w'(1 - \rho/d) \quad , \tag{131}$$

where d is the density of the platinum. The weight w is conveniently obtained from equations 130 and 131 by successive approximations.

It is extremely difficult to determine the exact solenoid current necessary to hold the float suspended at equilibrium in the solution. For this reason, Lamb and Lee (64) determined the minimum current necessary to make the float rise, while Geffcken, Beckmann, and Kruis (65) and MacInnes, Dayhoff, and Ray (66) extrapolated the average rate of rise to zero velocity.

A plot of $1/t$ against I, where t is the time required for the float to rise through a fixed distance, was found to give an unsatisfactory extrapolation curve with the present experimental arrangement. The curves were definitely non-linear, and to obtain the current corresponding to $1/t$ equal to zero, required extrapolation over a range equal to or greater than that covered by the experimentally determined points.

Extrapolation curves of $1/t^2$ vs. I were found to be very satisfactory. The curves were linear, except for high current values, and the range of extrapolation was very small.

The use of the quantity $1/t^2$ for extrapolation purposes was based on the following considerations. Under the influence of the magnetic field of the solenoid, the equation of motion for the float is closely approximated by

$$m(d^2x/dt^2) = M\left[f\ (\alpha_1,\ \alpha_2,\ \beta_1,\ \beta_2)\right] I + \rho V - mg. \quad (132)$$

In equation 132, m is the mass of the float system (float plus added platinum weights); x is the distance along the direction of motion; M is a constant which includes the magnetic coupling factor between the solenoid and the permanent magnet; α_1, α_2, β_1, and β_2 are the angles between the ends of the permanent magnet and the top and bottom turns of the solenoid; f is a function of the cosines of these angles; ρ is the density of the liquid; V is the volume of the float, and g is the gravitational acceleration. Since the distance through which the float moves is very small compared to the dimensions of the solenoid, the function of the angles, f, in equation 132 is essentially constant. Treating this factor as a constant; integrating the equation twice, and solving for $1/t^2$, gives

$$1/t^2 = AI + B + v_0/(x-x_0)t \quad , \qquad (133)$$

where A, B, V_0, and $x - x_0$ are constants. When the initial velocity, v_0, is equal to zero, $1/t^2$ is a linear function of

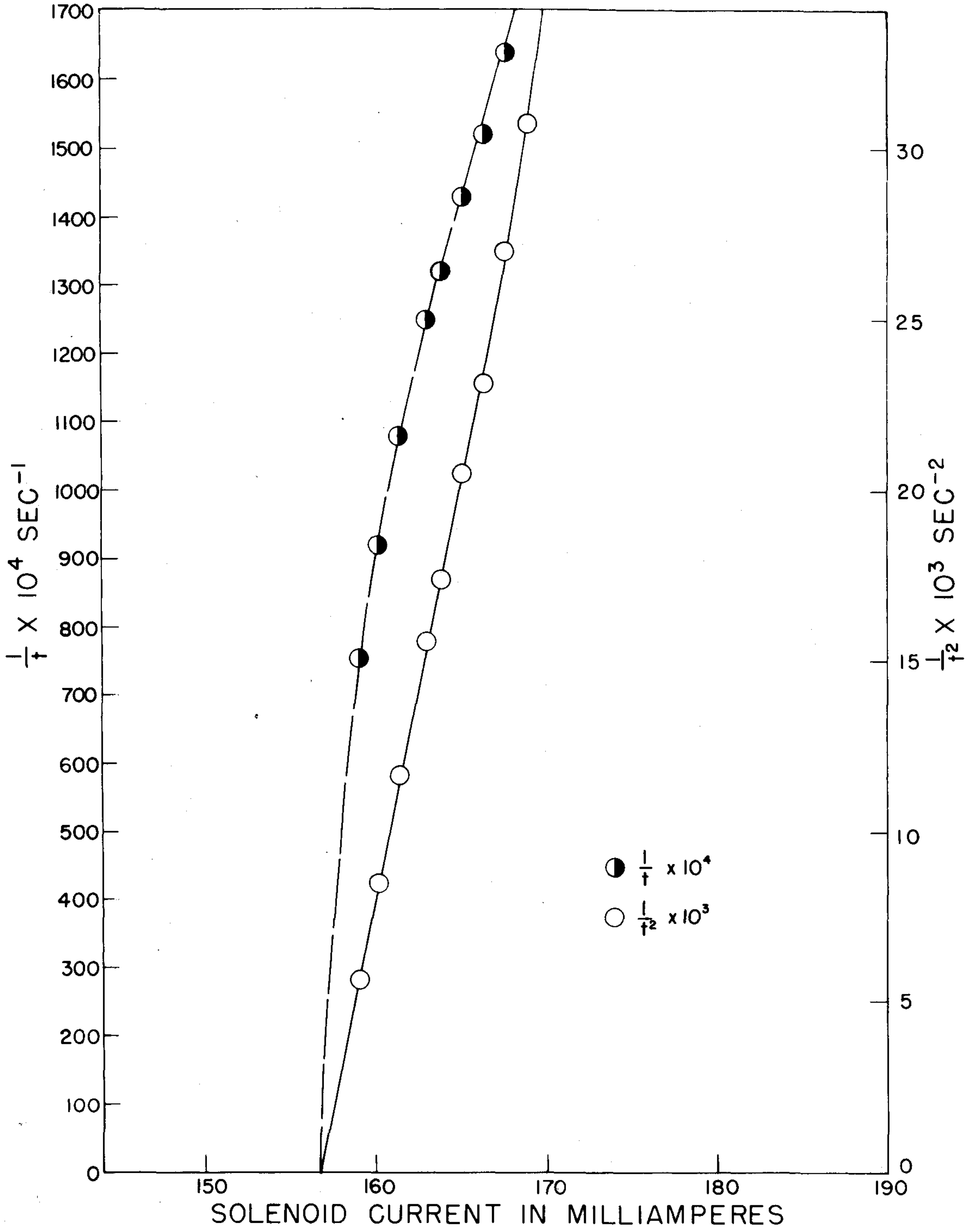
$\underline{I}$ within the limitations of the assumptions made in the integration of equation 132. However, it was found necessary to permit the float to rise through a distance of about 3 millimeters before timing in order to eliminate uncertain fluctuations in the rate of rise. As a result, $\underline{v_0}$, was not zero but approached zero as $\underline{1/t^2}$ became sufficiently small. The resultant curves were linear except for higher values of $\underline{I}$.

The two types of extrapolation curves are shown in Figure 1. Such extended curves were generally unnecessary, four or five points being adequate for extrapolation to the equilibrium current, $\underline{I_0}$.

B. Preparation of Materials

The rare earth oxides used in the experimental work for this thesis, were obtained from the following sources. Lanthanum oxide of 99.5 per cent purity and neodymium oxide of 75 per cent purity, obtained from Lindsay Power and Light Company were further purified at the Ames Laboratory of the Atomic Energy Commission by ion-exchange methods (7,8,9,10, 11,12,13,14,15). The erbium and ytterbium oxides were separated from Gadolinite ore by Dr. F. H. Spedding's Rare Earth Group at the Iowa State College Institute for Atomic

Figure 1. Extrapolation curves for equilibrium solenoid current


1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
$\frac{1}{t} \times 10^4$ SEC^{-1}
30
25
20
15
10
5
0
$\frac{1}{t^2} \times 10^3$ SEC^{-2}
150
160
170
180
190
SOLENOID CURRENT IN MILLIAMPERES
◐ $\frac{1}{t} \times 10^4$
○ $\frac{1}{t^2} \times 10^3$

Research and were purified by ion-exchange techniques. The Marsh sodium amalgam method (98,99) was used to extract the ytterbium from lutecium.

The rare earth oxides were analyzed for impurities of other rare earths and of common elements by emission spectrography (100). The purities of the oxides, as determined by Dr. V. A. Fassel's Spectrographic Group at the Ames Laboratory are given in Table 1. The limit of detection for the rare earth elements was about 0.02 to 0.03 per cent and for the common elements was about 0.01 per cent.

Table 1. Purity of rare earth oxides

Oxide	Analysis
La_2O_3	Less than 0.04% Pr_6O_{11}, 0.05% CeO_2, and 0.02% Nd_2O_3. Slight traces of iron, calcium, and magnesium detected prior to three precipitations from acid oxalate solution.
Nd_2O_3	No other rare earths or thorium detected. Slight trace of calcium detected prior to three precipitations from acid oxalate solution.
Er_2O_3	About 0.05% Ho_2O_3, 0.05% Y_2O_3, 0.05% Tm_2O_3, and 0.05% Yb_2O_3 detected.
Yb_2O_3	Less than 0.1% Lu_2O_3 detected. No other rare earths or common elements detected.

In order to remove any traces of iron, calcium, etc., the rare earth oxalates were precipitated three times from acid solutions with recrystallized Baker's Analyzed oxalic acid. After each precipitation, the rare earth oxalates were gathered in a fine sintered glass filter, dried at 120°C, and ignited to the oxides at about 1000° C.

Solutions of the rare earth salts were prepared by dissolving the oxides in pure acids.

Rare earth salts are thought to hydrolyze according to the following equilibrium:

$$RE^{+++} + H_2O \rightleftharpoons RE(OH)^{++} + H^{+} . \qquad (134)$$

Accordingly, whenever the solution contains six equivalents of the desired anion per mole of rare earth oxide, a small portion of the rare earth will be present as the basic cation, and the solution will be slightly acidic.

In preparing the rare earth chloride solutions, the dry oxides were added slowly to a slightly less than equivalent amount of approximately 6 normal acid. The excess oxides were removed by filtering the solutions through a fine sintered glass filter.

Due to the hydrolysis, slightly more than equivalent amounts of the oxides were dissolved. Some oxide was also present in colloidal form.

Aliquots of the solutions were titrated with 0.05 normal hydrochloric acid, the pH during the titration being followed with a Beckmann Model G pH meter. Typical strong acid-strong base titration curves were obtained. The equivalence points were determined from plots of $\underline{(\Delta\,\mathrm{pH}/\Delta\,\mathrm{ml})}$ vs. the average volume of titrant added.

The bulk solutions were adjusted to the pH values obtained from titrations of the aliquots, with a few drops of dilute acid, and the solutions were refluxed gently for from two to three hours. Aliquots of these solutions were then titrated with approximately 0.05 normal hydrochloric acid. In most cases it was found necessary to add a small amount of dilute base to the aliquots, prior to titration, in order to be able to follow the titration curve over a sufficiently extended range. For the concentrations of rare earth salts used in this work, the equivalence pH for the titration of the basic rare earth cations was several units below that of the strong acid-strong base equivalence point and there were no interferences. The bulk solutions were carefully adjusted to the pH values determined from titration of the aliquots. These solutions were found to be very stable and were relatively free of colloids as evidenced by very weak Tyndall effects.

Rare earth nitrate solutions were prepared in analogous manner except that Baker's Analyzed nitric acid was used in place of the hydrochloric acid.

In measuring the specific gravities of solutions of these salts, stock solutions of three concentrations were used for each salt. These concentrations were of approximately 25, 10, and one per cent, by weight. The solutions prepared by dissolving the oxides were adjusted to concentrations of about 25 weight per cent by the addition of distilled water. These solutions were analyzed and solutions of approximately 10 per cent and one per cent composition were prepared from accurately weighed amounts of the 25 per cent stock solutions and of distilled water. These solutions were stored in volumetric flasks with caps which could be greased to eliminate the possibility of evaporation.

The customary method for the analysis of solutions of rare earth salts consists in the precipitation of the rare earth oxalates and subsequent ignition to the oxides for weighing. However, the rare earth oxalates are slightly soluble due to the formation of complex ions such as $RE(C_2O_4)^+$ and $RE(C_2O_4)_2^-$ (101,102). This solubility is negligible for the light rare earths but becomes appreciable for the heavy rare earths resulting in errors in analyses by the oxalate precipitation method.

Recovery experiments were made on ytterbium chloride solutions prepared by dissolving known weights of freshly ignited ytterbium oxide in minimum amounts of hydrochloric acid. Precipitation with oxalic acid, filtration, and ignition to the oxide gave an average recovery of 98.26±0.14 per cent. Additional experiments were made by the direct precipitation of the ytterbium oxalate in the crucibles in which the oxides were to be weighed. A slight excess of oxalic acid was added to the solution in each crucible, and the samples were evaporated to dryness under infrared lamps. The dry residues were moistened with distilled water and a small quantity of nitric acid was added to each crucible. The samples were again ignited to dryness and ignited to the oxide at about 1000° C. An average recovery of 100.008±0.027 per cent was obtained by this method. The stock solutions of all the rare earth salts used in this research were analyzed by this procedure. The solutions of rare earth chlorides were also analyzed for chloride, by the standard gravimetric method. The chloride analyses were consistently lower than the oxide analyses by about 0.1 per cent. All calculations were therefore based on the oxide analyses since the titration curves obtained in the preparations of the solutions indicated that equivalent solutions were obtained.

The potassium chloride used in checking the calibration of the apparatus was prepared in the following manner. Baker's Analyzed potassium chloride was reprecipitated from aqueous solution saturated with hydrogen chloride gas. The salt was dried in an oven at 110° C. and fused in platinum crucibles at about 800° C. under an atmosphere of dry argon. The potassium chloride solutions were prepared by adding weighed amounts of the fused potassium chloride to weighed quantities of distilled water.

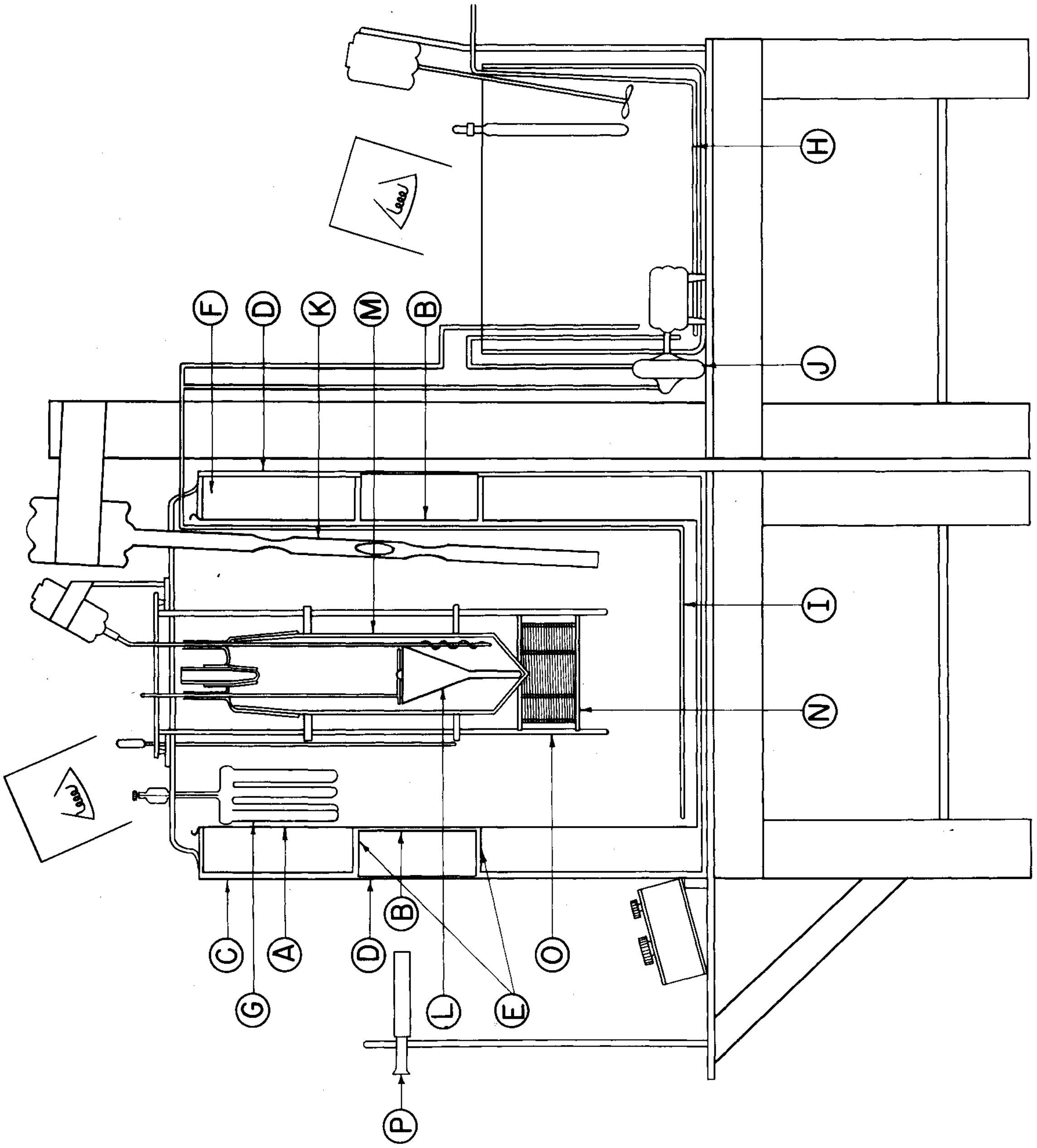
The distilled water used in all dilutions had a specific conductance of less than 1.0×10^{-6} mhos per centimeter. In every case, except for one series of measurements on neodymium nitrate solutions, the same sample of water was used in preparing the stock solutions and in making the dilutions.

C. Apparatus

1. Description

A diagram of the apparatus used in the experimental work for this thesis is given in Figure 2. The letters used in the following description refer to the lettering in this diagram.

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


F
D
K
M
B
H
J
I
N
C
A
G
D
B
L
E
O
P

For pure water at 25° C., the coefficient of expansion corresponds to a change in density of about 2.5×10^{-7} grams per milliliter per 0.001° C. Since similar values may be expected for dilute aqueous solutions, it was necessary that the temperature of the solutions be controlled to within one or two thousandths of a degree in order to obtain significant density measurements for solutions at extreme dilution. In order to obtain the best possible temperature control, an insulated constant temperature bath was constructed.

The basic component of the constant temperature bath was a 30 gallon stainless steel container, A. This container had an inside diameter of 18 inches and a depth of 27 inches.

Rectangular openings, about 4 inches by 7 inches, in opposite sides of the container were fitted with curved Plexiglass windows, B. These windows were made water-tight with rubber gaskets and were held in place by brass frames placed inside and outside the thin stainless steel walls. It was found necessary to heat the Plexiglass and form it to the curvature of the container before fastening it into place.

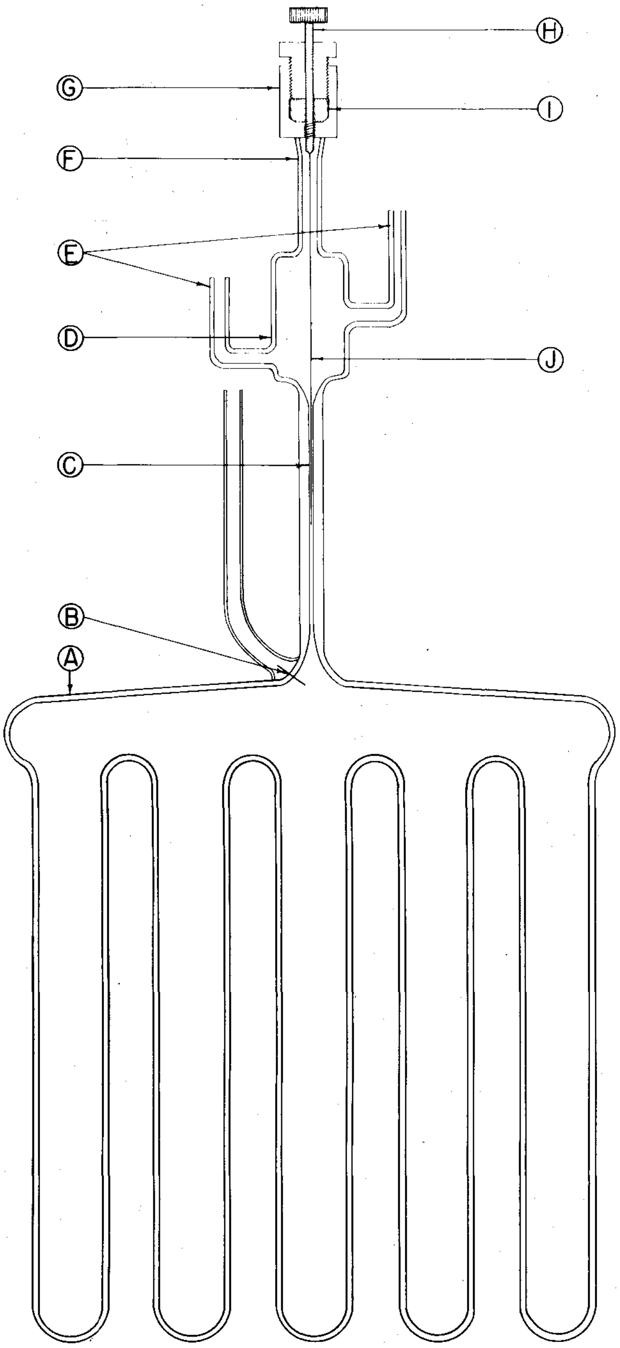
The stainless steel container was placed inside a wooden box, C, whose dimensions were 28 inches by 28 inches by 30 inches. This box had glass covered openings, D, to match the windows of the inner bath. The spaces between the windows of the container and the windows of the box were framed with plywood, E, and the remaining space, F, was filled with Zonolite insulating material. A wooden cover, fitted closely around the stainless steel container, was added to the box, and the completed unit was placed on a strong wooden stand in order to bring the windows to a convenient height.

A thermo-regulator, G, and Figure 3, similar to that designed by MacInnes and Dayhoff (66), was used to control the temperature of the bath. A mercury reservoir, in the shape of an arc with five suspended fingers, was constructed from 25 millimeter Pyrex tubing. After being filled with about 15 pounds of triple distilled mercury, the reservoir was "flamed out" by heating the walls with a flame while the reservoir was connected to a vacuum pump. This treatment resulted in a mirror-like surface for the walls of the reservoir.

A capillary tube of about 0.3 millimeter inside diameter was sealed to the reservoir. The upper end of this capillary was sealed to a glass expansion chamber with a capacity of about 15 milliliters.

To complete the filling of the thermo-regulator, the reservoir was heated until the expansion chamber was about half filled with mercury and additional clean mercury was added to the expansion chamber as the reservoir was allowed to cool. This procedure was repeated until the mercury

Figure 3. Diagram of thermo-regulator



Ⓐ MERCURY RESERVOIR OF 25 mm PYREX TUBING

Ⓑ PLATINUM WIRE SEALED THROUGH RESERVOIR WALL

Ⓒ PYREX CAPILLARY

Ⓓ EXPANSION CHAMBER

Ⓔ CONNECTIONS FOR HYDROGEN GAS

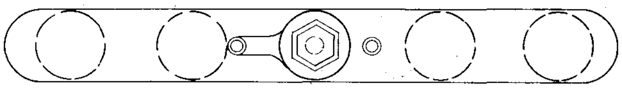
Ⓕ KOVAR SEAL

Ⓖ BRASS PACKING GLAND

Ⓗ NO. 8-24 SCREW

Ⓘ TEFLON WASHER THREADED TO FIT NO. 8-24 SCREW

Ⓙ FIVE INCH LENGTH OF NO. 28 CHROMEL-A WIRE SILVER SOLDERED TO NO. 8-24 SCREW



meniscus was about the middle of the capillary when the regulator was in thermal equilibrium with water at 25° C.

A small brass packing gland was sealed to the top of the expansion chamber through a Kovar seal. The cap of this packing gland was threaded to fit a number 8-24 screw to which a five inch length of number 28 Chromel-A wire was silver soldered. This wire, which extended into the glass capillary, provided the intermittant contact with the mercury in the reservoir. The permanent contact was made through a platinum wire sealed in the wall of the reservoir.

A small Teflon washer, threaded to fit the screw, was used as the packing for the packing gland. Final adjustment of the temperature was obtained by raising or lowering the wire in the capillary.

The electrical contacts from the thermo-regulator were connected to a Precision Scientific Company electronic relay. This relay was used to actuate two 350 watt heat lamps which were the only heating elements used for the bath. Only electronic controllers with rocker-type mercury switches were found to respond rapidly enough to be satisfactory.

In order to have a dry, non-oxidizing atmosphere around the metal to mercury contact in the regulator, dried hydrogen gas was passed through the regulator by means of two tubes on the sides of the expansion chamber. When it was found that the temperature control became less satisfactory after a brief period of operation, bubbling bottles, partially filled with mercury, were placed in the hydrogen train on either side of the thermo-regulator. The passage of hydrogen through these bottles gave small surges of pressure which prevented the mercury from sticking in the capillary. With adequate stirring and proper cooling for the bath, the regulator was found to control the temperature of the bath to within ±0.001° C. for extended periods of time.

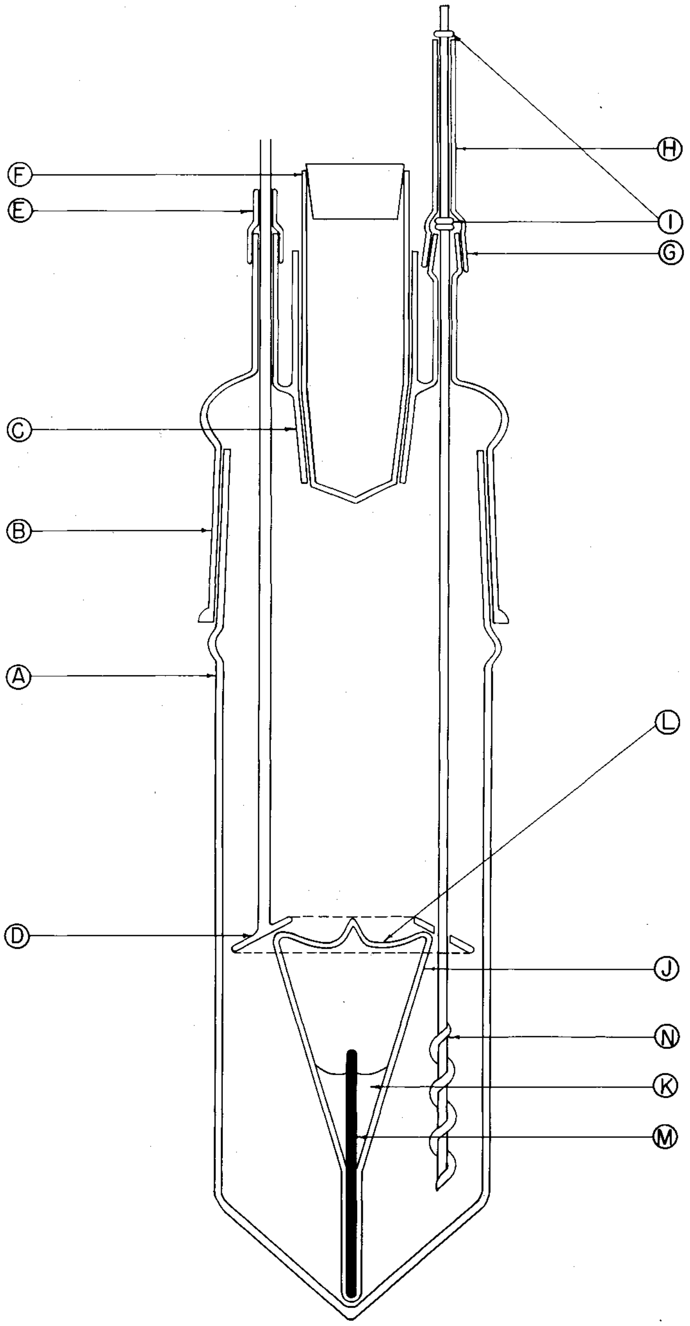
The cooling water for the water bath was obtained from a small auxiliary bath, H Figure 2, which had an independent temperature control. The water from this bath, which was maintained at a temperature about 3° C. lower than that of the large bath, was pumped through the cooling coils, I, by a small centrifugal pump, J. The temperature of this bath was controlled by a Precision Scientific Company Microset regulator and could be adjusted to compensate for large changes in room temperature. Two heat lamps were used as the heating elements for the small bath and the cooling coils for this bath were connected directly to the cold water main.

A large tubular turbine stirrer, K, was used in the larger water bath. This stirrer was mounted on a wooden upright from a heavy stand, entirely separated from the bath, so that the vibrations from the stirrer motor would not be transferred to the measuring apparatus.

The float, L Figure 2 and J Figure 4, was prepared from a conical Pyrex centrifuge tube of 100 ml capacity. The float contained a magnetized Cunife rod and was ballasted with lead shot fixed in place with Pyseal.

The float was prepared in the following manner. The lower graduated portion of the centrifuge tube was removed and a short length of Pyrex tubing, of internal diameter slightly greater than the diameter of the Cunife rod, was substituted. A four inch length of 3/16 inch diameter Cunife rod, which had previously been magnetized between the pole pieces of a strong electromagnet, was placed in the tube. The top of the centrifuge tube was depressed to form a receptacle for the platinum weights to be added during the course of a density measurement. A small hole was left in the center of the top to permit the addition of the lead shot and Pyseal. The estimated amount of Pyseal required to completely cover the lead shot was placed in the float. With the float clamped in a horizontal position, the Pyseal was melted and allowed to cool and adhere to the wall of the float. The float was then placed in distilled water at 25° C. and lead shot were added until the float sank to the edge of the opening in the top. With the float again fixed in a

Figure 4. Diagram of specific-gravity cylinder and float



Ⓐ CYLINDER OF 100 mm PYREX TUBING
Ⓑ NO. 103/60 STANDARD TAPER
Ⓒ NO. 40/50 STANDARD TAPER
Ⓓ HOLD-DOWN RING
Ⓔ RUBBER TUBING TO SUPPORT HOLD-DOWN RING
Ⓕ STOPPER
Ⓖ NO. 10/18 STANDARD TAPER
Ⓗ GLASS TUBING ATTACHED TO STANDARD TAPER JOINT. LUBRICATED WITH SILICONE GREASE
Ⓘ SMALL RUBBER O-RINGS
Ⓙ FLOAT
Ⓚ LEAD SHOT FIXED WITH PYSEAL
Ⓛ DEPRESSION TO HOLD PLATINUM WEIGHTS
Ⓜ MAGNETIZED CUNIFE ROD
Ⓝ STIRRER

vertical position, the Pyseal was melted and allowed to completely fill the spaces around the lead shot. The opening in the top was sealed and the float was again placed in distilled water at 25° C. An additional 50 milligram platinum weight was required to make the float sink.

The solution container or specific gravity cylinder, fabricated from 100 millimeter Pyrex tubing, is shown at M in Figure 2 and in greater detail in Figure 4. An approximately 45 degree cone was formed at the bottom of the cylinder and the top was sealed to the male portion of a Pyrex 103/60 standard taper joint. The total length of the cylinder was 14 inches. The cone in the bottom of the cylinder served two purposes, guiding the float to its rest position in the center of the cylinder and aiding in the reproducible positioning of the cylinder in the supporting frame.

A cap for the specific-gravity cylinder was constructed from the female portion of the 103/60 standard taper. A 2 1/2 inch length of 45 millimeter Pyrex tubing was sealed to the larger end of a female 40/50 standard taper. This was attached in the center of the cap, by means of a ring seal, with the smaller end of the taper extending inside the cap. Two three inch lengths of 10 millimeter Pyrex tubing were also sealed in the cap parallel to the axis of the 45 millimeter tubing, and a 10/18 standard taper male joint was attached to one of these tubes. The opening in the center of the cap was closed with a removable plug made by closing the smaller end of the male 40/50 standard taper joint. The glass tubing of this plug was packed with glass wool and the top was closed with a rubber stopper.

In order to prevent the top of the float from rising through the liquid-air interface, a "hold-down" device was introduced into the cylinder. This device consisted of a section of a Pyrex cone 3 1/4 inches in diameter at the bottom and 2 inches in diameter at the top. An 18 inch length of 6 millimeter Pyrex rod was attached to the device perpendicular to the base of the cone. This rod was passed through one of the 10 millimeter glass tubes in the cylinder cap. A short length of gum rubber tubing was used for a seal between the glass rod and the 10 millimeter glass tubing. The hold down ring could be raised or lowered by slipping the glass rod up or down through the rubber seal.

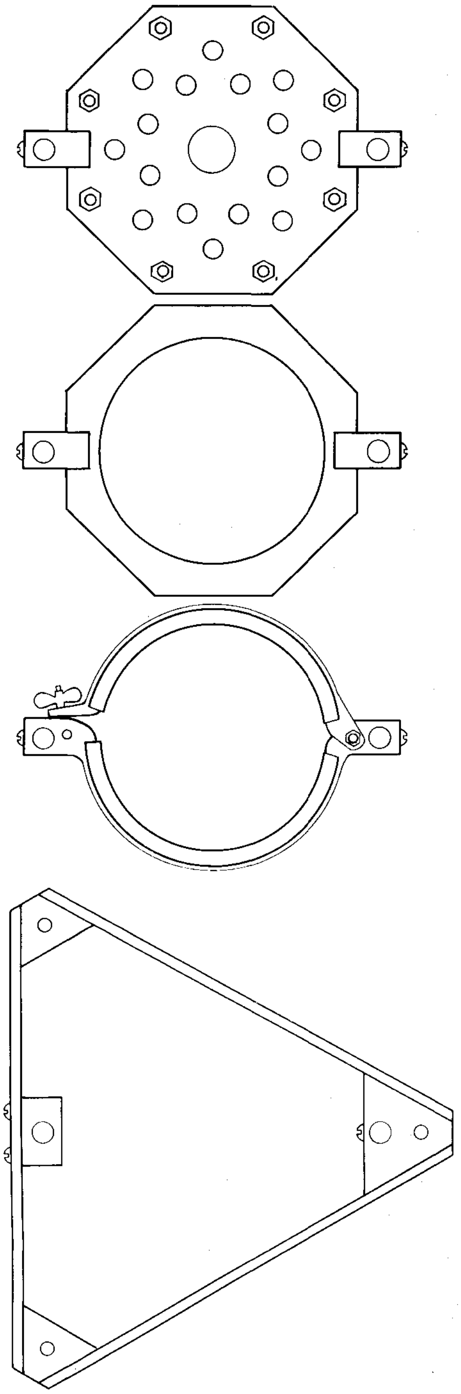
A small spiral type Pyrex stirring rod was placed in the cylinder. This rod extended through the Pyrex tubing in the cylinder cap which terminated in the 10/18 male joint. The 10/18 female joint was attached to a three inch length of Pyrex tubing of inside diameter slightly larger than the diameter of the stirring rod. This three inch length of tubing was lubricated with Corning High Vacuum Silicone

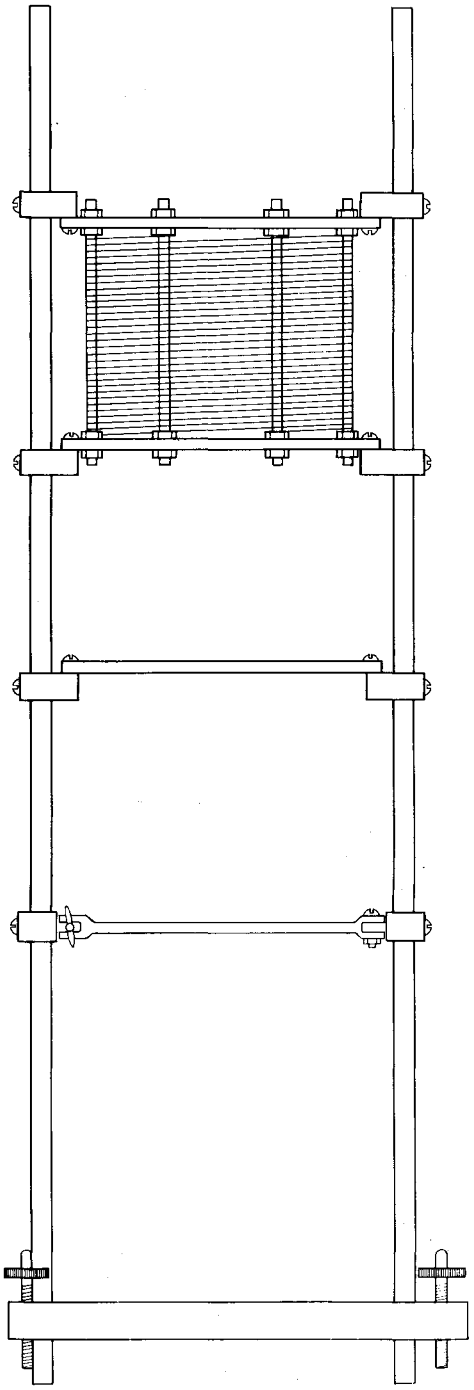
Grease and served as a bearing for the stirring rod. This grease was found to provide excellent lubrication while giving an air-tight seal. The stirrer was attached to an adjustable speed electric motor by a flexible coupling of gum rubber tubing.

The solenoid, shown at N in Figure 2 and also in Figure 5, consisted of 27 turns of number 24 Formvar coated wire wound on an octagonal shaped frame 6 1/2 inches across and 6 inches high. This frame was made from two octagonal Plexiglass plates and eight threaded 1/4 inch brass rods. The plates were cut from 1/4 inch Plexiglass stock and a 17/64 inch hole was drilled in each corner. The plates were spaced 5 1/2 inches apart on the threaded brass rods with a nut on both sides of each plate on the rods. A one inch hole, drilled in the center of the upper plate, was tapered to fit the conical bottom of the specific gravity cylinder. Additional holes were drilled in both plates to permit the free circulation of the water in the bath.

In preparing the solenoid, the Formvar coated wire was wound directly onto the frame of brass rods, the threads assisting in obtaining uniform spacing of the wires. The two lead wires were brought out through small holes in the top Plexiglass plate and out the top of the water bath. The

Figure 5. Diagram of solenoid and support for specific gravity cylinder





completed solenoid unit was fastened to the two brass support rods, O Figure 2, as shown in Figure 5.

The supporting unit for the solenoid and specific gravity cylinder was made so that the entire unit could be easily removed from the water bath. Two 5/8 inch brass rods, 34 inches long, were attached, at the top, to a triangular brass frame with sides 14 inches long. The three adjustable legs of this frame rested on the flat surface of a similar frame attached to the support rods of the water bath.

For the proper operation of the apparatus, it was necessary that the specific gravity cylinder be replaced in the same position relative to the solenoid each time after it had been removed for cleaning and filling. The large hole in the upper plate of the solenoid frame provided a means for locating the bottom of the cylinder. A third Plexiglass plate, containing a hole slightly larger than the diameter of the cylinder, was placed six inches above the solenoid. This plate was attached to the top plate of the solenoid frame with three threaded brass rods and to the two 5/8 inch support rods with brass clamps. A four inch diameter split ring clamp, padded with 3/8 inch Tygon tubing was placed between the support rods five inches above the third Plexiglass plate. This clamp served the dual function of aiding in the proper positioning of the cylinder and of holding the cylinder down against the buoyant force of the water in the water bath. The final vertical alignment of the solenoid, float, and cylinder was obtained by adjusting the legs of the triangular supporting frame. With this system it was found possible to replace the cylinder in an exact position each time after it had been removed.

The current for the solenoid was obtained from a constant voltage source of direct current constructed in the Electronics Shop at the Ames Laboratory. The circuit diagram for this regulator is given in Figure 6.

The electrical circuit for the solenoid, Figure 7, was very simple. A standard resistor, a decade box, a 25 ohm Helipot, and the solenoid were connected in series across the voltage source. A heavy duty double pole-double throw knife switch was wired to reverse the current through the solenoid when thrown to the alternate positions.

With a fixed potential at the voltage regulator, the current in the solenoid was adjusted by varying the resistance of the variable resistors, the fine adjustment being made with the Helipot. The current flowing in the solenoid circuit was determined by measuring the potential drop across the standard resistance. The standard resistance consisted of three one ohm Rubicon air cooled standard shunts connected

Figure 6. Circuit diagram for constant voltage power supply

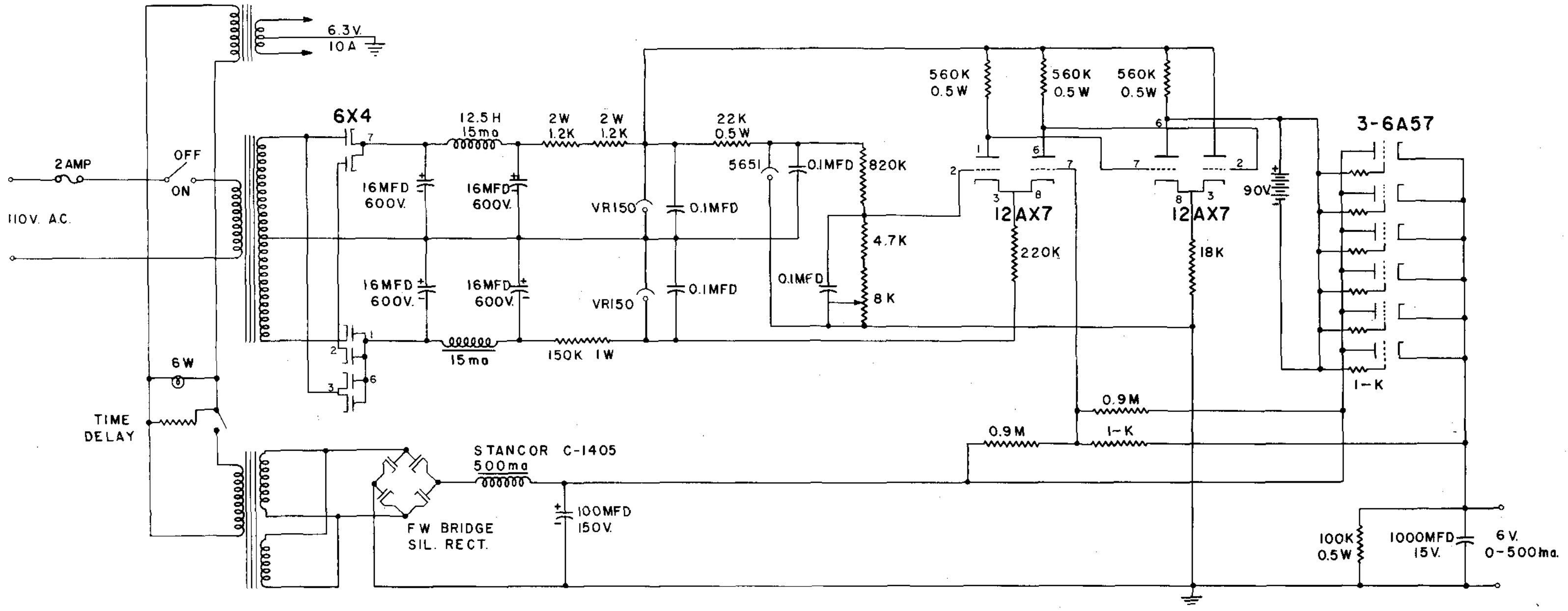
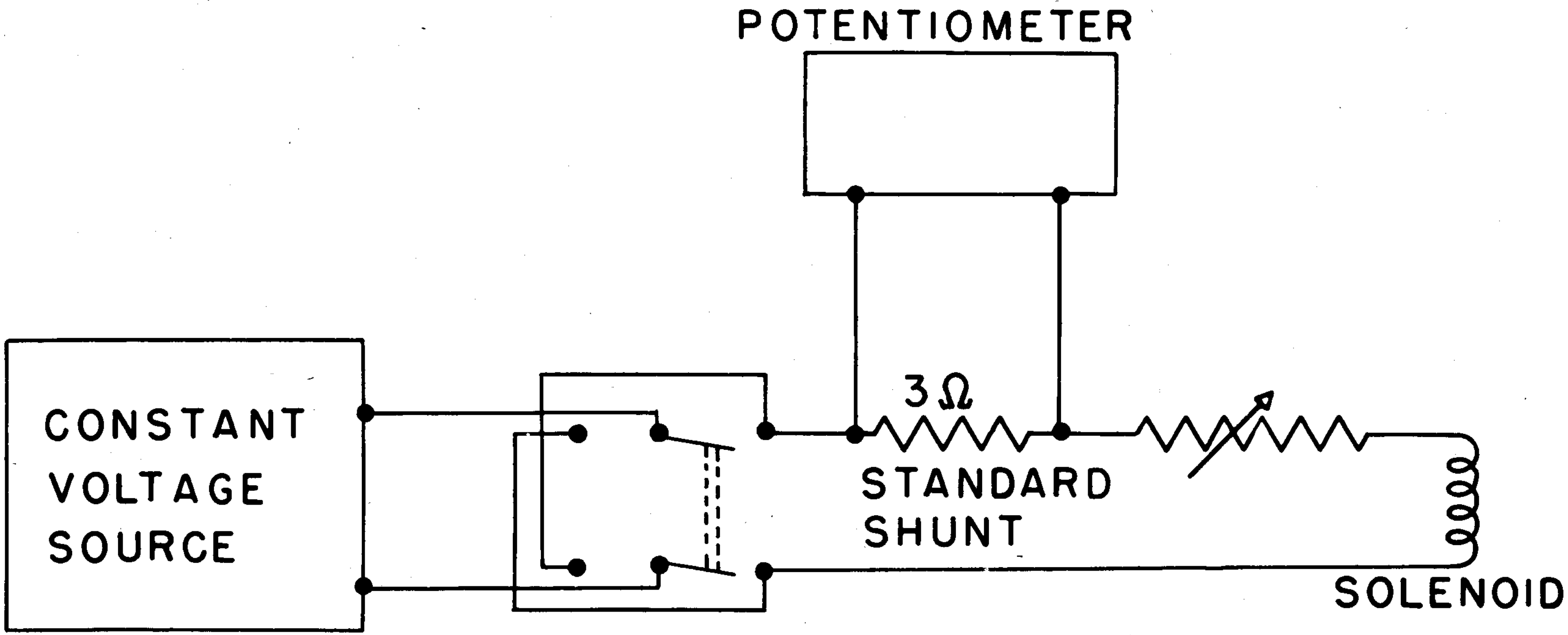

6.3V.
10A
2AMP
OFF
ON
110V. AC.
6X4
12.5H
15ma
2W
1.2K
2W
1.2K
22K
0.5W
5651
0.1MFD
820K
16MFD
600V.
16MFD
600V.
VR150
0.1MFD
4.7K
16MFD
600V.
16MFD
600V.
VR150
0.1MFD
0.1MFD
8K
15ma
150K 1W
6W
TIME
DELAY
STANCOR C-1405
500ma
FW BRIDGE
SIL. RECT.
100MFD
150V.
560K
0.5W
560K
0.5W
560K
0.5W
12AX7
220K
12AX7
18K
90V.
3-6A57
1-K
0.9M
0.9M
1-K
100K
0.5W
1000MFD
15V.
6V.
0-500ma.

Figure 7. Wiring diagram for solenoid circuit


POTENTIOMETER
CONSTANT VOLTAGE SOURCE
3 Ω
STANDARD SHUNT
SOLENOID

in series. The potential drop across the standard resistance was measured with a Rubicon type B potentiometer standardized against an Epply standard cell. The solenoid current was then obtained from Ohm's law.

The temperature of the water bath was measured with a 25 ohm platinum resistance thermometer and a type G-2 Mueller Bridge. The resistance thermometer was placed as close to the specific gravity cylinder as possible but was not placed in the cylinder, due to a lack of room.

A Gaertner Telemicroscope, shown at P in Figure 2, with an occular scale was used to measure the rate of rise of the float.

Platinum weights, to be added to the float, were made from annealed platinum wire. Weights of approximately 5, 10, 25, 50, 100, and 500 milligram denominations were constructed. The 5 milligram and 10 milligram weights were made from number 32 wire, the 25 milligram and 50 milligram from number 26 wire, the 100 milligram from number 22 wire, and the 500 milligram weights were made from number 8 wire. These weights were shaped in the form of equilateral triangles with a fourth leg extending upward from the plane of the triangle. These weights were coded by making small marks on the linear portions of the wire. Thus, 1011 indicated one mark on the portion of wire perpendicular to the plane of the triangle, no marks on the first leg of the triangle, one mark on the second leg, and one mark on the third leg, when the marks were read in a clockwise direction around the triangle. This code made it possible to keep an accurate record of the weights used for each solution. This was necessary since the weights were not of integral values and were weighed in groups after the density determinations were completed.

Three analytical type balances were used in connection with this work. An Ainsworth type FDJ microbalance was used to weigh the platinum weights added to the float. An Ainsworth type BB analytical balance was used for the necessary weighings in analytical procedures, and a Seko 2000 gram capacity solution balance was used in preparing solutions by weight and for weighing the amounts of stock solutions added to the specific gravity cylinder. Three sets of weights were used with these balances. An Ainsworth Grade A Precision Fractional series of weights, from 1 milligram to 1000 milligram was used with the microbalance. A set of Ainsworth Class S certified weights, of nominal values from 1 gram to 100 gram was used whenever larger weights were required for the microbalance and for all analytical weighings. A set of Sargent Class S lacquered brass weights, from 1 gram to 1000 gram was used with the solution balance.

Relative humidity was measured with a Taylor Humidiguide and the atmospheric pressure was measured with a Foucoult type mercury barometer.

2. Calibration

Several calibrations were necessary before the apparatus could be used for determining the specific gravity of solutions.

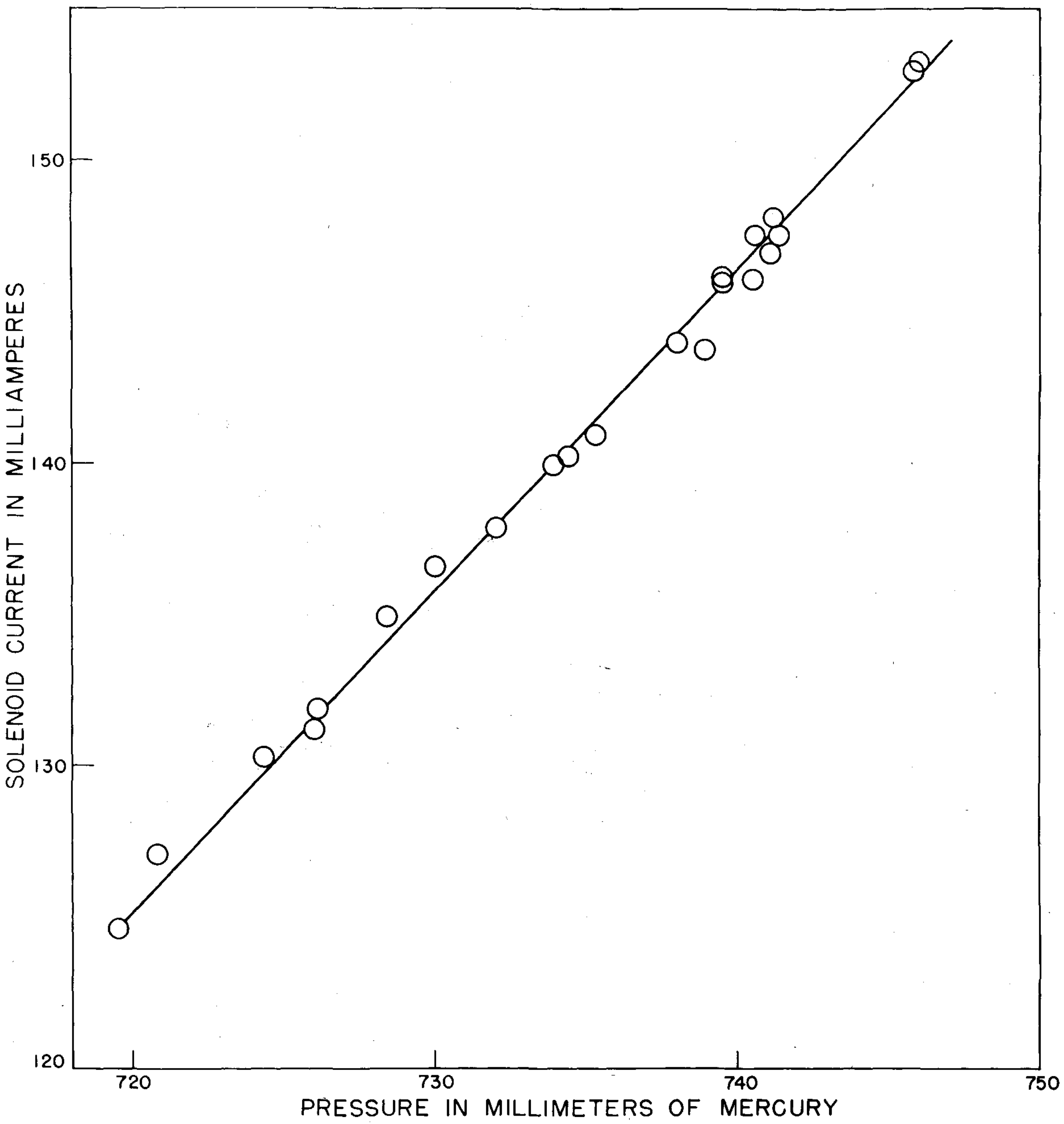
The solenoid current, I_o, necessary to maintain the float at equilibrium in the solutions was found to be strongly dependent on the atmospheric pressure. This was due, not to the compressibility of the solution, but to variation in the volume of the float with changes in the atmospheric pressure. A calibration factor for this variation was obtained by measuring the equilibrium current, I_o, for various values of the atmospheric pressure, P. The data for this calibration are given in Table 2 and are shown graphically in Figure 8. An average value of $\Delta I_o/\Delta P = 1.08 \pm 0.01$ milligram per millimeter was obtained. The pressure variation covered by this calibration was over a total range of 27.5 millimeters of mercury. The average variation in atmospheric pressure during a series of specific gravity determinations was found to be about plus or minus 10 millimeters. Table 2 also

Table 2. Calibration data for corrections on equilibrium solenoid current

P in mm. Hg	I_o in ma.	P	I_o	$\frac{\Delta I_o}{\Delta P}$	$I'_o(733.0)^a$	I'_o
740.5	146.1	7.5	8.0	1.07	138.1	-0.9
738.9	143.8	5.9	6.3	1.07	137.5	-1.5
719.5	124.6	-13.5	-14.4	1.07	139.0	±0.0
724.3	130.3	- 8.7	- 9.3	1.07	139.6	0.6
739.5	146.0	6.5	7.0	1.16	139.0	±0.0
739.5	146.2	6.5	7.2	1.11	139.2	0.2
740.6	147.6	7.6	8.1	1.07	138.8	-0.2
741.2	148.2	8.2	8.8	1.08	139.4	0.4
728.4	135.0	- 4.6	- 4.9	1.06	139.9	0.9
733.9	140.0	0.9	1.0	1.11	139.0	±0.0
741.4	147.6	8.4	9.0	1.07	138.6	-0.4
741.1	147.0	8.1	8.7	1.07	138.3	-0.7
726.1	131.9	- 6.9	- 7.4	1.07	139.3	0.3
745.8	153.0	12.8	13.7	1.07	139.3	0.3
730.0	136.6	- 3.0	- 3.2	1.07	139.8	0.8
746.0	153.3	13.0	13.9	1.07	139.4	0.4
738.0	144.0	5.0	5.4	1.08	138.6	-0.4
720.8	127.1	-12.2	-13.1	1.07	140.2	1.2
726.0	131.2	- 7.0	- 7.5	1.07	138.7	-0.3
735.3	141.0	2.3	2.5	1.09	138.5	-0.5
734.4	140.3	1.4	1.5	1.07	138.8	-0.2
732.0	137.9	- 1.0	- 1.1	1.10	139.0	±0.0
Average				1.08 ±0.01	139.0	±0.5

[a] Corrected to P = 733.0, the mean pressure for the series of measurements.

Figure 8. Variation in equilibrium solenoid current with pressure


SOLENOID CURRENT IN MILLIAMPERES
150
140
130
120
720
730
740
750
PRESSURE IN MILLIMETERS OF MERCURY

contains values of the equilibrium current, $\underline{I_o'}$, corrected to 733.0 millimeters, the mean pressure for the series of measurements. The average deviation in the equilibrium current of ±0.5 milliamperes corresponded to an uncertainty of $\pm 2.5 \times 10^{-7}$ in the specific gravity.

A second calibration was necessary to evaluate the factor, $\underline{\psi}$, for the conversion of the equilibrium solenoid currents to their weight equivalents. This factor was obtained from measurements of the equilibrium currents required with various total weights of platinum added to the float. The conversion factor was evaluated as $\psi = 5.254 \pm 0.020$ milligrams per milliampere. In general, the equilibrium solenoid current was less than 300 milliamperes so that the uncertainty in the factor $\underline{\psi}$ was not sufficient to introduce serious errors.

The stirrup weights of the microbalance and the set of Ainsworth fractional microbalance weights were calibrated by the Richard's substitution method (103). This calibration was referred to the value of the one gram weight from the Ainsworth Class S certified set of weights.

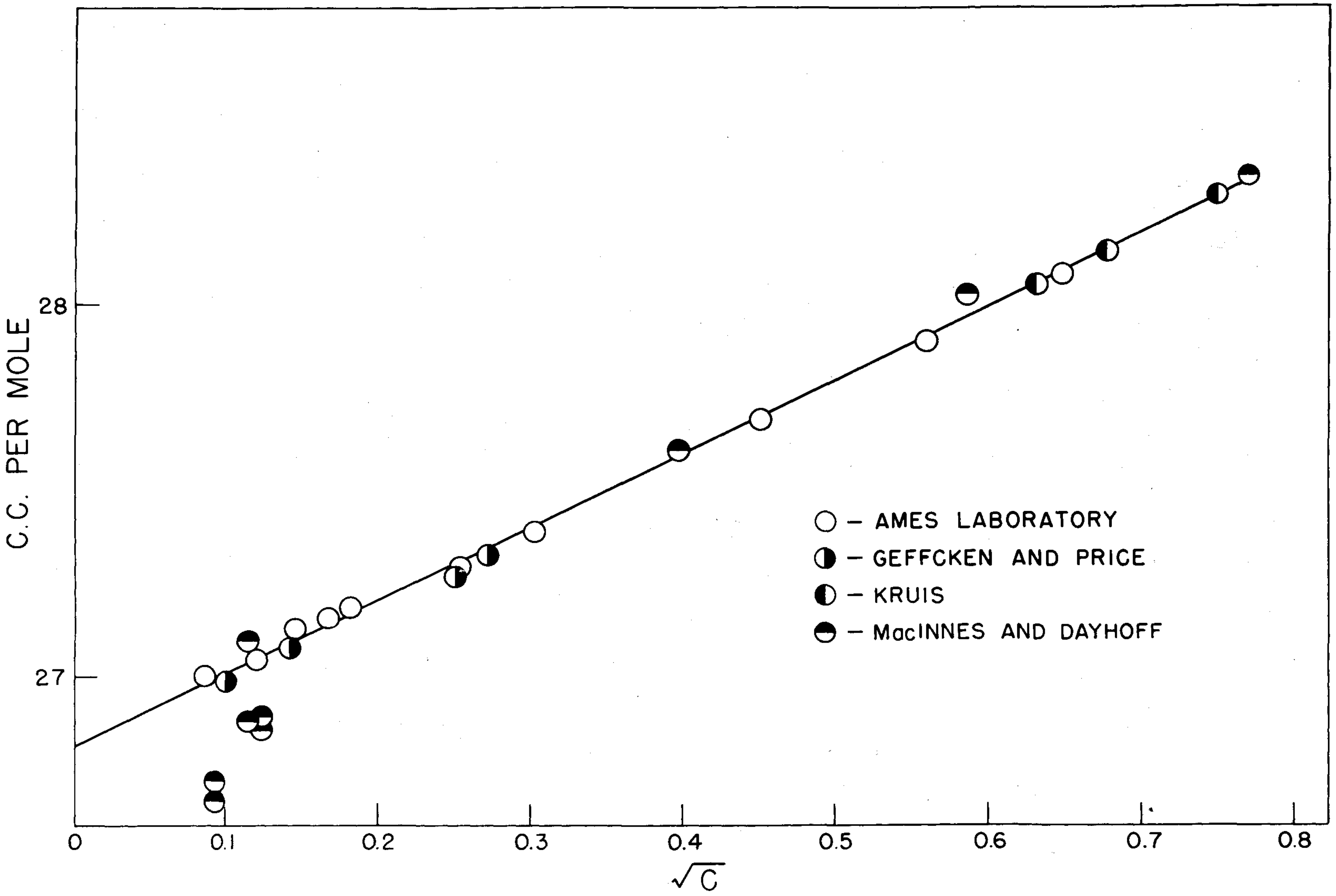
As a final check on the calibration of the apparatus, apparent molal volumes of aqueous solutions of potassium chloride at 25° C. were measured. The densities and apparent molal volumes obtained for potassium chloride are given in

Table 3 and shown graphically in Figure 9. Apparent molal volumes of potassium chloride as obtained by Geffcken and Price (78), Kruis (89), and MacInnes and Dayhoff (104) are shown in Figure 9 for comparison. The apparent molal volumes obtained from the measurements in this laboratory were in excellent agreement with those obtained by Geffcken and Price and by Kruis, but differed considerably from those obtained by MacInnes and Dayhoff for the more dilute solutions.

Table 3. Densities and apparent molal volumes of potassium chloride in aqueous solution at 25° C.

c	$c^{\frac{1}{2}}$	ρ	ϕ_v
0.0073477	0.085719	0.9974240	27.002
0.014282	0.119508	0.9977538	27.048
0.021085	0.145207	0.9981711	27.131
0.027121	0.164685	0.9983619	27.160
0.032763	0.18101	0.9986287	27.185
0.063825	0.25264	1.0000955	27.295
0.091028	0.30171	1.0013745	27.392
0.20142	0.44879	1.0065289	27.694
0.31232	0.55886	1.011668	27.908
0.41865	0.64703	1.016564	28.083

Figure 9. Apparent molal volumes of potassium chloride in aqueous solutions at 25° C.


C.C. PER MOLE
28
27
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
$\sqrt{C}$
○ – AMES LABORATORY
◑ – GEFFCKEN AND PRICE
◐ – KRUIS
⊖ – MacINNES AND DAYHOFF

D. Procedure

The procedure followed in measuring the specific gravities of solutions may be briefly described as follows.

Prior to making the measurements for solutions of each rare earth salt, the apparatus was thoroughly cleaned. The specific gravity cylinder, cylinder cap, hold down ring, stirring rod, and weight burette were cleaned with hot dichromate cleaning solution. These were then rinsed repeatedly with distilled water and were allowed to stand in distilled water for a period of several hours, after which they were dried and placed in the temperature-controlled balance room. The float was washed in a dilute solution of sodium hydroxide containing a small amount of Aerosol, rinsed with distilled water, washed in a dilute solution of hydrochloric acid, and repeatedly rinsed with distilled water. The float was then placed in a large desiccator containing Anhydrone, which was put in the balance room. When the float was thoroughly dry and was in thermal equilibrium with the balance room, it was weighed on an analytical balance. The float was then placed in a covered container filled with the distilled water used in preparing the solutions and placed in the thermostated weighing room. It was found that if the float was allowed to stand in the distilled water for several hours and was wet when placed in the distilled water in the specific-gravity cylinder, there was less tendency for small air bubbles to adhere to the walls of the float.

In order to prevent degassing of the water and solutions when they were placed in the water bath at 25° C., the temperature of the balance room was maintained at approximately 26° C. For higher temperatures, considerable difficulty was encountered due to condensation of water vapor along the upper wall of the specific-gravity cylinder when it was placed in the water bath at 25° C. The apparatus, solutions, and distilled water were allowed to come to thermal equilibrium with this room before being weighed.

Distilled water was weighed directly in the specific-gravity cylinder on the Seko solution balance. The empty specific gravity cylinder and cover were weighed. Approximately 800 grams of distilled water were added, and the wet float was lowered into the cylinder. The cylinder, water, float, and cover were weighed and the weight of water found by difference. All weights were corrected to vacuo.

The hold down ring and the glass stirring rod were placed in the cylinder, the 103/60 standard taper joint was greased with Lubriseal and the cylinder cap was placed in position. The cylinder was then placed in the constant temperature bath, and the stirrer was attached to the small variable speed electric motor.

A minimum period of two hours was allowed for the distilled water in the specific-gravity cylinder to come to equilibrium with the constant temperature bath. The equilibrium solenoid current, for the float in distilled water, was measured. The water was stirred and the equilibrium current was again measured. Since the equilibrium solenoid current for distilled water was fundamental for all the calculations for a series of solutions (equation 130), the measurements were repeated until the results were constant to within ±0.5 milliamperes over extended periods of time. The atmospheric pressure, at the time of each measurement, was recorded so that the proper correction could be made.

An appropriate quantity of approximately one per cent stock solution of the rare earth salt was weighed into the cylinder from a weight burette. The resulting concentration, $\underline{P}$, of the solution in the cylinder was given by

$$P = \frac{wP_o}{W + w} \qquad (135)$$

where $\underline{P_o}$ was the weight per cent concentration of the stock solution, $\underline{w}$ was the weight of stock solution added, and $\underline{W}$ was the weight of distilled water initially in the cylinder.

The solution in the cylinder was stirred in order to obtain a homogeneous concentration and thermal equilibrium. Platinum weights were added to the float until a solenoid current of from 80 milliamperes to 300 milliamperes would cause the float to rise at a measurable rate. In order to prevent the trapping of air bubbles, the weights were heated in a small gas flame just prior to being added to the float, and the weights added for each solution were recorded by the code previously described. The equilibrium solenoid current was determined. The solution was thoroughly stirred, permitted to stand for about one hour and the current was again determined. Agreement of these measurements to within ±0.5 milliamperes was taken as evidence that the solution was homogeneous and was in thermal equilibrium with the water bath.

Additional portions, sufficient to give solutions of the desired concentrations, of the approximately one per cent, 10 per cent, and 25 per cent stock solutions were weighed into the cylinder. For each solution, the necessary amount of platinum weight was added and the equilibrium solenoid current was determined.

The amount of platinum to be added for each solution was estimated from a plot of the weight of platinum, $\underline{w}$, vs. the concentration, $\underline{P}$. This plot was linear, within the accuracy required for estimating the weight to be added, and passed through zero at zero concentration. The weight of platinum required for the first solution was found by trial, and the approximate weights required for the remainder of the solutions were estimated from the line determined by the weight added for a solution of this concentration and the zero intercept. It was generally possible to estimate the proper amount of platinum to within ±10 milligrams.

On completion of the measurements on a series of solutions, the specific-gravity cylinder was removed from the water bath for cleaning and refilling. The weights were removed from the float, washed in dilute nitric acid, rinsed in distilled water, and ignited to red heat in a gas flame. The weights were weighed in groups, each group being made up of the weights added to the float for one concentration of solution. In this manner, the total weighing error was smaller than would have been possible by summing the individual weights.

The specific gravity for each solution was calculated by successive approximations from the equations

$$S = \frac{W + w - I_0 \psi}{W - I_0^0 \psi} \qquad (136)$$

and

$$w = w'(1 - \rho/d) \quad . \qquad (137)$$

The molar concentration, c, was obtained from the weight per cent, P, and the density, ρ, by use of the relationship

$$c = \frac{10\rho P}{M_2} \quad , \qquad (138)$$

where M_2 is the molecular weight of the solute.

The apparent molal volumes were calculated by use of equation 112.

E. Results

Specific gravities of aqueous solutions of four rare earth chlorides and of four rare earth nitrates were determined by the procedure previously described.

From the specific gravities and the known concentrations of the solutions, the apparent molal volume ϕ_v, was calculated for each concentration by means of equation 112. Empirical equations of the form given by equation 107, containing five adjustable parameters, were fitted to the data on the apparent molal volumes for each salt. From these equations, the partial molal volume, $\bar{V}_2$, was obtained by use of equation 108. This operation resulted in an empirical equation for the partial molal volumes of each salt.

The specific gravities, ρ/ρ_0, apparent molal volumes, ϕ_v, and partial molal volumes, $\bar{V}_2$, for aqueous solutions of the rare earth chlorides are given in Tables 4 through 7. The partial and apparent molal volumes for the chlorides are shown graphically in Figures 10 through 13. Theoretical limiting slopes for the apparent and partial molal volumes are shown in the figures as short straight lines labeled ϕ and $\bar{V}_2$ respectively.

In the tables, the concentrations are given in moles of solute per 1000 grams of water. The quantity Δ is the difference between the experimentally determined apparent molal volume, for a solution of the given molal concentration, and the apparent molal volume as calculated from the empirical equation given below the table. The empirical equation for the partial molal volumes of each salt is also given below each table. The apparent and partial molal volumes are given in cubic centimeters per mole. The values for the specific gravities are given to only six decimal places for the more concentrated solutions. Hydrostatic pressure corrections would have been necessary in order to obtain the seventh

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

m	$m^{1/2}$	ρ/ρ_o	ϕ_v	ϕ_v calc.^{a}	Δ	$\bar{V}_2{}^b$
0.0010079	0.031747	1.0002324	14.8	14.92	-0.12	15.41
0.0060338	0.077677	1.0013816	16.35	16.20	+0.15	17.16
0.011564	0.10753	1.0026400	17.01	16.88	+0.13	18.04
0.021850	0.14782	1.0049727	17.68	17.68	±0.00	19.01
0.043068	0.20753	1.0097570	18.63	18.64	-0.01	20.13
0.081550	0.28557	1.018379	19.63	19.65	-0.02	21.35
0.13642	0.36935	1.030573	20.62	20.61	+0.01	22.67
0.20020	0.44744	1.044626	21.50	21.48	+0.02	24.04
0.26290	0.51274	1.058325	22.22	22.25	-0.03	25.21
0.33836	0.58169	1.074661	23.00	23.03	-0.03	26.29
			Average		±0.05	

$$^a\phi_v = 13.8639 + 36.044\ m^{1/2} - 87.540\ m + 134.52\ m^{3/2} - 75.634\ m^2.$$

$$^b\bar{V}_2 = 13.8639 + 54.065\ m^{1/2} - 175.08\ m + 336.31\ m^{3/2} - 226.90\ m^2.$$

Figure 10. Partial and apparent molal volumes of lanthanum chloride in aqueous solutions at 25° C.

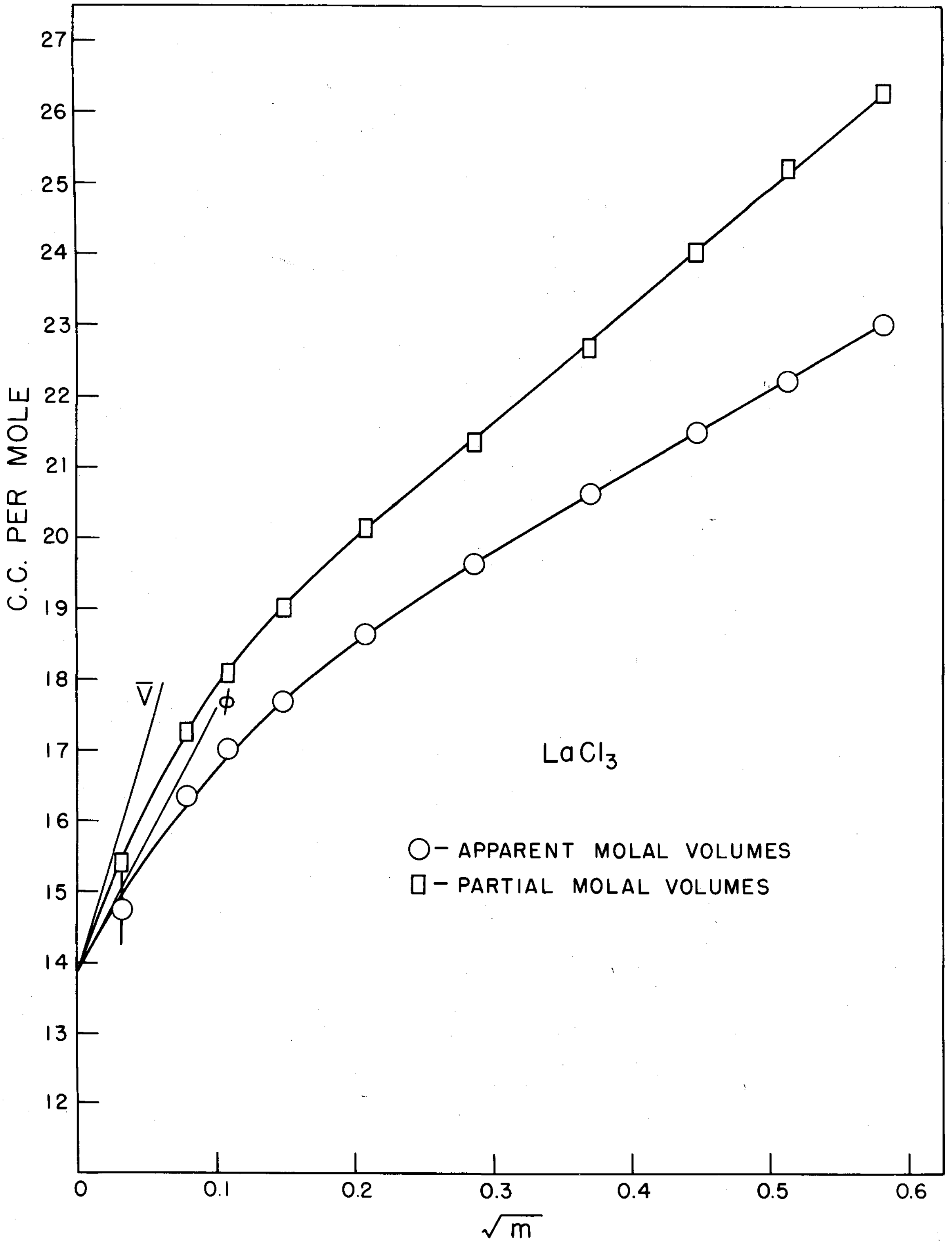

C.C. PER MOLE
27
26
25
24
23
22
21
20
19
18
17
16
15
14
13
12
0
0.1
0.2
0.3
0.4
0.5
0.6
$\sqrt{m}$
$\bar{V}$
ϕ
$LaCl_3$
○ – APPARENT MOLAL VOLUMES
□ – PARTIAL MOLAL VOLUMES

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

m	$m^{1/2}$	ρ/ρ_o	ϕ_v	$\phi_{v\,\mathrm{calc.}}^{a}$	Δ	$\bar{V}_2^{b}$
0.0019068	0.043667	1.0004564	11.3	11.34	-0.04	11.77
0.0035523	0.059601	1.0008488	11.7	11.65	+0.05	12.25
0.0057770	0.076007	1.0013785	12.04	11.96	+0.08	12.67
0.013893	0.11787	1.0033057	12.70	12.71	-0.01	13.73
0.022808	0.15102	1.0054145	13.22	13.27	-0.05	14.50
0.059781	0.24450	1.014089	14.70	14.67	+0.03	16.37
0.11433	0.33813	1.026795	15.90	15.88	+0.02	17.92
0.16258	0.40321	1.037953	16.63	16.64	-0.01	18.89
0.20852	0.45664	1.048514	17.20	17.22	-0.02	19.67
0.24922	0.49922	1.057825	17.66	17.67	-0.01	20.31
0.29202	0.54039	1.067553	18.14	18.11	+0.03	20.96
0.35220	0.59347	1.081188	18.67	18.67	+0.00	21.88
			Average		±0.03	

$^{a}\phi_v = 10.455 + 21.129\ m^{1/2} - 17.554\ m + 5.7320\ m^{3/2} + 5.3420\ m^2.$

$^{b}\bar{V}_2 = 10.455 + 31.694\ m^{1/2} - 35.108\ m + 14.330\ m^{3/2} + 16.026\ m^2.$

Figure 11. Partial and apparent molal volumes of neodymium chloride in aqueous solutions at 25° C.

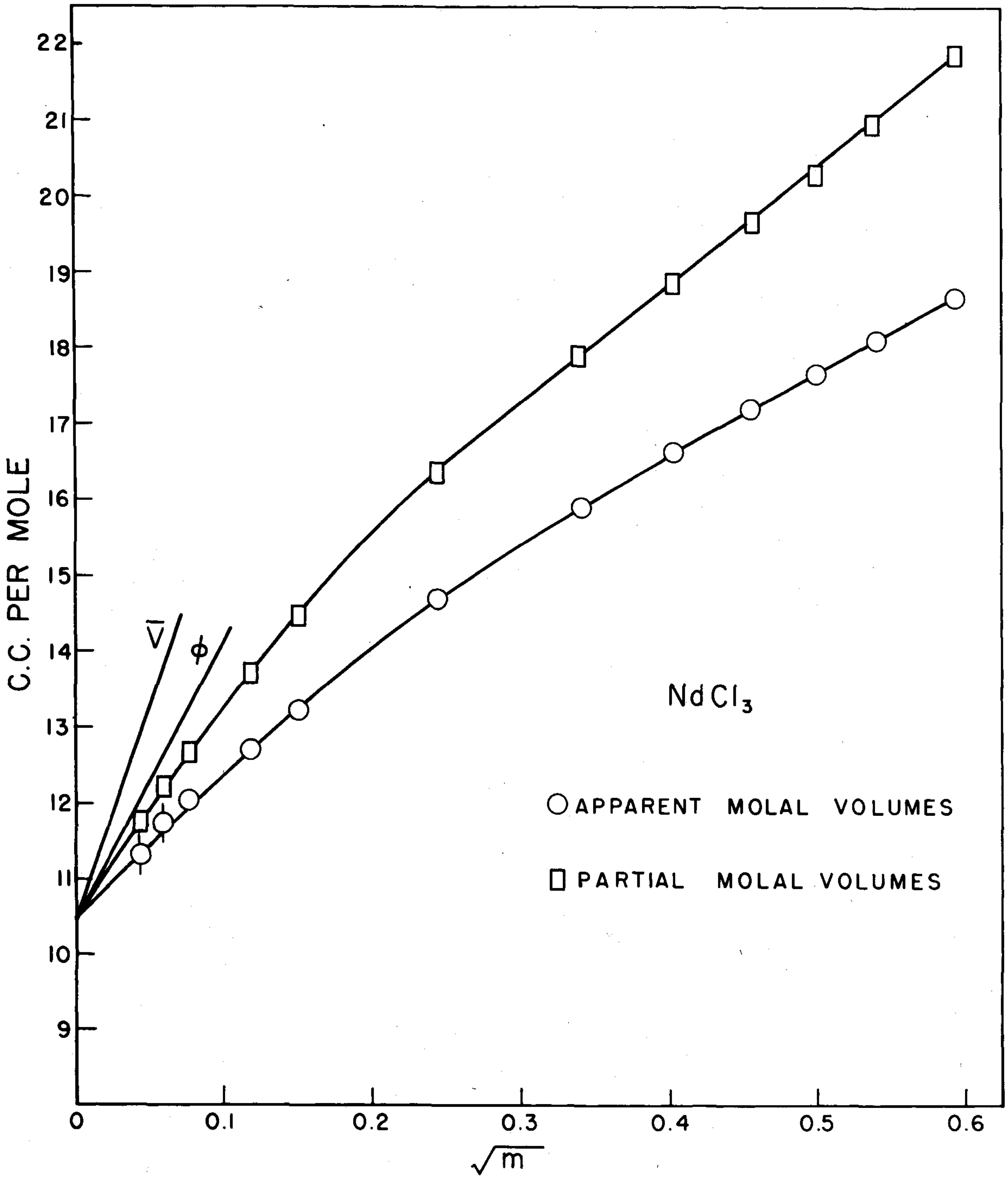

C.C. PER MOLE
22
21
20
19
18
17
16
15
14
13
12
11
10
9
0
0.1
0.2
0.3
0.4
0.5
0.6
$\sqrt{m}$
$\bar{V}$
ϕ
NdCl$_3$
○ APPARENT MOLAL VOLUMES
▯ PARTIAL MOLAL VOLUMES

Table 6. Specific gravities, apparent molal volumes and partial molal volumes of erbium chloride in aqueous solutions at 25° C.

m	$m^{1/2}$	ρ/ρ_o	ϕ_v	ϕ_v calc.^{a}	Δ	$\bar{V}_2{}^b$
0.0013548	0.036808	1.0003496	15.6	12.59	----	12.96
0.0051332	0.071646	1.0013364	13.25	13.23	+0.02	13.86
0.012211	0.12211	1.0038698	14.01	14.03	-0.02	14.89
0.024682	0.15711	1.0063926	14.53	14.51	+0.02	15.58
0.044390	0.21069	1.011464	15.19	15.20	-0.01	16.49
0.083929	0.28970	1.021579	16.16	16.15	+0.01	17.89
0.13393	0.36596	1.034279	17.08	17.01	-0.07	19.35
0.18634	0.43167	1.047515	17.81	17.83	-0.02	20.25
0.26177	0.51163	1.066414	18.67	18.65	-0.02	20.96
			Average		±0.02	

$^a\phi_v = 11.804 + 23.292\ m^{1/2} - 54.438\ m + 116.22\ m^{3/2} - 93.172\ m^2.$

$^b\bar{V}_2 = 11.804 + 34.938\ m^{1/2} - 108.88\ m + 290.55\ m^{3/2} - 279.52\ m^2.$

Figure 12. Partial and apparent molal volumes of erbium chloride in aqueous solutions at 25° C.

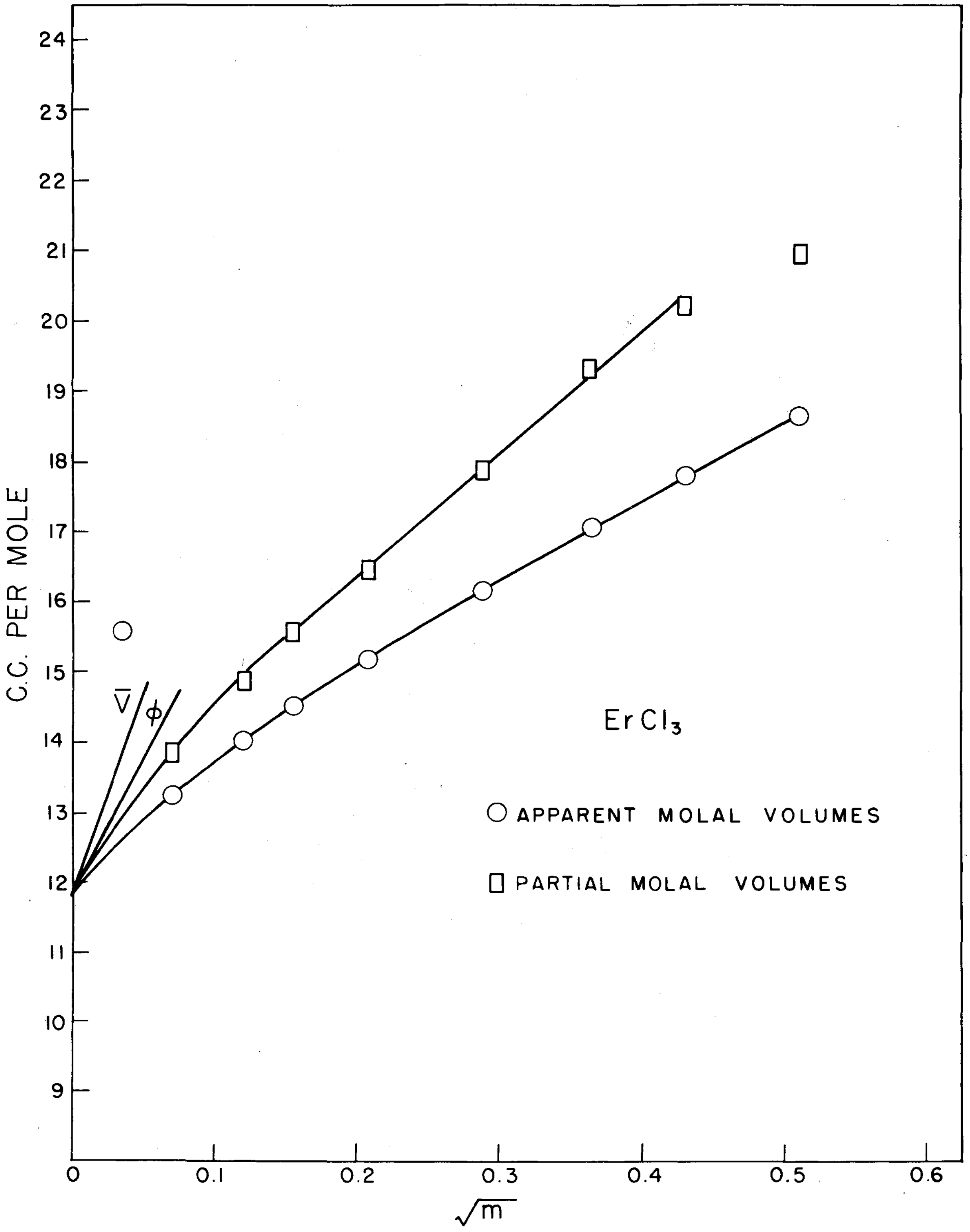
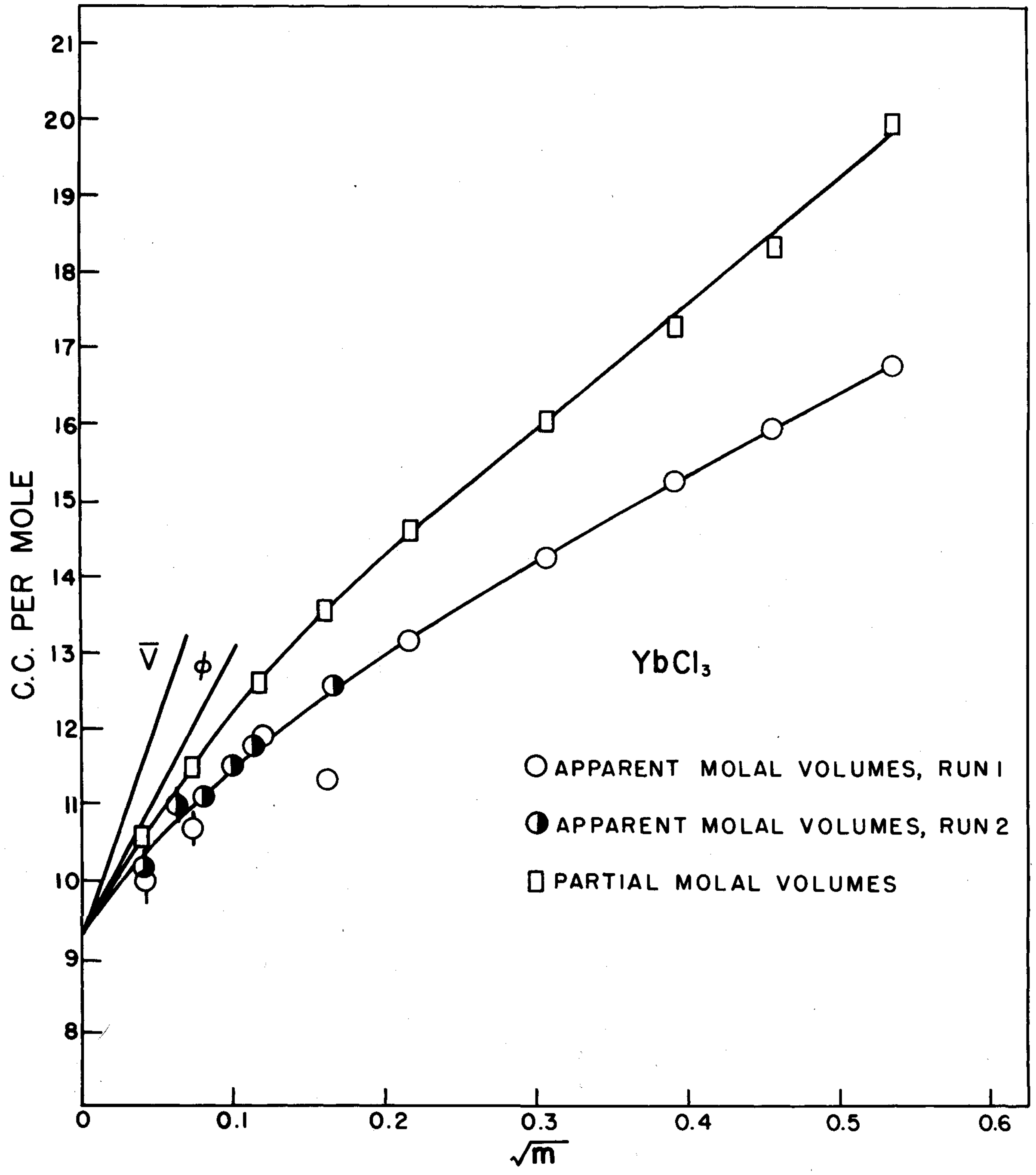

C.C. PER MOLE
24
23
22
21
20
19
18
17
16
15
14
13
12
11
10
9
0
0.1
0.2
0.3
0.4
0.5
0.6
$\sqrt{m}$
$\bar{V}$
ϕ
$ErCl_3$
○ APPARENT MOLAL VOLUMES
□ PARTIAL MOLAL VOLUMES

Figure 13. Partial and apparent molal volumes of ytterbium chloride in aqueous solutions at 25° C.


C.C. PER MOLE
21
20
19
18
17
16
15
14
13
12
11
10
9
8
0
0.1
0.2
0.3
0.4
0.5
0.6
$\sqrt{m}$
$\bar{V}$
ϕ
$YbCl_3$
○ APPARENT MOLAL VOLUMES, RUN 1
◐ APPARENT MOLAL VOLUMES, RUN 2
☐ PARTIAL MOLAL VOLUMES

figure, which due to the uncertainties in the concentrations, was not significant for these solutions.

Data on the specific gravities, apparent molal volumes, and partial molal volumes of solutions of the rare earth nitrates are tabulated in Tables 8 through 13. The apparent and partial molal volumes of the nitrates are shown graphically in Figures 14 through 17.

Three series of measurements were made on neodymium nitrate solutions. The data given in Table 9 (run number one) and in Table 10 (run number two) were obtained from measurements using the same stock solutions of neodymium nitrate. The distilled water used in making the dilutions in run number one was from the same sample of water used in preparing the stock solutions, whereas, the water used in making the dilutions for run number two was from a second sample of water. Data given in Table 11 (run number three) were obtained from a second series of neodymium nitrate stock solutions. The same sample of distilled water was used in preparing the stock solutions and in making the dilutions.

The data given in Tables 9 and 11 were used to evaluate the parameters in the empirical equation for the apparent molal volumes of the neodymium nitrate solutions.

Table 8. Specific gravities, apparent molal volumes, and partial molal volumes of lanthanum nitrate in aqueous solutions at 25° C.

m	$m^{1/2}$	ρ/ρ_o	ϕ_v	$\phi_{v\,\text{calc.}}{}^{a}$	Δ	$\overline{V}_2{}^{b}$
0.0016268	0.040334	1.0004477	49.9	50.00	-0.1	50.87
0.0048436	0.069596	1.0013258	51.29	51.09	+0.20	52.11
0.0070899	0.084202	1.0019394	51.45	51.49	-0.04	52.60
0.015612	0.12495	1.0042530	52.46	52.42	+0.04	53.67
0.032556	0.18043	1.0088315	53.35	53.41	-0.06	54.87
0.059182	0.24327	1.015965	54.47	54.41	+0.06	56.39
0.074284	0.27256	1.019982	55.01	54.90	+0.11	57.20
0.12520	0.35384	1.033430	56.21	56.26	-0.05	59.41
0.22172	0.47088	1.058493	57.92	57.81	+0.11	58.67
			Average		±0.09	

$^{a}\phi_v = 48.307 + 52.961\ m^{1/2} - 224.87\ m + 586.07\ m^{3/2} - 544.48\ m^2.$

$^{b}\overline{V}_2 = 48.307 + 79.442\ m^{1/2} - 449.75\ m + 1465.2\ m^{3/2} - 1633.4\ m^2.$

Figure 14. Partial and apparent molal volumes of lanthanum nitrate in aqueous solutions at 25° C.

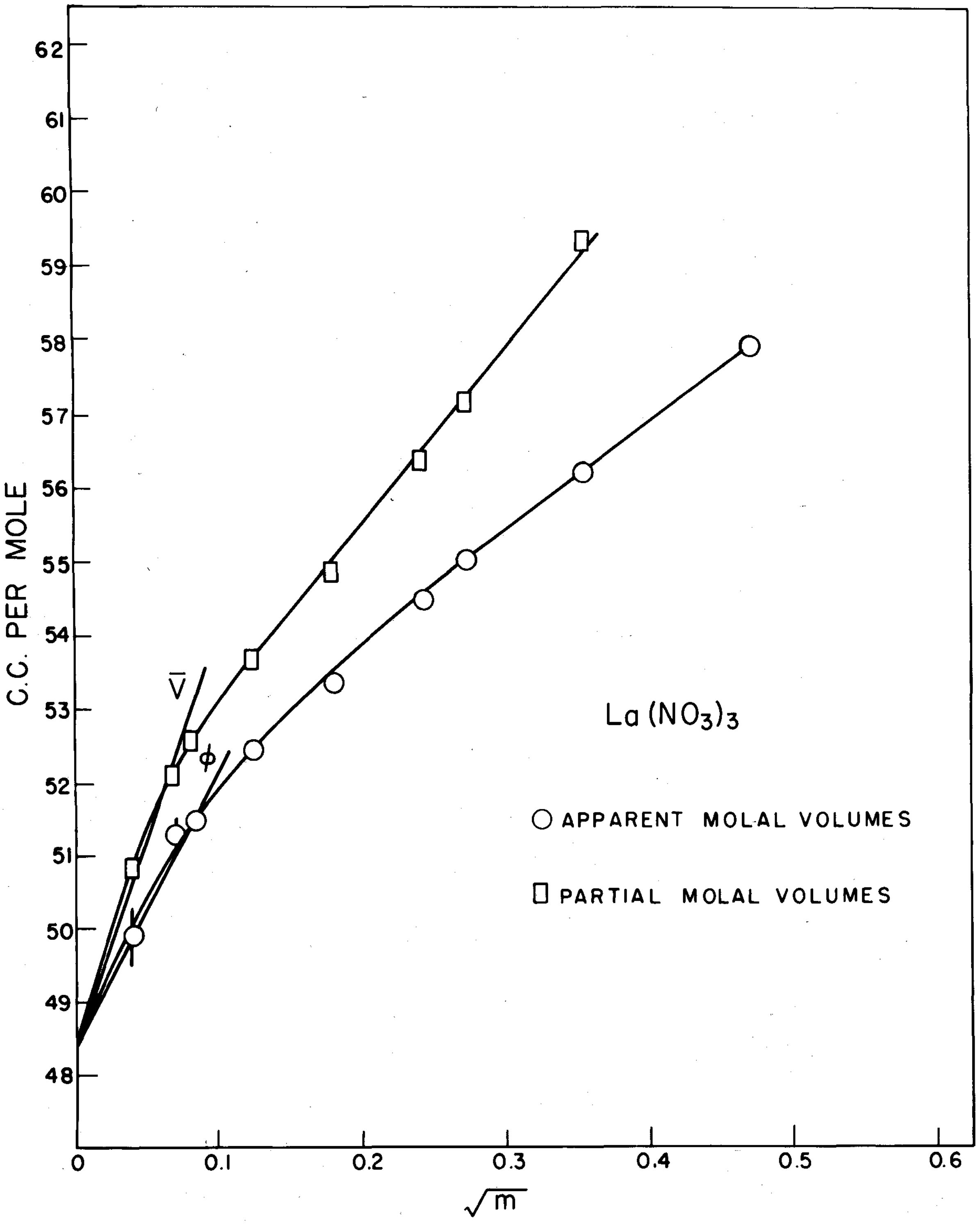

C.C. PER MOLE
62
61
60
59
58
57
56
55
54
53
52
51
50
49
48
0
0.1
0.2
0.3
0.4
0.5
0.6
$\sqrt{m}$
$\bar{V}$
ϕ
$La(NO_3)_3$
○ APPARENT MOLAL VOLUMES
▯ PARTIAL MOLAL VOLUMES

Table 9. Specific gravities, apparent molal volumes, and partial molal volumes of neodymium nitrate in aqueous solutions at 25° C., run number one

m	$m^{1/2}$	ρ/ρ_0	ϕ_v	$\phi_v{}^a$ calc.	Δ	$\overline{V}_2{}^b$
0.0011246	0.033534	1.0003196	46.2	45.89	+0.27	46.57
0.0050452	0.071029	1.0014275	47.38	47.29	+0.09	48.53
0.011316	0.10638	1.0031882	48.54	48.44	+0.10	50.06
0.020338	0.14261	1.0057071	49.54	49.48	+0.06	51.40
0.037437	0.19349	1.010449	50.79	50.75	+0.04	53.00
0.074034	0.27209	1.020499	52.49	52.42	+0.07	55.10
0.10765	0.32810	1.029637	53.55	53.48	+0.03	56.49
0.15808	0.39760	1.043209	54.76	54.72	+0.04	58.15
0.24462	0.49459	1.066158	56.29	56.33	-0.04	60.22
			Average		±0.08	

$^a\phi_v = 44.444 + 46.171\ m^{1/2} - 95.234\ m + 147.50\ m^{3/2} - 91.923\ m^2.$

$^b\overline{V}_2 = 44.444 + 69.256\ m^{1/2} - 190.47\ m + 368.74\ m^{3/2} - 275.77\ m^2.$

Table 10. Specific gravities, apparent molal volumes, and partial molal volumes of neodymium nitrate in aqueous solutions at 25° C., run number two

m	$m^{1/2}$	ρ/ρ_0	ϕ_V	ϕ_V^a calc.	Δ	$\bar{V}_2^b$
0.0012637	0.035834	1.0003592	46.2	45.98	+0.22	46.70
0.0051126	0.071503	1.0014462	47.49	47.31	+0.18	48.55
0.011278	0.10526	1.0031763	48.65	48.39	+0.26	49.99
0.19445	0.13945	1.0054557	49.59	49.40	+0.19	51.30
0.041426	0.20354	1.011543	51.22	50.98	+0.24	53.32
0.076555	0.27669	1.021172	52.77	52.52	+0.25	55.34
0.11771	0.34309	1.032335	54.00	53.77	+0.23	57.13
0.17913	0.42680	1.048802	55.33	55.44	-0.11	59.87
0.25864	0.50857	1.069810	56.61	56.59	+0.02	61.79
			Average		±0.19	

$^a\phi_V = 44.444 + 46.171\ m^{1/2} - 95.234\ m + 147.50\ m^{3/2} - 91.923\ m^2.$

$^b\bar{V}_2 = 44.444 + 69.256\ m^{1/2} - 190.47\ m + 368.74\ m^{3/2} - 275.77\ m^2.$

Table 11. Specific gravities, apparent molal volumes, and partial molal volumes of neodymium nitrate in aqueous solutions at 25° C., run number three

m	$m^{1/2}$	ρ/ρ_o	ϕ_v	$\phi_v{}^a$ calc.	Δ	$\bar{V}_2{}^b$
0.0012393	0.035204	1.0003528	45.8	45.96	-0.16	46.66
0.0035244	0.059451	1.0009998	46.7	46.88	-0.18	47.96
0.012172	0.10943	1.0034298	48.48	48.52	-0.04	50.15
0.022695	0.15065	1.0063664	46.90	49.70	-0.10	51.67
0.039961	0.19990	1.011152	50.80	50.90	-0.10	53.18
0.071466	0.26733	1.019790	52.26	52.33	-0.07	54.98
0.11723	0.34239	1.032277	53.66	53.74	-0.08	56.84
0.17740	0.42120	1.048399	54.98	55.14	-0.16	58.75
0.27193	0.52146	1.073355	56.58	56.74	-0.16	60.66
			Average		-0.13	

$^a\phi_v = 44.444 + 46.171\ m^{1/2} - 95.234\ m + 147.50\ m^{3/2} - 91.232\ m^2.$

$^b\bar{V}_2 = 44.444 + 69.256\ m^{1/2} - 190.47\ m + 368.74\ m^{3/2} - 255.77\ m^2.$

Figure 15. Partial and apparent molal volumes of neodymium nitrate in aqueous solutions at 25° C.

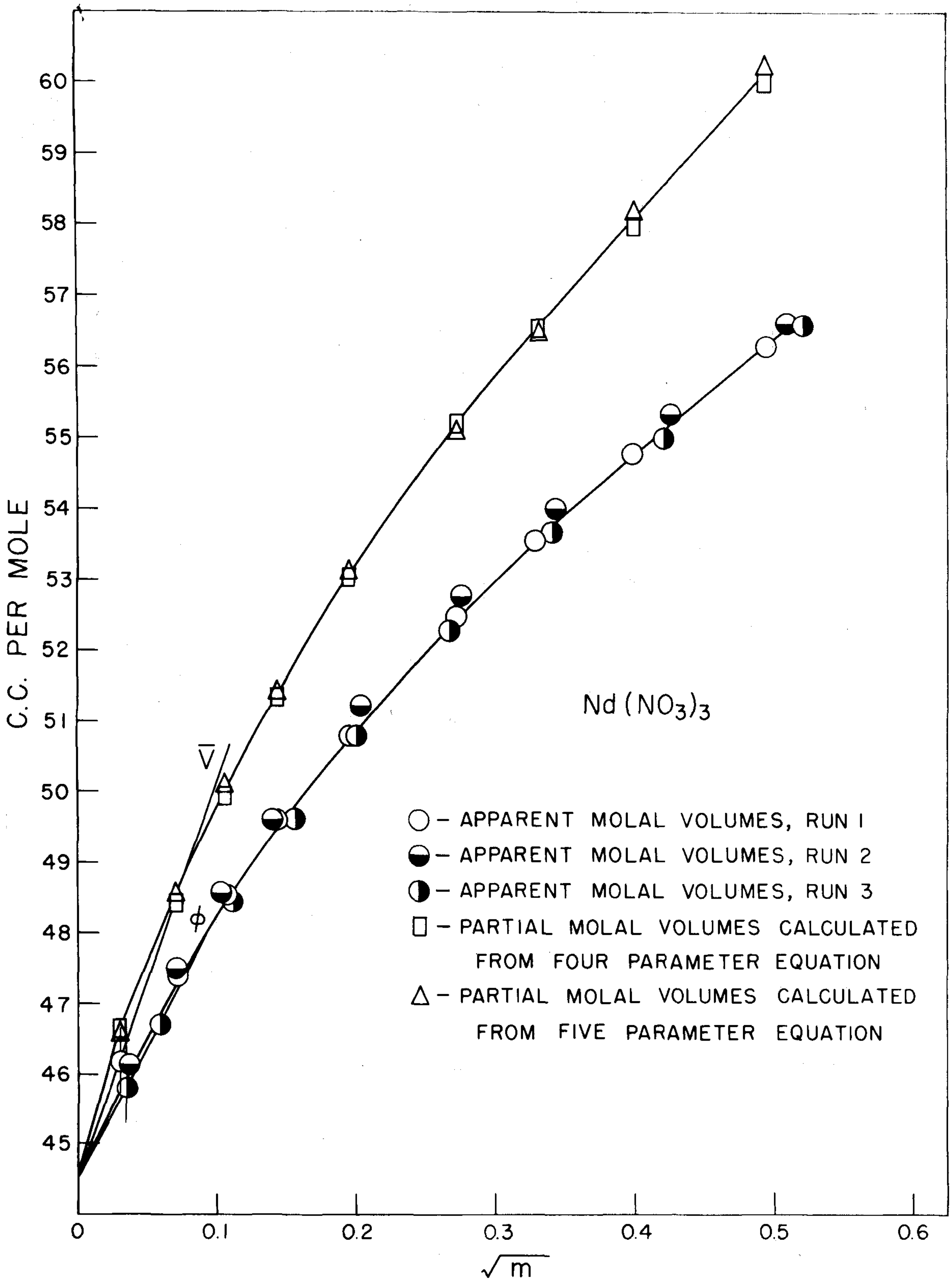

60
59
58
57
56
55
54
53
52
51
50
49
48
47
46
45
C.C. PER MOLE
0
0.1
0.2
0.3
0.4
0.5
0.6
$\sqrt{m}$
$\bar{V}$
ϕ
$Nd(NO_3)_3$
○ – APPARENT MOLAL VOLUMES, RUN 1
◒ – APPARENT MOLAL VOLUMES, RUN 2
◐ – APPARENT MOLAL VOLUMES, RUN 3
□ – PARTIAL MOLAL VOLUMES CALCULATED FROM FOUR PARAMETER EQUATION
△ – PARTIAL MOLAL VOLUMES CALCULATED FROM FIVE PARAMETER EQUATION

Table 12. Specific gravities, apparent molal volumes, and partial molal volumes of erbium nitrate in aqueous solutions at 25° C.

m	$m^{1/2}$	ρ/ρ_o	ϕ_v	ϕ_v^a calc.	Δ	$\bar{V}_2^b$
0.00096372	0.031044	1.0002959	46.3	46.24	+0.06	46.52
0.0034672	0.058883	1.0010361	46.69	46.74	-0.05	47.26
0.011424	0.10688	1.0034914	47.57	47.56	+0.01	48.45
0.020437	0.14296	1.0062330	48.08	48.14	-0.06	49.26
0.034725	0.18635	1.010559	48.77	48.80	-0.03	50.14
0.067084	0.25901	1.020300	49.75	49.76	-0.01	51.35
0.10936	0.33070	1.032931	50.59	50.58	+0.01	52.33
0.15716	0.39643	1.047098	51.28	51.25	+0.03	53.20
0.21845	0.46739	1.065087	52.05	51.95	-0.10	54.36
			Average		±0.04	

$^a\phi_v = 45.679 + 18.327\ m^{1/2} - 2.6032\ m - 41.929\ m^{3/2} + 53.567\ m^2.$

$^b\bar{V}_2 = 45.679 + 27.491\ m^{1/2} - 5.2063\ m - 104.82\ m^{3/2} + 160.70\ m^2.$

Figure 16. Partial and apparent molal volumes of erbium nitrate in aqueous solutions at 25° C.

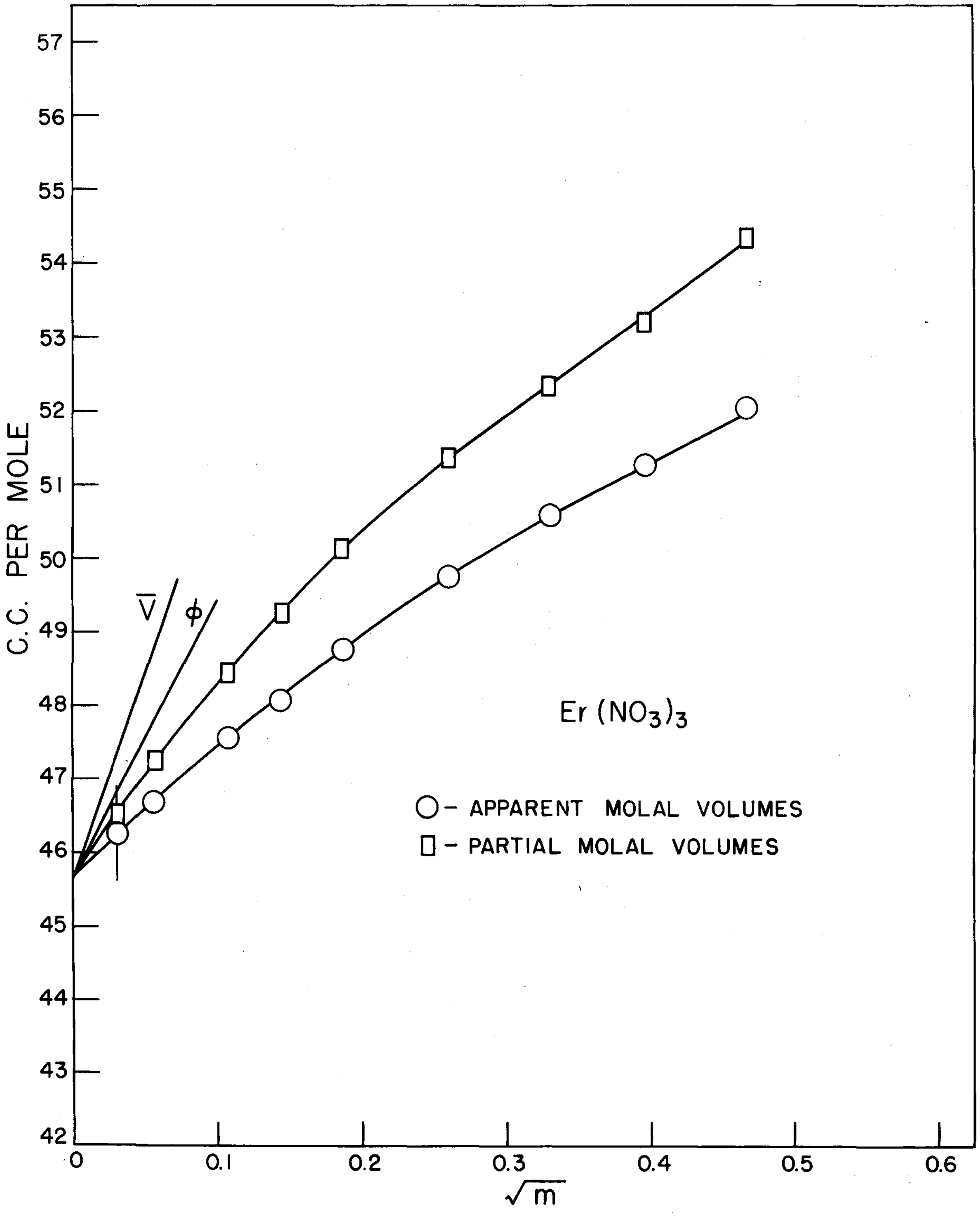

57
56
55
54
53
52
51
50
49
48
47
46
45
44
43
42
C.C. PER MOLE
0
0.1
0.2
0.3
0.4
0.5
0.6
$\sqrt{m}$
$\bar{V}$
ϕ
$Er(NO_3)_3$
○ - APPARENT MOLAL VOLUMES
☐ - PARTIAL MOLAL VOLUMES

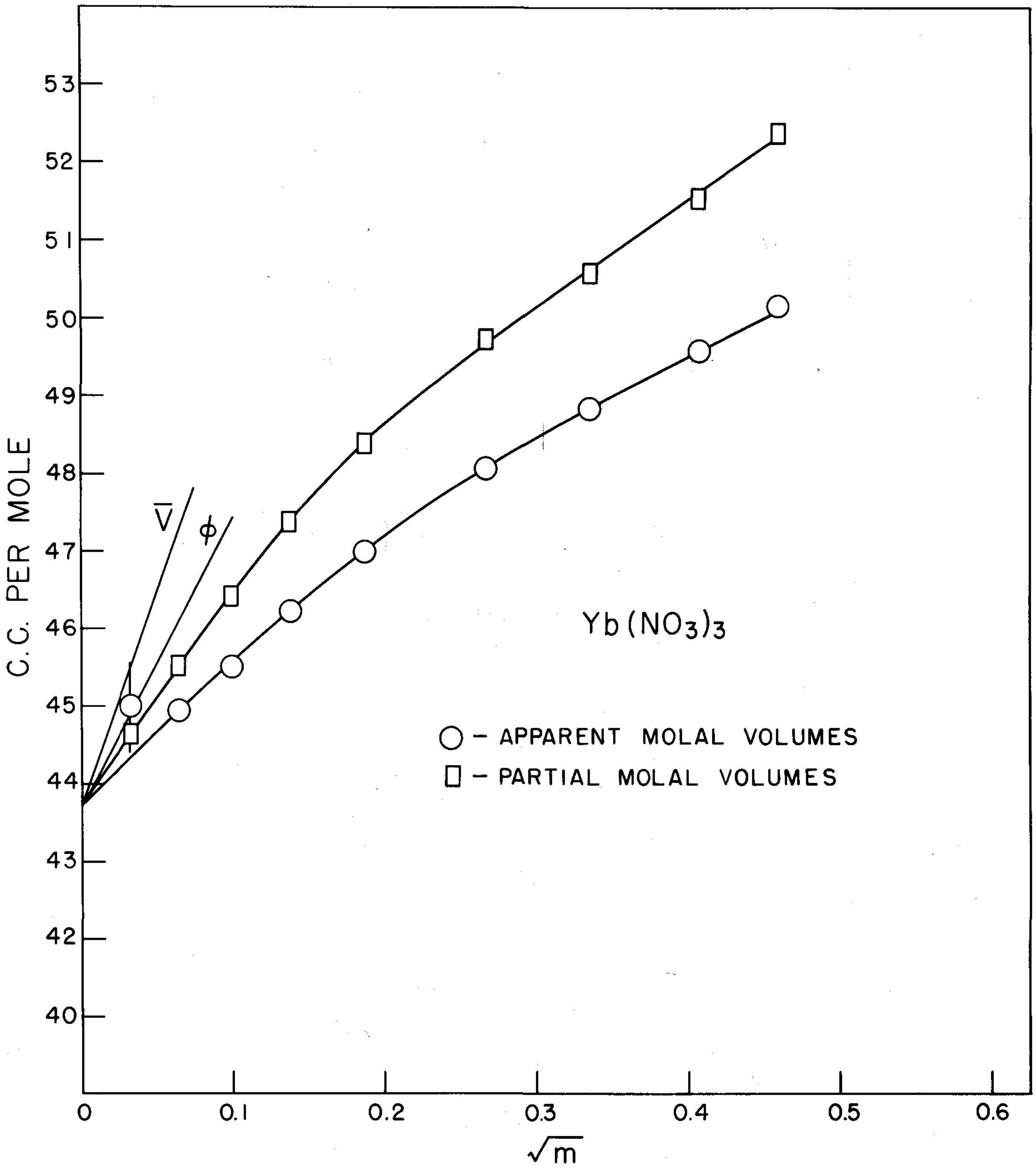
Table 13. Specific gravities, apparent molal volumes, and partial molal volumes of ytterbium nitrate in aqueous solutions at 25° C.

m	$m^{1/2}$	ρ/ρ_o	ϕ_v	ϕ_v calc.[a]	Δ	$\overline{V}_2$[b]
0.00098479	0.031382	1.0003091	45.1	44.34	+0.76	44.64
0.0039407	0.062775	1.0012379	44.95	44.93	+0.02	45.52
0.0095753	0.097853	1.0030024	45.50	45.57	-0.07	46.44
0.018736	0.13688	1.0058586	46.24	46.25	-0.01	47.38
0.034522	0.15880	1.010760	47.00	47.02	-0.02	48.40
0.070976	0.26641	1.022008	48.08	48.10	-0.02	49.72
0.11126	0.33356	1.034344	48.85	48.86	-0.01	50.59
0.16509	0.40631	1.050700	49.59	49.57	+0.02	51.52
0.21017	0.45844	1.064275	50.17	50.08	+0.09	52.39
			Average		±0.10	

[a] $\phi_v = 43.726 + 19.590\ m^{1/2} - 2.9351\ m - 50.955\ m^{3/2} + 65.590\ m^2.$

[b] $\overline{V}_2 = 43.726 + 29.386\ m^{1/2} - 5.8501\ m - 127.39\ m^{3/2} + 196.77\ m^2.$

Figure 17. Partial and apparent molal volumes of ytterbium nitrate in aqueous solutions at 25° C.


C.C. PER MOLE
53
52
51
50
49
48
47
46
45
44
43
42
40
0
0.1
0.2
0.3
0.4
0.5
0.6
$\sqrt{m}$
$\bar{V}$
ϕ
$Yb(NO_3)_3$
○ - APPARENT MOLAL VOLUMES
☐ - PARTIAL MOLAL VOLUMES

A second empirical equation,

$$\phi_v = 44.821 + 37.791\ m^{1/2} - 43.580\ m + 27.988\ m^{3/2}\ , \quad (139)$$

was found to represent the data for neodymium nitrate solutions reasonably well but not as accurately as the five parameter equation. Partial molal volumes for neodymium nitrate, as determined by the use of equation 139, are also shown in Figure 15.

F. Experimental Errors

The accuracy with which the specific gravities and the apparent molal volumes can be determined is fixed by the errors in the measurements of a number of experimental quantities. The apparatus, as previously described, was designed to minimize these errors as much as possible. The experimental errors in certain of these quantities had a negligible influence on the specific gravities and apparent molal volumes over most of the concentration range studied; however, the effect of errors in some of the measurements varied greatly with the concentration of the solutions.

The quantities on which the specific gravity and apparent molal volume depend are: the temperature, $\underline{T}$, the concentration, $\underline{c}$, the weight of the float, $\underline{W}$, the weight of platinum, $\underline{w}$, added to the float, the equilibrium solenoid current, $\underline{I_o}$, and the calibration factor $\underline{\psi}$. The influence of fluctuations in the temperature was discussed in connection with the description of the apparatus and amounted to an uncertainty of about ±2.6 x 10^{-7} in the specific gravity. The uncertainties in the specific gravity, $\underline{S}$, and the apparent molal volume, $\underline{\phi_v}$, due to uncertainties in the experimental quantities listed above, may be determined by differentiating equations 130 and 112 with respect to these quantities.

Equation 113, namely,

$$d\phi_v = \frac{-1000}{c}\, dS \qquad (113)$$

gives the uncertainty, $\underline{d\phi_v}$, in the apparent molal volume due to the error, $\underline{dS}$, in the specific gravity. The influence of uncertainties in the various quantities on the specific gravity, $\underline{S}$, will first be examined and these will be related to the uncertainties in $\underline{\phi_v}$ through equation 113.

The absolute values of the uncertainties in the specific gravity due to errors in the various experimental quantities are shown in Figure 18, and the corresponding uncertainties in the apparent molal volume are shown in Figure 19.

Figure 18. Variations in dS with concentration due to uncertainties in values of experimental quantities

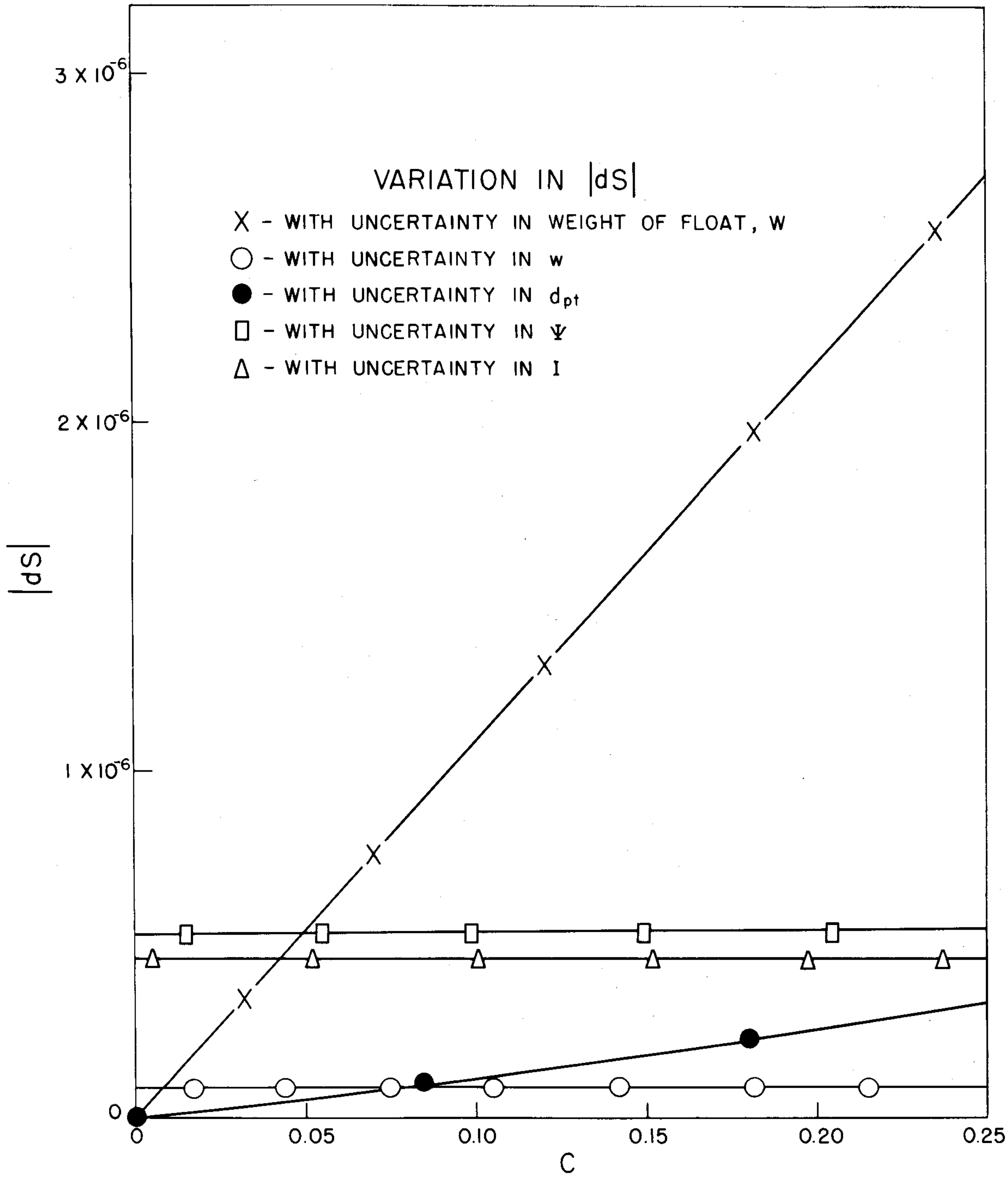
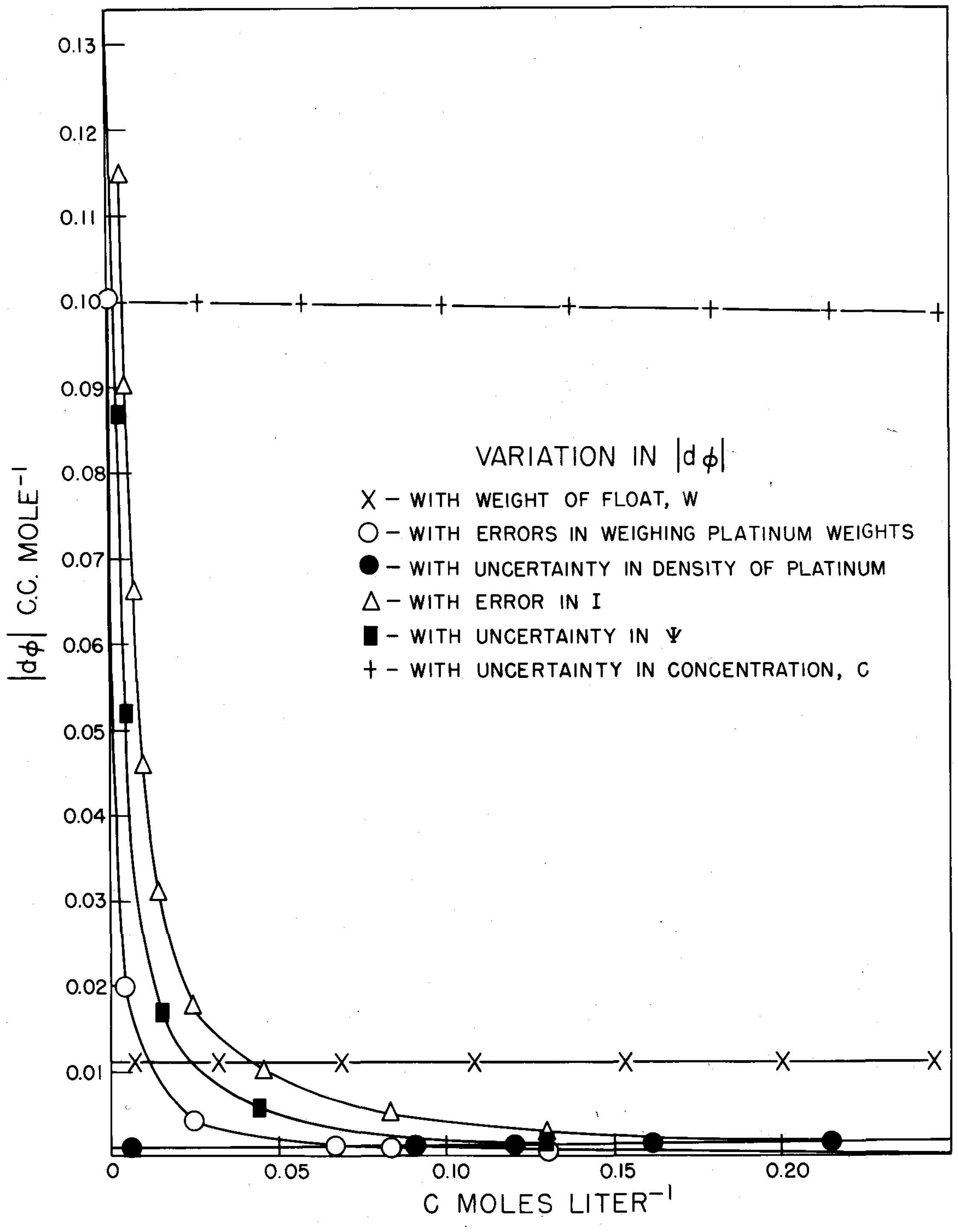

VARIATION IN |dS|
X - WITH UNCERTAINTY IN WEIGHT OF FLOAT, W
○ - WITH UNCERTAINTY IN w
● - WITH UNCERTAINTY IN d_{pt}
□ - WITH UNCERTAINTY IN Ψ
Δ - WITH UNCERTAINTY IN I
|dS|
3 X 10⁻⁶
2 X 10⁻⁶
1 X 10⁻⁶
0
0
0.05
0.10
0.15
0.20
0.25
C

Figure 19. Variations in $|d\phi|$ with concentration due to uncertainties in values of experimental quantities


VARIATION IN $|d\phi|$
X – WITH WEIGHT OF FLOAT, W
○ – WITH ERRORS IN WEIGHING PLATINUM WEIGHTS
● – WITH UNCERTAINTY IN DENSITY OF PLATINUM
△ – WITH ERROR IN I
■ – WITH UNCERTAINTY IN Ψ
+ – WITH UNCERTAINTY IN CONCENTRATION, C
$|d\phi|$ C.C. MOLE^{-1}
0.13
0.12
0.11
0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
0.05
0.10
0.15
0.20
C MOLES LITER^{-1}

Differentiation of equation 130 with respect to the weight of the float, W, gives

$$dS = \frac{DdW - NdW}{D^2} = \frac{(D - N)dW}{D^2} \qquad (140)$$

where D is equal to $W - I_o^o \psi$ and N is equal to $W + w - I_o \psi$. Since $D - N$ increases negatively with increasing concentration, the absolute value of the error in S due to the uncertainty, dW, in the weight of the float increases with increasing concentration. For erbium chloride solutions, an apparent uncertainty of ±5 milligrams in the weight of the float leads to errors in the specific gravity ranging from zero at infinite dilution to $\pm 3 \times 10^{-6}$ at 0.3 molar. The influence of this error on the apparent molal volume is almost constant at $d\phi_v$ equal to 0.011 cubic centimeters over the same concentration range. This is due to the fact that $D - N$ is very nearly a linear function of the concentration, so that the substitution of equation 140 into equation 113 gives

$$d\phi_v = -\frac{1000 \times \text{Const.}}{D^2}\, dW. \qquad (141)$$

The effect on the specific gravity, S, of errors in the weight, w, of the platinum weights is obtained by differentiating equation 130 with respect to w. Thus

$$dS = \frac{dw}{D} . \tag{142}$$

The probable uncertainty of ±0.01 milligrams in the weighing of the platinum weights leads to an uncertainty of about $\pm 9 \times 10^{-8}$ in the specific gravity. The resulting uncertainty in the apparent molal volume is appreciable only for extremely dilute solutions. There is an additional uncertainty in the weight of the platinum arising from the uncertainty in the density of the platinum weights. The weight of platinum, w, corrected for the buoyancy of the solution, is given by

$$w = w' (1 - \rho/d) \tag{143}$$

where w' is the weight of the platinum in vacuo, ρ is the density of the solution, and d is the density of platinum.

Differentiation of equation 143 with respect to d gives

$$dw = - \frac{w'}{D^2} d(d) . \tag{144}$$

A value of 21.428 ± 0.002 grams per cubic centimeter for the density of annealed platinum wire, as determined by MacInnes, Dayhoff, and Ray (66), was used in all calculations. This value is in excellent agreement with that obtained by Kahlbaum and Sturm (105). The error in S due to the uncertainty in the density of platinum increases with increasing concentration. For a 0.26 molar erbium chloride solution, dS is equal to $\pm 3.5 \times 10^{-7}$. The effect of the uncertainty in the density of platinum on the apparent molal volume is negligible over the entire concentration range studied.

Differentiation of equation 130 with respect to the equilibrium solenoid current, I_o, gives

$$dS = \frac{N \psi \, dI_o^o - D \psi \, dI_o}{D^2} \quad . \qquad (145)$$

The maximum error will arise when the errors in I_o and I_o^o are in opposite directions. Substituting $dI_o^o = - dI_o$ and $N \simeq D$ gives

$$dS \simeq \frac{2 dI_o^o}{D} \quad . \qquad (146)$$

An uncertainty of ±0.5 milliamperes in the equilibrium solenoid current gives an uncertainty in S of about $\pm 5 \times 10^{-7}$. The error in the partial molal volume, ϕ_v, due to this uncertainty in the current, increases very rapidly with decreasing concentration for solutions of concentration less than about 0.01 molar.

The uncertainty in the specific gravity due to the uncertainty in the calibration factor $\underline{\psi}$ is obtained by differentiation of equation 130 with respect to $\underline{\psi}$, which gives

$$dS = \frac{NI_0^0 d\psi - DI_0 d\psi}{D^2} \quad . \tag{147}$$

Substituting $\underline{N \simeq D}$ gives

$$dS \simeq \frac{(I_0^0 - I_0)d\psi}{D} = \frac{\Delta I d\psi}{D} \quad . \tag{148}$$

The maximum value of $\underline{\Delta I}$ was about 300 milliamperes and $\underline{d\psi}$ was about ±2 x 10^{-7} grams per milliampere. Substitution of these values into equation 148 gives a value of ±5 x 10^{-7} for $\underline{dS}$. The uncertainty in the apparent molal volume due to the uncertainty in the calibration factor, $\underline{\psi}$, increases rapidly with decreasing concentration for extremely dilute solutions.

The most serious limitation on the accurate determinations of the apparent molal volumes was due to the uncertainties in the concentrations of the solutions. These uncertainties were due to two factors, the limitation in the precision of the analytical method used, and errors made in weighing quantities of stock solutions into the cylinder. The uncertainties in the apparent molal volumes resulting from errors in the concentrations of the stock solutions were about ±0.10 to ±0.15 cubic centimeters per mole. The uncertainties due to errors in the weights of stock solution were estimated to be less than ±0.05 cubic centimeters per mole.

IV. DISCUSSION OF RESULTS

The errors involved in the determination of apparent and partial molal volumes were discussed in the preceding section of this thesis. The largest error, that due to uncertainties in the concentrations of the solutions, limited the accuracy in the measurement of these quantities to about ±0.15 cubic centimeters per mole. Fortunately, the change in the partial and apparent molal volumes between neighboring elements was sufficiently large to show significant changes above the errors in the measurements.

In general, the partial and apparent molal volumes of the rare earth salts, as determined from this research, were found to deviate markedly from the simple limiting laws, equations 97 and 104, at very low concentrations. The limited amount of data now available seems to indicate that the heavy rare earth salts show greater deviation from the limiting slopes for the partial and apparent molal volumes than do the salts of the lighter rare earths. This change is in the direction to be expected from the increasing extent of hydrolysis and greater facility of ion-pair formation with increasing atomic number.

Comparison of the experimentally determined values of the apparent and partial molal volumes, at moderate concentrations, with the values predicted by more general theoretical equations is not possible at the present stage of investigation. In the theoretical section of this thesis, a number of the difficulties arising in the theoretical treatment of solutions of unsymmetrical polyvalent electrolytes were discussed. The effect of such factors as the higher order terms of the complete solution of the Poisson-Boltzmann equation on the apparent and partial molal volumes cannot be determined until further information is available for a number of partial differential coefficients. As a result, extrapolation formulas such as that derived by Owen and Brinkley (95), equation 121, cannot now be employed.

Rare earth salts of the types investigated in this research might be expected to exhibit considerable association of the Bjerrum type (5). From equation 82, $\underline{q}$ is seen to equal 10.5 angstroms for 3-1 type electrolytes. The average value of the mean distance of closest approach, $\underline{a}^o$, is about 5.7 angstroms for the rare earth chlorides (22), and 4.5 angstroms for the three rare earth nitrates for which data are available (24). These are well within the limits for which association might be expected. If association of this type is present, the effect was not apparent in the data for the activity coefficients which were found to be in excellent agreement with the Debye-Hückel theory up to concentrations of about 0.1 molar (106). Again more data are needed for a number of partial differential coefficients before the theory can be compared with the experimentally determined values for apparent and partial molal volumes.

There is no simple correlation between the partial or apparent molal volumes, as determined in this study, and the mean distances of closest approach, $\underline{a}^{o}$, as determined from measurements of activity coefficients. This is, perhaps, to be expected. The quantity $\underline{a}^{o}$ is defined precisely but is treated as an adjustable parameter in the activity coefficient equations. As a consequence, little significance can be attached to the exact numerical values obtained, although, for the rare earth salts, they are of the order of magnitude to be expected for the sum of the crystal ionic radii plus the diameter of a water molecule. Furthermore, partial and apparent molal volumes depend on volume changes throughout the solution as a whole while the mean distances of closest approach result from interionic forces which may have only secondary effects on volume changes in the solvent.

Empirical equations of the form given by equation 107 were used for the calculation of the partial molal volumes. Extrapolations to infinite dilution by equations of this type do not yield as accurate values as may be obtained by the use of theoretical extrapolation formulas. However, in the absence of the proper theoretical equations, the empirical equations were used to obtain the values of the apparent molal volumes at infinite dilution. The additivity of these limiting values is surprisingly good considering the errors introduced by the uncertainties in the concentrations of the solutions and the use of empirical equations for the extrapolations.

The apparent molal volumes of the rare earth salts at infinite dilution do not vary regularly with atomic number. For both the chlorides and the nitrates, the limiting value of the apparent molal volume of the neodymium salt falls between the values for the erbium and ytterbium salts. The apparent molal volumes of neodymium nitrate in solutions of moderate concentrations are larger than the apparent molal volumes of erbium nitrate at the same concentrations. At lower concentrations the values for neodymium nitrate cross over the values for erbium nitrate to reach a limiting value between those of erbium nitrate and ytterbium nitrate.

The irregular change of apparent molal volumes at infinite dilution with atomic number may result from a change in the hydration number of the rare earth ions. As the ions become larger, with decreasing atomic number, a second coordination number may become possible, resulting in an equilibrium being established between rare earth ions having different coordination numbers. There is crystallographic evidence for a change in the hydration of rare earth salts, in crystal form, in the neighborhood of praseodymium, and x-ray measurements on lanthanum sulfate enneahydrate (107) have shown that oxygen coordination numbers of 9 and 12 exist for lanthanum ions in the same crystal. In dilute solutions, where the positive and negative ions are separated by greater distances than in the crystal, it is possible that the larger coordination number may be carried forward for one or two additional elements.

The exact effect, on the apparent molal volume, of a change in the coordination number of the rare earth ions cannot be predicted. However, if the volume of a solution is given by

$$V = V_{solute} + n_1 V_1^o + \Delta v_{H_2O} , \qquad (149)$$

where $\underline{V_{solute}}$ is the volume of the solute, exclusive of the volume of the hydration water, and $\underline{\Delta V_{H_2O}}$ is the change in volume of the water, then from equation 99,

$$\phi_v = v_{solute} + \Delta v_{H_2O} . \qquad (150)$$

At infinite dilution,

$$\phi_v^o = v^o_{solute} + \Delta v^o_{H_2O} \quad , \qquad (151)$$

where $\underline{v^o_{solute}}$ is the volume occupied by one mole of solute and $\underline{\Delta v^o_{H_2O}}$ is the net change in the volume of the water resulting from the addition of one mole of solute to an infinite quantity of water. The volume occupied by the solute is unknown. However, for a given coordination number, $\underline{v^o_{solute}}$ and $\underline{\Delta v^o_{H_2O}}$ should vary smoothly with changes in ionic radii, while a change in coordination number may result in discontinuities in both quantities with the major change occurring in $\underline{\Delta v_{H_2O}}$. Thus, if ions of some rare earths can exist in solution with two coordination numbers and others with only one, the apparent molal volumes at infinite dilution should fall into two series. Furthermore, since $\underline{\Delta v^o_{H_2O}}$ is negative, an increase in the absolute magnitude of this quantity with an increase in coordination number for the lighter rare earth ions would lead to a predicted behavior in qualitative agreement with the experimental results.

Apparent molal volumes increase more rapidly with concentration for neodymium nitrate and lanthanum nitrate than for the other rare earth salts studied. This may also be due to an equilibrium between lanthanum ions or neodymium ions having two coordination numbers. The chloride ions, being roughly of the same size as the water molecules, should be able to displace a water molecule from the hydration shell of a cation without greatly disturbing other water molecules in the shell. The more bulky nitrate ion should have a greater steric effect on the water molecules of the ions with the larger coordination number, driving the equilibrium in the direction of the smaller coordination number. As a result of this change in equilibrium, the apparent molal volumes would tend to shift toward the higher values to be expected for the smaller coordination number. The larger coordination number should be more stable for the lanthanum ion than for the neodymium ion and the shift in the apparent molal volumes of lanthanum nitrate should be less pronounced.

At the present time, there are not sufficient data for definite conclusions to be reached. The proposed explanation of the apparent anomalies in the apparent molal volumes leads to qualitative agreement with the experimental results, but additional data are needed for other rare earth salts before this explanation can be verified or an alternative one proposed.

A number of other properties of solutions of rare earth salts also exhibit irregularities in the neighborhood of neodymium. Equivalent conductances at infinite dilution of rare earth chlorides (19,22), bromides (21), nitrates, sulfates, and perchlorites (24) change slowly from lanthanum to neodymium and decrease rapidly beyond neodymium. Similar behavior was observed for the transference numbers of rare earth chlorides (106).

Since the apparent molal volumes depend strongly on the interaction of the ions and the solvent, it might be reasonable to expect that apparent anomalies in the apparent molal volumes should be reflected in such properties as the heats, free energies, and entropies of solution and the heats, free energies, and entropies of formation of the hydrated ions. At the present time, data on these properties are too limited for comparison. Furthermore, the volume effects may arise from different arrangements of the water molecules which are nearly equivalent in energy and entropy. In this case the apparent anomalies should not appear in the other thermodynamic properties.

Additional information which might be correlated with data for the partial and apparent molal volumes might be obtained from Raman spectra of the solutions, from ultrasonic interferometry, and from measurements of diffusion coefficients. A very versatile Raman spectroscope and recorder have recently been described by T. F. Young (108). Raman spectra may provide some information on the strength of ion-pair or complex ion formation between the rare earth ion and the anion present in the solution. In addition, some idea of the extent of the cationic hydration might be obtained from the frequency shifts and changes in intensities of certain lines arising from the water molecule. Some studies of the Raman effect in aqueous solutions of rare earth salts have been reported in the literature, but the studies should be extended to include salts of the heavy rare earths.

A recent review on the effects and uses of ultrasonic waves was given by Barnartt (109), and a simple technique for the measurements of diffusion coefficients has been described by Harned (110).

There are a number of interesting empirical and semi-empirical relations which have been applied to partial and apparent molal volumes. As data are accumulated for more rare earth salts, it would be of interest to see how the apparent molal volumes fit into the divisions, such as that made by Fajans and Johnson (111), of the apparent molal volumes into apparent ionic volumes. Data for the apparent ionic volumes of the cations might then be used in a study of the applicability of the single parameter activity coefficient equation derived by Stokes and Robinson (112,113).

The extension of specific gravity measurements to other rare earth salts might be facilitated by a change in apparatus. The magnetically controlled quartz fiber balance can be made extremely sensitive (114). A displacement bulb constructed as an integral part of the balance arm would make such a balance an ideal tool for the measurement of specific gravities since the entire balance can be placed inside the solution chamber. An arrangement whereby a small number of weights could be added or removed from the balance, as required, would remove one of the most time consuming steps of the present procedure. This apparatus would be ideally suited to the extension of measurements to higher concentrations since the balance can be constructed in quite small dimensions.

V. SUMMARY AND CONCLUSIONS

A. Summary

An apparatus for the precise determination of the specific gravities of solutions was constructed and calibrated. This apparatus was an adaptation of that originated by Lamb and Lee (64) and modified by Geffcken, Beckmann, and Kruis (65) and MacInnes, Dayhoff, and Ray (66), and consisted essentially of a well thermostated constant temperature bath and a magnetically controlled float.

Specific gravities were calculated by successive approximations from the equations

$$S = \rho/\rho_0 = \frac{W + w - I_0 \psi}{W - I_0^0 \psi} \quad , \qquad (130)$$

and

$$w = w' \, (1 - \rho/d_{pt}) \quad , \qquad (131)$$

where the various quantities are as defined on page 59.

Apparent molal volumes were calculated from the equation

$$\phi_v = \frac{1000}{c}(1 - \rho/\rho_o) + M_2 / \rho_o . \qquad (112)$$

As a final check on the calibration of the apparatus, the apparent molal volumes of potassium chloride in aqueous solutions at 25° C. were determined. The values obtained for the apparent molal volumes were found to be in excellent agreement with those obtained by Geffcken and Price (78) and Kruis (89). The apparent molal volumes of potassium chloride are given in Table 3 and shown graphically in Figure 9.

Specific gravity measurements were made on aqueous solutions of lanthanum, neodymium, erbium, and ytterbium chlorides and nitrates at 25° C. The concentration range covered was from about 0.001 molar to about 0.3 molar.

Apparent molal volumes of the rare earth salts were calculated from the specific gravities by means of equation 112.

Empirical equations of the form

$$\phi_v = a + bm^{1/2} + cm + dm^{3/2} + km^2 \qquad (107)$$

were fitted to the data for the apparent molal volumes of each salt. These equations were used for extrapolations to infinite dilution, and for the calculation of the partial molal volumes.

Partial molal volumes were calculated from the empirical equation for each salt by use of the relation

$$\bar{V}_2 = m\left(\frac{\partial \phi_v}{\partial m}\right)_{T,P,n_j} + \phi_v \quad . \tag{108}$$

This operation resulted in empirical equations of the form

$$\bar{V}_2 = a + (3/2)bm^{1/2} + 2cm + (5/2)dm^{3/2} + 3km^2 \tag{109}$$

for the partial molal volumes of each salt. The empirical equations for the apparent and partial molal volumes are given under the table of data for each salt.

A tentative interpretation of two apparent anomalies in the apparent molal volumes was given.

B. Conclusions

1. The apparent and partial molal volumes of the rare earth salts in aqueous solutions show significant deviations from the limiting laws at low concentrations. The deviations from the limiting slopes appear to be greater for the heavy rare earth salts than for salts of the lighter elements.

The experimentally determined values of the apparent and partial molal volumes cannot be compared with the values predicted by more general theoretical equations until data are available for several partial differential coefficients introduced in the theoretical development.

2. The apparent molal volumes of the rare earth salts at infinite dilution appear to fall into two series. Data obtained in this investigation seem to indicate that lanthanum and neodymium salts are members of one series while erbium and ytterbium salts belong to a second series. The appearance of two series can be explained qualitatively by assuming an equilibrium to exist between rare earth ions having different coordination numbers. This tentative explanation may be verified or invalidated as further data are accumulated.
3. Apparent molal volumes increase more rapidly with increasing concentration for lanthanum nitrate and neodymium nitrate than for the other salts investigated. An equilibrium between ions having different coordination numbers was suggested as a possible explanation of the change in the limiting apparent molal volumes with atomic number. If such equilibria

exist, the behavior of lanthanum nitrate and neodymium nitrate may result from shifts in the equilibria for the larger lanthanum and neodymium ions in the presence of nitrate ions.

4. Measurements of partial and apparent molal volumes should be extended to include more rare earth salts. The salts studied in this investigation were chosen to provide a preliminary survey of the series. Had these salts been restricted to a more limited range of the rare earth series or exclusively to either the nitrates or the chlorides, it is probable that some of the more interesting results would not have been observed. However, the distribution of the eight salts between the light and heavy elements and between the chlorides and the nitrates leaves large gaps in the data. It is particularly important that data be obtained for rare earth salts between neodymium and erbium.

VI. LITERATURE CITED

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