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VOLUME-TEMPERATURE RELATIONSHIPS OF SOME

RARE-EARTH CHLORIDE SOLUTIONS

by

Wayne Merlyn Gildseth

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I. INTRODUCTION

The past few years have given rise to a renewed interest in the study
of electrolytic solutions which has been revealed by new theoretical
attacks on the problem and by experimental investigations over much wider
ranges of temperature, composition, and other such physical conditions.
Exemplifying the above is the theoretical solution of the conductance
problem by Fuoss and Onsager in which ions are represented as charged
spheres rather than point charges (1), the extension of the above theory
to associated electrolytes by Fuoss (2, 3), the application of electronic
computer techniques to electrolytic solution theory by Guggenheim (4), the
very precise measurements of the dielectric constant of water at different
temperatures by Vidulich and Kay (5) and Owen, et al. (6), the very precise
x-ray diffraction study of water by Danford and Levy (7), the x-ray dif-
fraction study of hydrolytic species in aqueous zinc chloride solutions by
Kruh and Standley (8), and the theoretical calculations of various physical
properties of water made by Frank and Wen (9) and Nemethy and Scheraga
(10). The reasons for this renewed interest are in part due to the greater
availability of electronic computers, better experimental techniques and
instrumentation, and to the fact that a thorough theoretical understanding
of electrolytic solutions still remains as one of the major unsolved
problems of physical chemistry. In order to thoroughly understand electro-
lytic solutions, it is necessary to gain an insight into the nature of the
chemical species and the solvent and ionic structures present in these
solutions. Numerous investigative approaches into the study of electrolytic

solutions such as the study of fused salts and the use of x-ray diffraction techniques are presently in use. In addition to these methods, experimental determinations of physical properties are needed to test any proposed theories and to provide insight into the nature of electrolytic solutions.

Electrolytic solutions containing trivalent cations have, to date, presented some of the severest tests for electrolytic solution theories. Basically, this is due to the fact that it is the square of the charge which is important in electrolytic solution theory. In addition, electrolytic solutions containing trivalent cations undergo considerable solvation, solvolysis, and association. Of all the trivalent cations available, the Group IIIa elements of yttrium, lanthanum and the rare-earth elements beginning with cerium (atomic number 58) and ending with lutetium (atomic number 47) are of particular interest for several reasons. First of all, with the development of large-scale ion exchange techniques, these elements are now readily available in fairly large amounts and in high purity. A good discussion of this topic and an excellent list of references is given by Jack E. Powell (11). These elements will each form several water soluble salts which are quite stable over wide ranges of concentration and temperature, and although they undergo considerable solvolysis, particularly at the higher concentration, they are in general much better in this respect than most other trivalent cations. Also, the elements mentioned have similar electronic structures. This is especially true for the rare-earth elements in which the 4f subshell is filled up as the atomic number increases. Since the 4f electrons are well screened by the 5s5p subshells and since the ions are solvated, the chemical properties of these elements

in aqueous solution are very similar. Furthermore, as the 4f subshell is filled, the atomic radii of these elements decreases giving rise to the familiar "Lanthanide Contraction". This regular decrease in atomic radii and similarity in chemical properties would lead one to expect that the physical properties of their electrolytic solutions would also change in a regular manner. However, this has not been found to be the case, and in itself poses some interesting problems, as well as providing information regarding differences in solvation, solvolysis, and association.

Of all the thermodynamic and transport properties of electrolytic solutions available for study, some of the least studied are the thermodynamic properties which are second derivatives of free energy, such as partial molal compressibility, partial molal expansibility, and partial molal heat capacity. This is in part due to the experimental difficulties involved and to the fact that the error in these properties is extremely large for the dilute concentration range in which the present electrolytic solution theories are effective. Nevertheless, these properties are of interest at higher concentrations for the study of the effects of such phenomena as solvation, solvolysis, and association on physical properties of electrolytic solutions, as well as for general insight into the nature of electrolytic solutions. With these considerations in mind, this report is concerned with measurements of densities of water and aqueous solutions of lanthanum and neodymium chlorides over a range of temperatures from 20 to 80° C. The lanthanum and neodymium chloride solutions are examined over a range of concentrations from 0.1 molal to almost saturation at 25° C.

With these data, it is possible to calculate cubical coefficients of thermal expansion for water and solutions. In addition, apparent molal volumes and expansibilities of the solutions and partial molal volumes and expansibilities of water and the solutions can be calculated.

II. GENERAL THEORY

A. General Thermodynamics

Thermodynamics attempts to macroscopically describe the state of matter through the formulation of the intrinsic properties of matter such as composition, temperature, pressure, and volume. In the thermodynamic development to be presented below, it will be assumed that such external properties as electrical, magnetic, and gravitational fields of force are being held constant.

The first and second laws of thermodynamics define respectively, the internal energy and entropy of a system. The composition, temperature, pressure, volume, internal energy, and entropy of a system at equilibrium are all functions of state. This simply means that their values depend only on the state of the system in question, and that they are independent of the previous history of the system. Using these six functions of state, three other functions of state, namely, enthalpy, Gibb's free energy, and the Helmholtz work function can also be defined.

In systems hiving more than one component, the chiemical potential of component "i" can be defined as:

$$\mu_i = (\partial F / \partial n_i)_{T,P,n_j}$$

in which μ_i is the chemical potential of the ith component of the system, F is the Gibb's free energy of the system, and n_i is the number of moles of the ith component in the system.

The various functions of state of the system are related according to the following differential equations:

$$dF = - SdT + VdP + \sum_{i=1}^{n} \mu_i dn_i \qquad (2.2)$$

$$dA = - SdT - PdV + \sum_{i=1}^{n} \mu_i dn_i \qquad (2.3)$$

$$dE = TdS - PdV + \sum_{i=1}^{n} \mu_i dn_i \qquad (2.4)$$

and

$$dH = TdS + VdP = \sum_{i=1}^{n} \mu_i dn_i \qquad (2.5)$$

in which F, A, E, H, S, T, V, and P are the Gibb's free energy, Helmholtz work function, internal energy, enthalpy, entropy, temperature, volume, and pressure, respectively.

In addition to being functions of state, F, A, H, E, S, and V are also extensive properties. An extensive property is a homogeneous function of first degree in the amount of material present. If G is an extensive property of the system, such that

$$G = G(T, P, n_1, n_2, \ldots), \qquad (2.6)$$

and λ is some constant, then

$$\lambda G = G(T, P, \lambda n_1, \lambda n_2, \ldots). \qquad (2.7)$$

Furthermore, according to Euler's theorem on homogeneous functions (12),

$$G = \sum_{i=1}^{n} n_i \left(\partial G / \partial n_i \right)_{T,P,n_j}. \qquad (2.8)$$

The partial derivative, $(\partial G/\partial n_i)_{T,P,n_j}$, is called the partial molal G, and

is symbolized $\overline{G}_i$. It is seen from Equation 2.1 that the chemical potential

of a component is nothing more than the partial molal free energy of that

component. Differentiation of Equation 2.6 under conditions of constant

temperature and pressure gives

$$dG = \sum_{i=1}^{n} \overline{G}_i dn_i .$$ (2.9)

However, differentiation of Equation 2.8 gives

$$dG = \sum_{i=1}^{n} n_i d\overline{G}_i + \sum_{i=1}^{n} \overline{G}_i dn_i .$$ (2.10)

Solving Equations 2.9 and 2.10 simultaneously, the relationship

$$\sum_{i=1}^{n} n_i d\overline{G}_i = 0$$ (2.11)

is obtained for conditions of constant temperature and pressure. This

relationship is the Gibbs-Duhem equation in its most general form. This

equation is particularly valuable when the partial molal quantity of one

component of a two component system is known as a function of concentration,

and the corresponding quantity for the other component is desired.

One of the most difficult thermodynamic problems for chemists has been

the comparison of the chemical potentials of a particular component at

different concentrations. To alleviate this difficulty, G. N. Lewis defined

the absolute activity (13). According to the current usage, the chemical

potential of a component is defined as

$$\mu_i = \mu_i^o + RT \ln a_i$$ (2.12)

in which μ_i^0 is the chemical potential at some arbitrary standard state at which the activity is taken to be unity, and a_i is the activity of the ith component.

With electrolytic solutions, it is customary to express the concentration either as molarity, c = moles of salt per liter of solution, or molality, m = moles of salt per 1000 grams of solvent. In these cases, the activity of the salt is defined such that

$$\lim_{c \to 0} (a_2/c) = 1 \qquad (2.13)$$

$$or$$

$$\lim_{m \to 0} (a_2/m) = 1 \qquad (2.14)$$

where the subscript "2" refers to the salt.

If the salt dissociates according to the equation

$$A_{\nu+}B_{\nu-} = \nu_+ A^{+z+} + \nu_- B^{-z-} \qquad (2.15)$$

into

$$\nu = \nu_+ + \nu_- \qquad (2.16)$$

ions, the activity of salt may be written as

$$a_2 = (a_+^{\nu+}) \cdot (a_-^{\nu-}) . \qquad (2.17)$$

In Equation 2.17, a_+ and a_- refer to cationic and anionic activities, respectively. Since individual ionic activities can not be determined experimentally, it is convenient to define a mean ionic activity, $a_\pm$, as

$$a_\pm = (a_2)^{1/\nu} \qquad (2.18)$$

The concentrations of the cationic and anionic species are, respectively,

$$m_+ = \nu_+ m \tag{2.19}$$

and

$$m_- = \nu_- m, \tag{2.20}$$

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

$$m_\pm = (m_+^{\nu_+} m_-^{\nu_-})^{1/\nu}. \tag{2.21}$$

If we define the activity coefficient of the salt, γ_2, as

$$\gamma_2 = \frac{a_2}{m}, \tag{2.22}$$

it follows from Equations 2.18 and 2.21 that

$$\gamma_\pm = \frac{a_\pm}{m_\pm} \tag{2.23}$$

in which $\gamma_\pm$ is the mean ionic molal or practical activity coefficient of the salt. From Equations 2.12, 2.18, and 2.23 it is now seen that

$$\mu_2 = \mu_2^o + \nu RT \ln a_\pm \tag{2.24}$$

or

$$\mu_2 = \mu_2^o + \nu RT \ln (\gamma_\pm m_\pm) \tag{2.25}$$

or

$$\mu_2 = \mu_2^o + \nu RT \ln (\gamma_\pm m) + RT \ln (\nu_+^{\nu_+} \nu_-^{\nu_-}). \tag{2.26}$$

B. General Theory of Electrolytic Solutions

The history of electrolytic solution theory is essentially the history
of electrochemistry. It might be said that the study of electrolytic
solutions began with the study of electrolysis which finally culminated
in Faraday's observations on electrolysis in 1834 (14). Following Faraday's
observations, considerable work was done on electrolytic solutions,
including the precise conductivity measurements of Kohlrausch and his co-
workers during the years 1869 to 1880. In 1887, Arrhenius (15) published
his ionization theory of electrolytes in which he proposed that when an
electrolyte dissolves, there is an equilibrium between ions and un-
dissociated molecules. This hypothesis leads to the result that at low
concentrations the equivalent conductance should vary linearly with con-
centration. The osmotic pressure studies of van't Hoff (16) seemed to
support the Arrhenius theory. In addition, Ostwald was able to show that
the conductance data of many systems obeyed his famous dilution law (17)
which was derived from the hypothesis of Arrhenius. This law is still
obeyed with weak electrolytes. However, the conductance work of
Kohlrausch and his co-workers on strong electrolytes led Kohlrausch to
conclude that at low concentrations the equivalent conductance of electro-
lytes were linear with either the square or cube root of concentration,
rather than being linear with concentration as predicted by the Arrhenius
theory. As time passed, x-ray diffraction studies on salts showed that
the crystals were composed of ions rather than neutral molecules. This
result, among other considerations, indicated that strong electrolytes such

as sodium chloride were completely dissociated into ions in dilute aqueous solutions. Sutherland (18), Noyes (19), and Bjerrum (20) were among those who adopted this point of view. About this time, several people attempted to develop a mathematical theory of electrolytic solutions. Notable among these was the work of Milner (21) whose theory was based on the hypothesis that the salt was completely dissociated into ions and that the deviations from ideal solution behavior were due to electrostatic inter- actions between the ions. Unfortunately, Milner's theory depended on the numerical evaluation of a slowly converging series which could not be put into a compact form. The highlight in the development of the modern theory of electrolytic solutions came in 1923 when Debye and Hückel published their theory (22). Although Debye and Hückel used essentially the same hypothesis as did Milner, they introduced the concept of an ionic "atmos- phere". This new concept plus the use of the Poisson equation made it possible to derive a compact mathematical expression which enabled them to calculate the limiting laws for various thermodynamic properties of dilute electrolytic solutions. According to the Debye-Hückel theory in its simplest form, the mean rational activity coefficient is given by

$$\ln (f_\pm) = -\frac{1}{\nu} \sum_{i=1}^{p} \nu_i z_i^2 \left[\frac{\pi N \epsilon^6}{1000 (kDT)^3} \right]^{1/2} \cdot S^{1/2}, \qquad (2.27)$$

where ν is the total number of moles of ions formed by the dissociation of one mole of the salt present in the solution, ν_i is the number of moles of ions of kind "i" formed by the above dissociation, z_i is the charge on the ion of kind "i", N is Avogadro"s number, ϵ is the electronic charge, k is Boltzmann's constant, D is the dielectric constant of the solvent, and

$$S = \sum_{i=1}^{s} c_i z_i^2$$

in which c_i is the concentration of the ith kind of ion in moles per liter. The quantity "S" is sometimes called the ionic strength of the solution, and was defined empirically by Lewis and Randall (23) in 1921, two years before the advent of the Debye-Hückel theory.

Since the introduction of the Debye-Hückel (22) theory, several attempts have been made to extend the theory to higher concentrations. Notable among these attempts was Bjerrum's theory of ionic association (24) in which Bjerrum introduced the ionic pair concept. Also, Onsager and Fuoss made improvements on the theory in the area of conductance (25). Other than minor improvements in the theory, no real advances have been made since that time. One of the attempts to attack the problem from another viewpoint is the cluster theory approach by Mayer (26). At present, it can probably be said that the theory of electrolytic solutions as expressed by the Debye-Hückel theory is accepted as being correct for very dilute solutions. However, the state of affiars in very concentrated solutions is far from being understood. For this reason, one can probablv expect to see a great deal of work being done in the future on concentrated solutions extending into the fused salt range over wide ranges of temperature. It would seem that an attack on solution theory from this point of view is in order, and for this reason, extensive experimental data over wide ranges of concentration and temperature are needed to help establish new theories of electrolytic solutions and to test any such theories which are proposed.

III. EXPERIMENTAL APPARATUS AND PROCEDURES

A. Preparation of Materials

1. Mercury

The mercury used during this research was obtained from the special materials group of the Ames Laboratory of the Atomic Energy Commission. The purification scheme which they used is given below:

a. The mercury was filtered through a 25 pound capacity gold adhesion principle filter which removed exterior impurities such as acids, dirt, oxides, and oil. Mercury from this filter was then run through a nitric acid tower which removed the more easily oxidizable impurities.

b. Next, 25 pound batches of the mercury were oxidized in a motor-driven oxifier for two or more hours. In this oxifier, the mercury was agitated in such a manner as to produce a thick spray, and in this way, air was carried into the body of the mercury and the skin formations of the mercury were broken up, releasing the microscopic particles of mercury which they had entrapped. With this treatment, all elements except the noble metals were effectively removed.

c. Mercury from the oxifier was filtered through another 25 pound gold adhesion principle filter, and then passed through a second nitric acid tower.

d. Finally, the mercury was distilled with a vacuum still. Impurities remaining in the still have been analyzed, and they were found to be the noble metals, silver, gold, palladium, etc., in that order.

e. The distilled mercury was then placed in clean Pyrex bottles which had been dried by heating.

Mercury purified according to the above scheme has been used success-
fully in polarographs for several years.

As an added precaution, the mercury used in this research was pinholed
immediately before using. A separatory funnel containing a piece of
filter paper with a number of pinholes placed directly above the holes in
the separatory funnel was used to pinhole the mercury. Particular care was
exercised to keep dust or grease from contacting the mercury after it was
pinholed. Mercury left in the separatory funnel after pinholing was
discarded. Also, the top portion of the pinholed mercury was discarded to
prevent any surface contamination.

According to the investigations of Lawrence (27), Hildebrand (28), and
Hulett (29), the method of mercury purification used in this research
should yield mercury of high purity.

2. Water

The water used in this research to prepare solutions, and also the
water on which density measurements were made, was purified according to
the following scheme:

a. Condensed steam from high pressure steam lines was passed through
an ion exchanger and then piped into the laboratory as tap distilled water.

b. This tap distilled water was then triply distilled with a tin
lined Barnsted still. The first distillation was from alkaline permanganate.
After the third distillation, the conductance water entered a tin lined
tank which was protected from the air with a carbon dioxide and dust
filter. The conductance of the water from this tank was approximately 5 x
10^{-7} mho. The conductance of the water on which density determinations were

made was checked following the density measurements and was found to be 7×10^{-7} mho. However, following the density determinations the water came into contact with air, and hence, the conductance may have increased somewhat due to the absorption of carbon dioxide from the air.

3. Rare-earth chloride solutions

One stock solution each of lanthanum chloride and neodymium chloride was prepared. All other lanthanum and neodymium chloride solutions were prepared by dilution of the corresponding stock solution with conductance water. For the purpose of preparing the stock solutions, approximately two kilograms each of lanthanum oxide and neodymium oxide were obtained from the rare-earth separation group of the Ames Laboratory of the Atomic Energy Commission. These oxides were analyzed for the presence of certain impurities by emission spectrography. A summary of the analytic results is given in Table 1.

Preparation of a rare-earth chloride stock solution consisted of dissolving a slight excess of the oxide in warm hydrochloric acid. The hydrochloric acid used was the middle one-third portion of the distillate from reagent grade hydrochloric acid which had been diluted to the approximate constant boiling composition with conductance water before distillation. The excess oxide was removed from the solution by filtration. The solution was again heated and a sufficient amount of the distilled hydrochloric acid was added to the solution to destroy most of the basic rare-earth colloid in the solution. Several 25 milliliter aliquots were then taken from the solution. Half of these were titrated with 0.05 N hydrochloric acid. The rest were first acidified with 1 N hydrochloric

Table 1. Spectrographic analyses of lanthanum and neodymium oxides

Element analyzed for	Lanthanum oxide	Neodymium oxide
Cu	very faint trace	possible trace
Ca	less than 0.03%[a]	much less than 0.05%
Fe	not detected	not detected
La	not analyzed	not detected
Ce	less than 0.03%	not detected
Pr	less than 0.03%	less than 0.08%
Nd	less than 0.02%	not analyzed
Sm	not analyzed	less than 0.06%

[a]The percentages reported as "less than" are the lower limits of the analyses. The actual amount of impurity could therefore be much less than the amount indicated.

acid and then back titrated with 0.05 N sodium hydroxide. In both cases, the titrations were followed with a Sargent Model D Recording Titrator using a glass pH indicating electrode and a calomel reference electrode. From the resulting pH versus milliliter plots, the equivalence point of the solution was determined. The results of these pH titrations are given in Table 2.

The stock solution was then titrated to its equivalence pH with 6 N distilled hydrochloric acid. Following this titration, the solution was heated for several hours, allowed to cool, and the volume of the solution was adjusted to its volume before heating by the addition of conductance water. Due to the reaction of the hydrochloric acid with basic species in

Table 2. Equivalence point determination of lanthanum and neodymium
chloride stock solutions

Titrant	Equivalence pH for lanthanum chloride	Equivalence pH for neodymium chloride
HCl	2.48	1.97
HCl	2.49	1.95
NaOH	2.49	1.95
NaOH	2.50	1.96

the solution, the pH usually rises during the heating period. The pH was
again adjusted, and the solution was again heated. This procedure was
repeated until the pH no longer rose during the heating period. The
solution was then filtered through a sintered glass funnel and placed in a
tightly stoppered Pyrex flask.

Before analyzing the lanthanum chloride and neodymium chloride stock
solutions, their equivalence points were redetermined. In both cases, the
results confirmed the earlier determinations. As the pH's of the stock
solutions had, however, risen slightly during standing, a final pH adjust-
ment was made on each with distilled hydrochloric acid. There was little,
if any, Tyndall cone effect formed by shining a small beam of light through
the solutions, indicating that the amount of colloid present in each
solution was extremely small.

An oxide analysis for the rare-earth content was carried out on each
rare-earth chloride stock solution. Three weighed samples of each solution

were placed in porcelain crucibles, and a ten per cent excess of a saturated solution of twice recrystallized oxalic acid was added to each crucible to precipitate the rare-earth ion as the oxalate. Infrared lamps were then used to evaporate the water from the crucibles, and ignition of the rare-earth oxalate to the oxide was carried out in a muffle furnace at 900° C. The amount of oxide formed was determined by weight.

A chloride analysis was also carried out on each rare-earth chloride stock solution. These analyses were carried out potentiometrically with a previously standardized silver nitrate solution as the titrant. The electrode system used was a silver indicating electrode and a sleeve type calomel electrode in which ammonium nitrate was used in the outer sleeve.

In addition, a sulfate analysis was carried out on the lanthanum chloride stock solution. A ten per cent excess of three molar sulfuric acid was added to porcelain crucibles containing previously weighed samples of the stock solution. These samples were then allowed to evaporate to crystals very slowly, and were finally dried with infrared lamps. The excess sulfuric acid was driven off as sulfur trioxide by heating with a Meeker burner, and the samples were ignited in a muffle furnace at 700° C. The amount of lanthanum sulfate was determined by weight.

All of the analyses described above are capable of about 0.05% precision. The results of the analyses are given in Table 3.

Table 3. Analyses of lanthanum chloride and neodymium chloride stock solutions

Type of analysis	Mean molality for lanthanum chloride	Mean molality for neodymium chloride
oxide	3.3891 molal	3.4246 molal
chloride	3.3834 molal	3.4222 molal
sulfate	3.3853 molal	————————

B. Apparatus and Procedures

The determination of densities of liquids and solutions is an old problem. Hence, one should not be surprised to find numerous experimental methods available. Bauer and Lewin (30) describe a number of methods which have been used, the relative precision and accuracy of the methods, and the general problems involved in the determination of densities of liquids and solutions. Pycnometric, buoyancy, and dilatometric methods are the three general methods most commonly used.

Pycnometric methods are usually used for a liquid or a solution of constant composition at a single temperature. These methods are capable of determining densities accurately to about five parts per million.

Buoyancy methods are capable of accuracy to one part per ten million or better. Hence, they are particularly valuable for comparisons of liquids or solutions exhibiting small changes in densities as are found with very dilute solutions, variances in isotopic composition, etc. Great ingenuity can be exercised with the buoyancy method. For example, the

magnetic float method as introduced by Lamb and Lee (31) has proven to be very valuable for very precise density determinations.

Dilatometric methods are used primarily in determining changes in density caused by a slow reaction or by a change in temperature. They are capable of accuracy to about one part in one million or better.

Since this research was concerned with changes in density with temperature, and since an accuracy of at least a few parts per million was desired, a dilatometric method was the most logical one to use.

The experimental apparatus and procedures to be used had to satisfy the following criteria:

1. The method must be capable of determining changes in density with temperature with an accuracy of a few parts per million over a temperature range of 20 to 80° C.

2. The temperature must be controlled and measured with an accuracy of ± 0.001° C.

3. The water and solutions must be kept air-free during the density determinations.

4. The concentrations of the air-free solutions must be known to 0.1%.

5. The change in volume of the dilatometer containing the water or solution with temperature must be known.

6. It would be desirable to know the absolute density of the solutions to a few parts per one hundred thousand.

7. Since a considerable number of concentrations must be examined at a number of temperatures, the method must be as efficient as possible.

Descriptions of dilatometric apparatus which are capable of accurately measuring the change in density of a liquid or solution with temperature have been given by Gibson and Loeffler (32); Geffcken, Kruis, and Solana (33); Jones, Taylor, and Vogel (34); and Owen, White, and Smith (35), among others.

In the apparatus described by Jones, et al. (34), the dilatometer served as a mercury temperature regulator in addition to measuring the density changes. They claimed that their apparatus was capable of determining volume changes with an accuracy of $\pm 3 \times 10^{-4}$ cubic centimeters. Since their dilatometer had a volume of about 275 cubic centimeters, this meant that they could accurately determine changes in density to about two parts per million. The primary objection to their method as applied to this research was one of efficiency.

With certain modifications, the dilatometer described by Owen, et al. (35) was the one adopted as a basis for this research. With their apparatus, they claimed to be able to determine changes in volume with an accuracy of $\pm 1 \times 10^{-4}$ milliliters. Furthermore, they used ten dilatometers simultaneously which gave this method considerable experimental efficiency.

For this research, ten dilatometers were constructed from Pyrex glass by the glass shop in accordance with the diagram given in Figure 1. In this diagram, the male standard tapers A, G, and F were sizes 10/30, 14/20, and 29/42, respectively. The 29/42 taper was shortened with an ordinary glass saw. The capillary arm, D, was approximately 0.7 millimeter I.D. capillary tubing, and the Pyrex tubing connecting D with G was ten millimeter
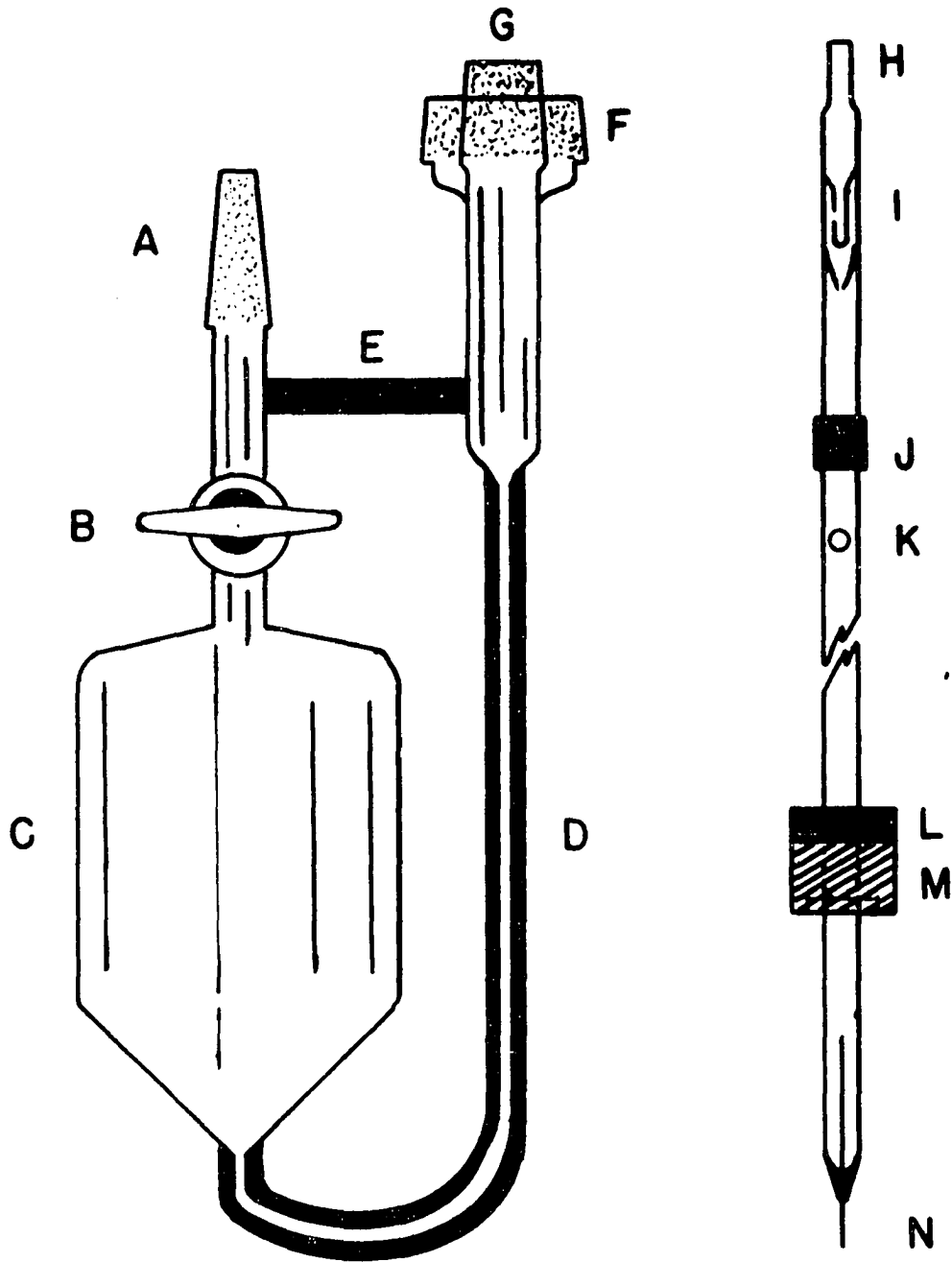
Figure 1. Dilatometer and withdrawal pipette

Pyrex tubing. The body of the dilatometer, C, was constructed from 56 millimeter Pyrex tubing and had a volume of about 130 milliliters. The side arm brace, E, of the dilatometer was four millimeter solid Pyrex rod, and the stopcock, B, was a two millimeter straight bore Pyrex stopcock. Out of an assortment of approximately one hundred stopcocks, ten shell and plug combinations were picked which showed good mating and were vacuum tight. In order to insure good mating and vacuum tightness, each of the ten combinations were mated together with a fine glass grinding compound. These shell and plug combinations were marked so that each plug was always used with the proper shell.

In cleaning the dilatometers, the excess Dow-Corning high vacuum stopcock grease was first wiped from the exterior parts of the dilatometers. Then the dilatometers were cleaned with 6 N nitric acid which reacts with and dissolves any mercury droplets remaining in the dilatometers. Next, the dilatometers were rinsed with tap distilled water, kerosene, acetone, and tap distilled water in the order given. They were then filled with chromic acid cleaning solution and completely submerged in the same cleaning solution. The cleaning solution containing the dilatometers was heated for several hours, and after cooling, the dilatometers were rinsed twice with tap distilled water and filled a third time with tap distilled water. This tap distilled water was allowed to remain in the dilatometers for one day, at which time they were rinsed twice with conductance water and twice with acetone in this order. Finally, the dilatometers were dried by using a water aspirator to pull clean, dry air through each dilatometer for a period of fifteen minutes.

Mercury was added to the dilatometer through the standard taper, G. Care was taken to insure that there were no air bubbles formed at the mercury-glass interface.

The addition of water or solution to a dilatometer was more complex than was the case with mercury since not only must the problem of air bubble formation be considered, but the water or solution must be kept air-free. The apparatus and method used in adding water or solution to a dilatometer was essentially the same as that used by Jones, et al. (34). The filling apparatus is described in Figure 2, and the following procedure was followed.

In the filling apparatus, A was attached to a vacuum pump, B was open to the atmosphere, C was a thermocouple vacuum gauge, D was a cold trap, E was a degassing burette, and M was a drying tube filled with anhydrous magnesium perchlorate. The stopcocks at B, K, L, and those attached to the cold trap were three-way stopcocks, whereas H, I, J, N, and P were two-way stopcocks. The shaded tubing was vacuum rubber tubing.

First, a clean, dry degassing burette was attached to the apparatus at J with the stopcock, N, open. The burette was sealed off with a piece of sealed glass tubing at the ball joint, O. The burette was then evacuated and the stopcock, N, was closed. In this manner, the bore of the stopcock, N, was evacuated.

Then the degassing burette was removed, and about 200 milliliters of water or solution were added to it. The burette was again attached to the system as shown in Figure 2 with the stopcocks K and L turned in such a
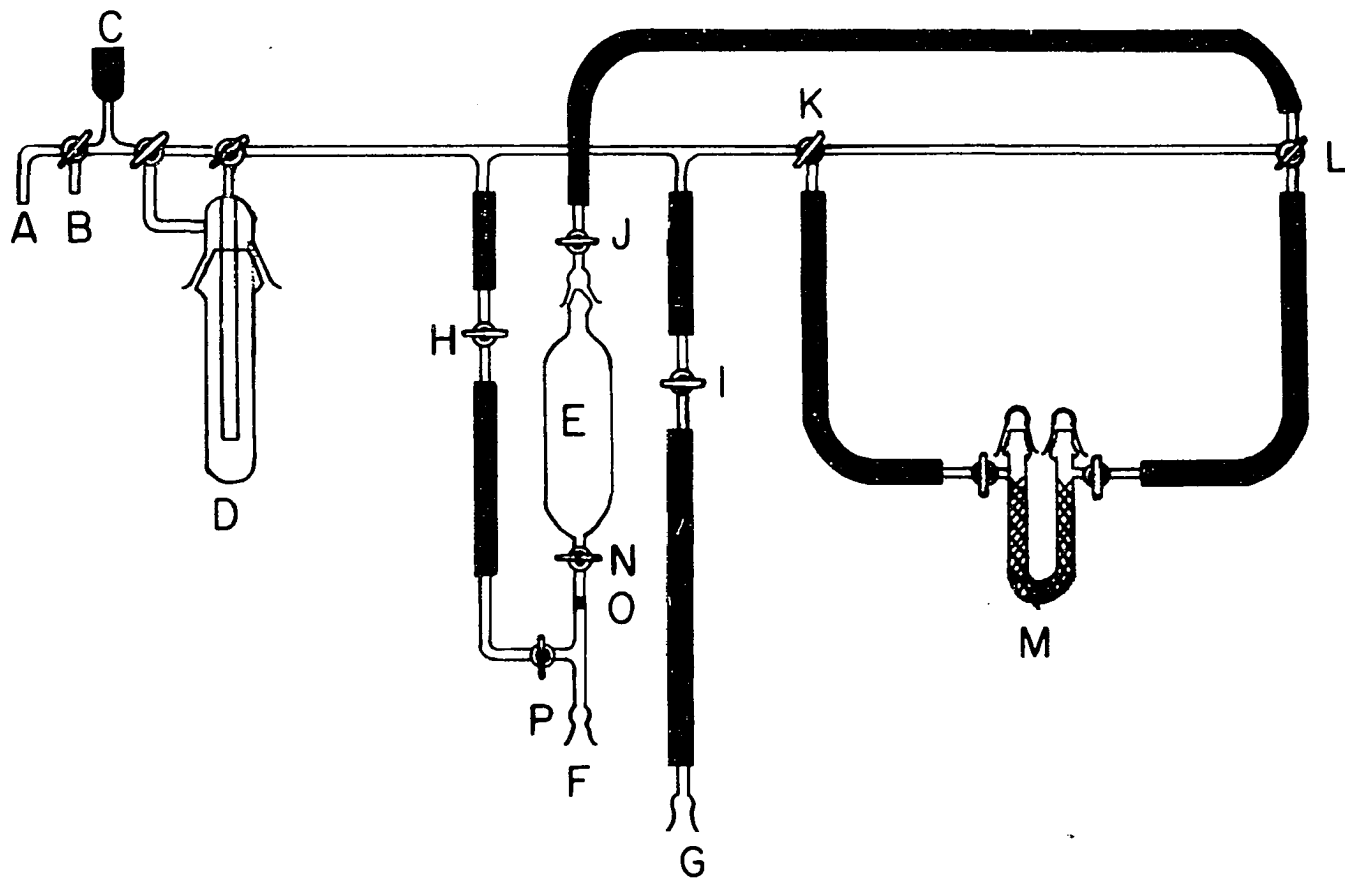
Figure 2. Vacuum apparatus for adding water or solutions to the dilatometers

manner that the water vapor driven off during the degassing process passed through M. A vacuum was then pulled on the water or solution until the liquid no longer bubbled. At this point, the stopcock J was closed so that the water or solution could be kept air free.

Next, the standard tapers F and G were attached, respectively, to the tapers A and G of the dilatometer to which about 25 milliliters of mercury had previously been added. Dow-Corning high vacuum stopcock grease was used on the taper, A, of the dilatometer, but a greaseless vacuum seal at G was made by adding mercury to the well around the taper, G, of the dilatometer formed by the Taper, F. The stopcock, B, of the dilatometer, and the stopcocks H, I, and P of the filling apparatus were opened. With K closed, the dilatometer was then evacuated to about ten microns or better. P and I were then closed and N was opened. The vapor pressure of the water or solution plus the force of gravity caused the liquid to enter the evacuated dilatometer. Due to the vapor pressure of the water or solution formed in the dilatometer during filling, a small amount of atmospheric pressure had to be introduced into the degassing burette at J to complete the filling of the dilatometer. When enough water or solution had been added to the dilatometer, the stopcock B of the dilatometer was closed and the filling was complete.

Since the weights of mercury and water or solution added to the dilatometers had to be known, it was necessary to weigh the empty dilatometers, the dilatometers containing mercury, and the dilatometers containing mercury and water of solution. These weighings were made with a Model B-5 Mettler balance. This is a single pan balance which has a

total capacity of 1000 grams and a sensitivity of 0.1 milligram. The
weights of mercury and water were corrected to vacuum and were known to a
few tenths of a milligram. During the calibration runs with mercury, the
dilatometers were completely filled with mercury and weighed about two
kilograms. A large two pan solution balance with a capacity of two kilograms
and a sensitivity of 0.2 milligrams was used to weigh the dilatometers
filled with mercury. The weight of mercury was corrected to vacuum and
was known to a few milligrams.

The constant temperature bath used in this research was similar to
the one described by Owen, et al. (35). A diagram of the bath is given in
Figure 3, and a description of it is given below.

The outer bath, A, was 30 inches x 30 inches x 30 inches, and was filled
with tap distilled water. The copper inner bath, B, was 15 inches wide,
18 inches long, and 16 inches deep, and was filled to a depth of about 10
inches with tap distilled water. F and F' in the diagram indicate brass
trays in the inner bath which held the ten dilatometers, five to a side.
Actually, each tray section was composed of two trays, one on top of the
other, in which there were holes into which the dilatometers were placed.
C and C' in the inner bath were stirrers, and D was a platinum resistance
thermometer used in measuring the temperature of the inner bath. The outer
bath was stirred with the centrifugal pump, J. During a run, only the
temperature of the outer bath was controlled. A thermistor having a
resistance of 100,000 ohms at 25° C and a change in resistance per degree
Centigrade of four per cent of the total resistance was used as one arm
of a Wheatstone bridge. One of the other arms of this bridge was composed
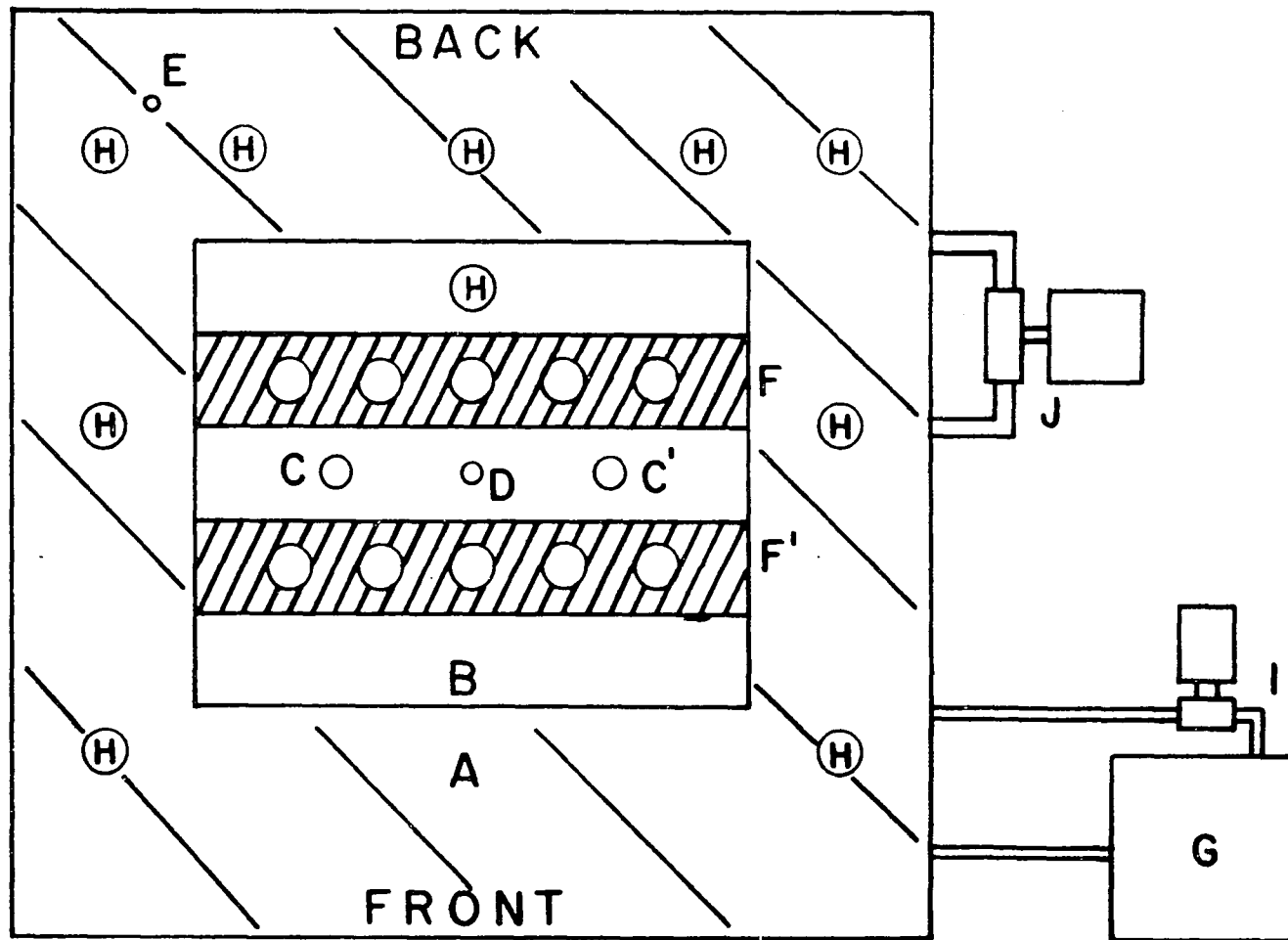
Figure 3. Constant temperature bath apparatus

of variable resistances. By adjusting these variable resistances, it was possible to balance the bridge at any temperature between 20 and 80° C. Two six volt dry cell batteries were used as a voltage source for the bridge, and the signal controlled a thyratron tube which in turn controlled certain heaters in the outer bath through a magnetic relay. There were nine heaters in the outer bath and one in the inner bath. These heaters were all labeled H in Figure 3. A 100 watt, a 300 watt, and a 500 watt heater, all in the outer bath, could be used as control heaters in any combination desired. All of the other heaters could be used only as continuous heating elements, and were used to raise the temperature of the inner and outer baths and for continuous heating when the outer bath was being controlled at the higher temperatures. Below 30° C, cold tap water was continuously passed through copper coils in the outer bath during the periods of temperature control. Above 30° C, a constant temperature bath, G, kept about 3° C below the temperature of the outer bath was used as a cooling source. Water from this auxilliary bath was circulated through the copper coils mentioned above with a small centrifugal pump, I. The temperature of the outer bath was controlled in this manner to ± 0.01° C. In order to prevent any temperature cycling from being conducted into the inner bath, 1/2 inch transite board was used to insulate the inner bath from the outer. The tops of both baths were covered with 1/2 inch plywood, and wool strips were placed on the plywood above the inner bath for added insulation. With the above method of temperature control, it was found possible to hold the temperature of the inner bath constant to 0.001° C for a period of one-half hour or longer over the entire temperature range of 20

to 80° C. The temperature of the inner bath was measured with a Leeds and Northrup platinum resistance thermometer which had been calibrated by the National Bureau of Standards. Ice point readings made with this thermometer have been reproducible over the past two years. The resistance of the platinum resistance thermometer was measured with a Model G-2 Leeds and Northrup Mueller Bridge. With this method, it was possible to accurately determine the temperature of the inner bath to 0.001° C over the entire experimental temperature range.

After the dilatometers had been filled and weighed, they were placed in the inner constant temperature bath. Withdrawals of mercury were made from these dilatometers at regular temperature intervals from 20 to 80° C. When calibrating with mercury, temperature intervals of seven degrees Centigrade were used, whereas with water and solutions, temperature intervals of five degrees Centigrade were used. At each withdrawal temperature, the temperature of the inner bath was adjusted to within 0.1° C of the temperature at which the outer bath was controlling. Following this temperature adjustment, about five hours were required for the temperature of the inner bath to become constant.

The withdrawals of mercury from the dilatometers were made with ten withdrawal pipettes, one constructed specifically for each dilatometer. A diagram of such a withdrawal pipette is given in Figure 1. M was a cylindrical piece of plexiglass glued firmly to a cylindrical ring of hard rubber, J, and to the seven millimeter glass tubing of the pipette. The dotted line at the bottom of the cylindrical plexiglass ring indicates a

circular indentation which was cut into the bottom of the ring. This circular indentation was designed to fit over the male standard taper, G, of the dilatometer. By introducing the withdrawal pipette into the side arm of the dilatometer until the plexiglass ring was firmly seated on the standard taper, G, of the dilatometer, the depth to which the pipette penetrated could be reproduced. N was a piece of 0.5 millimeter O.D. stainless steel tubing which just barely entered the capillary tubing of the dilatometer when M of the pipette was fitted over G of dilatometer. K was a hole blown out of the pipette glass tubing for the purpose of removing mercury from the pipette. During a withdrawal, K was closed with a length of tightly fitting rubber tubing, J. The design of the weight pipette at I was necessary to prevent mercury from escaping from the pipette during a withdrawal. The total length of the pipette was about 12 inches. In making a withdrawal, H of the pipette was attached to a vacuum system in which the pressure was 211 ± 2 millimeters of mercury less than the atmospheric pressure. This pressure drop was sufficient to cause the mercury in the dilatometer side arm to be forced into the withdrawal pipette until the level of the mercury fell below that of the stainless steel tubing, N, of the pipette. The vacuum system used consisted of a vacuum pump, two 40 liter Pyrex bottles in series, and a mercury manometer. With the two large Pyrex bottles, it was possible to withdraw from all dilatometers successively without raising the reduced pressure by more than 4 millimeters of mercury. With this withdrawal system, it was possible to reproduce the mercury levels in the capillary tubing of the dilatometers to about ± 1 x 10^{-4} milliliter.

At the higher temperatures, it was found that during a withdrawal, some of the air above the surface of the water in the inner bath was drawn into the withdrawal pipettes. Since this air was saturated with water vapor at a temperature above room temperature, water condensed in the withdrawal pipettes. In order to prevent this, Pyrex glass tubes with 29/42 female standard tapers at one end, and large enough in diameter to accept the withdrawal pipettes, were attached to the corresponding 29/42 male standard tapers of the dilatometers. Through holes cut into the top of the inner bath, these tubes extended to about one inch above the top of the inner bath. The tubes were left in place throughout the entire run, and between withdrawals they were covered to prevent the entry of dust into the dilatometer side arm.

Occasionally, a droplet of mercury would remain in the sidearm of a dilatometer following a withdrawal. With the aid of a pencil flashlight, visual checks of these occurrences could be made. It was found that the droplet of mercury left behind could be pushed into the mouth of the capillary tubing with a length of stainless steel tubing, and by making another withdrawal, the mercury could be removed in most cases. As a matter of course, the above procedure was followed with all dilatometers following the main withdrawal, regardless of whether or not the presence of mercury droplets in the dilatometer sidearm was visually confirmed. Using this procedure, the number of incomplete withdrawals during a run were very few.

The amount of mercury withdrawn from each dilatometer at each withdrawal temperature was determined by weight. The withdrawal pipettes were weighed using an ordinary analytical chainomatic balance which had a

capacity of 200 grams and a sensitivity of 0.1 milligram. For added efficiency, the balance was magnetically damped. A tare was used in weighing the weight pipettes in order to minimize the errors caused by surface effects and changes in the density of air. The weights used were calibrated according to the method of Richards (36), except that the transposition method rather than the substitution method was used (37). The weight in vacuum of mercury withdrawn could be accurately determined to about 0.1 milligram.

One of the difficulties encountered in this research was the large number of calculations which had to be made. Also, it was desirable to fit the data to a number of higher order polynomial equations using the method of least squares. For these reasons, most of the calculations described in the following chapters were carried out with a 7074 IBM computer. A computer program for fitting polynomial equations to experimental data according to the method of least squares was obtained from the computer services group of the Ames Laboratory of the Atomic Energy Commission. Other programs used were written specifically for the problem at hand.

IV. CALIBRATION OF DILATOMETERS

A. Introduction

The determination of the change in density of water or a solution with temperature requires that the change in volume of the dilatometer with temperature requires that the change in volume of the dilatometer with temperature be known. Also, the weight of mercury, water, or solution in the stopcock plug bore of the dilatometer must be known since this liquid does not contribute to the expansion of the liquid in the body of the dilatometer with an increase in temperature, but constitutes part of the weight of the liquid added to the dilatometer. The determination of the volume of each dilatometer as a function of temperature and the determination of the volume of the stopcock plug bore of each dilatometer at room temperature constitute what is called the calibration of the dilatometer.

The volume of a glass vessel can be determined from the weight of a liquid of known density required to fill the vessel. Water and mercury are often used since they are liquids at room temperature; they can be obtained in high purity; and their densities, at least at room temperature, are known with considerable accuracy.

The most widely accepted densities of water from 0 to 40° C are those determined by Chappuis (38) and Thiesen, Scheel, and Diesselhorst (39). The density values of Chappuis are generally accepted as a standard in this country and by the International Bureau of Weights and Measures. Furthermore, the density values of Chappuis are represented in units of grams per milliliter by the Tilton and Taylor equation (40) given by

$$1 - d = \frac{(t - 3.9863)^2}{508929.2} + \frac{t + 288.9414}{t + 68.12963}. \qquad (4.1)$$

This equation represents the Chappuis data to about one part per million over the temperature range of 0 to 42° C, and shall be used in this research to provide density values for water up to 40° C.

The density values of mercury used in this research were determined by Beattie, et al. (41). They used vitreous silica bulbs and determined densities of mercury over the temperature range of 0 to 350° C. In 1956, Cook (42) reviewed the various measurements of the expansion of mercury with temperature, and he concluded that the density data of Beattie, et al. were the best available at that time.

The density values of mercury in units of grams per milliliter according to the expansion data of Beattie, et al. can be represented to one part in the fifth decimal place by the equation

$$d = 13.59546/(1 + at + bt^2 + ct^3 + dt^4) \qquad (4.2)$$

in which

$a = 1.814401 \times 10^{-4}$,

$b = 7.016 \times 10^{-9}$,

$c = 2.8625 \times 10^{-11}$, and

$d = 2.617 \times 10^{-14}$.

B. Calibration of Stopcock Plug Bores

The volume of each stopcock plug bore was determined from the weight of mercury required to fill the plug bore at room temperature. The mean of three or four such determinations for each dilatometer and the mean

absolute deviations of these determinations from their mean are given in Table 4. It will be noticed that the data for dilatometer number VII is missing. The stopcock shell and plug combination of this dilatometer was found to be faulty, and therefore only nine dilatometers could be used.

Table 4. Calibration of the stopcock plug bores of the dilatometers at room temperature

Dilatometer number	Mean volume (ml)	Mean absolute deviation x 10^4 (ml)
I	0.0520	2.7
II	0.0442	0.2
III	0.0358	0.4
IV	0.0460	1.9
V	0.0481	0.7
VI	0.0444	1.3
VIII	0.0503	0.8
IX	0.0478	0.9
X	0.0531	1.7

C. Calibration of Dilatometers with Mercury

Two calibration runs were made with mercury over the temperature range of 20 to 80° C. The first calibration run with mercury was made prior to any runs on water or solutions, and the second run was made following the

runs on water and solutions. There were no significant differences between the results of these two runs, indicating that the expansion of the dilatometers with temperature remained the same during this research.

In order to obtain equations representing the volume of the dilatometers as a function of temperature, the temperature of each withdrawal, the mean withdrawal temperature for each temperature interval, and the change in volume of each dilatometer per degree Centigrade for each temperature interval were calculated. The volumes of the dilatometers at the various temperatures were calculated from the weights of mercury in the dilatometers at these temperatures and the corresponding densities of mercury as calculated from Equation 4.2. The method of determining these weights of mercury was described in the previous chapter.

The withdrawal temperatures were calculated from the measured resistances of the platinum resistance thermometer at the various temperatures by carrying out successive approximations on the equation

$$t = \frac{R_t - 25.56602}{0.10035209} + 0.0149154\, t\, (0.01t - 1) \tag{4.3}$$

in which t is the temperature in degrees Centigrade, and R_t is the measured resistance. The form of Equation 4.3 is given in the National Bureau of Standards circular accompanying the platinum resistance thermometer, and the constants in this equation obtained from a National Bureau of Standards calibration of the platinum resistance thermometer together with an ice point calibration performed in this laboratory. For each temperature interval, the mean temperature of the interval, t_{avg}, and the change in

volume of each dilatometer divided by the total temperature change of the interval, $\Delta V/\Delta t$, were calculated.

The resulting withdrawal temperatures and values of t_{avg} and $\Delta V/\Delta t$ for dilatometer number III obtained from the two calibration runs on mercury are given in Table 5. These data are representative of those obtained from the other dilatometers, being no better than the data from some of the other dilatometers and not much better than that of the remainder of the dilatometers. It will be noticed that the $\Delta V/\Delta t$ values, particularly for the first run, are somewhat erratic. This is due to small droplets of mercury which were not removed during the withdrawal. Fortunately, such an occurrence, which yields a high value of $\Delta V/\Delta t$, is almost always corrected during the next withdrawal which in turn yields a low value for $\Delta V/\Delta t$. In this way, the inconsistencies cancel each other to a considerable extent.

As is shown in Figure 4, the $\Delta V/\Delta t$ values are linear with respect to t_{avg}. For each dilatometer an empirical equation of the form

$$\Delta V/\Delta t = a + b\, t_{avg} \qquad (4.4)$$

was obtained by the method of least squares. Since it is found that second order polynomials satisfactorily represent the volumes of the dilatometers as functions of temperature, Equation 4.4 can be replaced by

$$dV/dt = a + bt \qquad (4.5)$$

where the parameters a and b have the same values for each dilatometer in Equation 4.5 as they did in Equation 4.4. This equivalence of equations is a consequence of the familiar law of the mean of calculus. Carrying out the

Table 5. Mercury calibration data for dilatometer number III

Run number 1			Run number 2		
Withdrawal temperature (°C)	Mean withdrawal temperature (°C)	$(\Delta V/\Delta t) \times 10^4$ (ml/deg)	Withdrawal temperature (°C)	Mean withdrawal temperature (°C)	$(\Delta V/\Delta t) \times 10^4$ (ml/deg)
19.082			19.341		
	22.058	12.8		22.723	12.8
25.035			26.105		
	28.564	13.3		29.573	12.9
32.092			33.041		
	35.535	12.7		36.489	13.0
38.979			39.938		
	42.427	13.2		43.366	13.0
45.875			46.795		
	49.295	13.1		50.272	13.1
52.714			53.751		

Table 5 (Continued)

Run number 1			Run number 2		
Withdrawal temperature (°C)	Mean withdrawal temperature (°C)	$(\Delta V/\Delta t) \times 10^4$ (ml/deg)	Withdrawal temperature (°C)	Mean withdrawal temperature (°C)	$(\Delta V/\Delta t) \times 10^4$ (ml/deg)
	56.299	16.5		57.250	13.4
59.885			60.751		
	63.305	9.7		64.274	13.2
66.726			67.797		
	70.036	13.5		71.356	13.6
73.347			74.915		
	76.709	13.0		78.854	12.8
80.071			82.793		
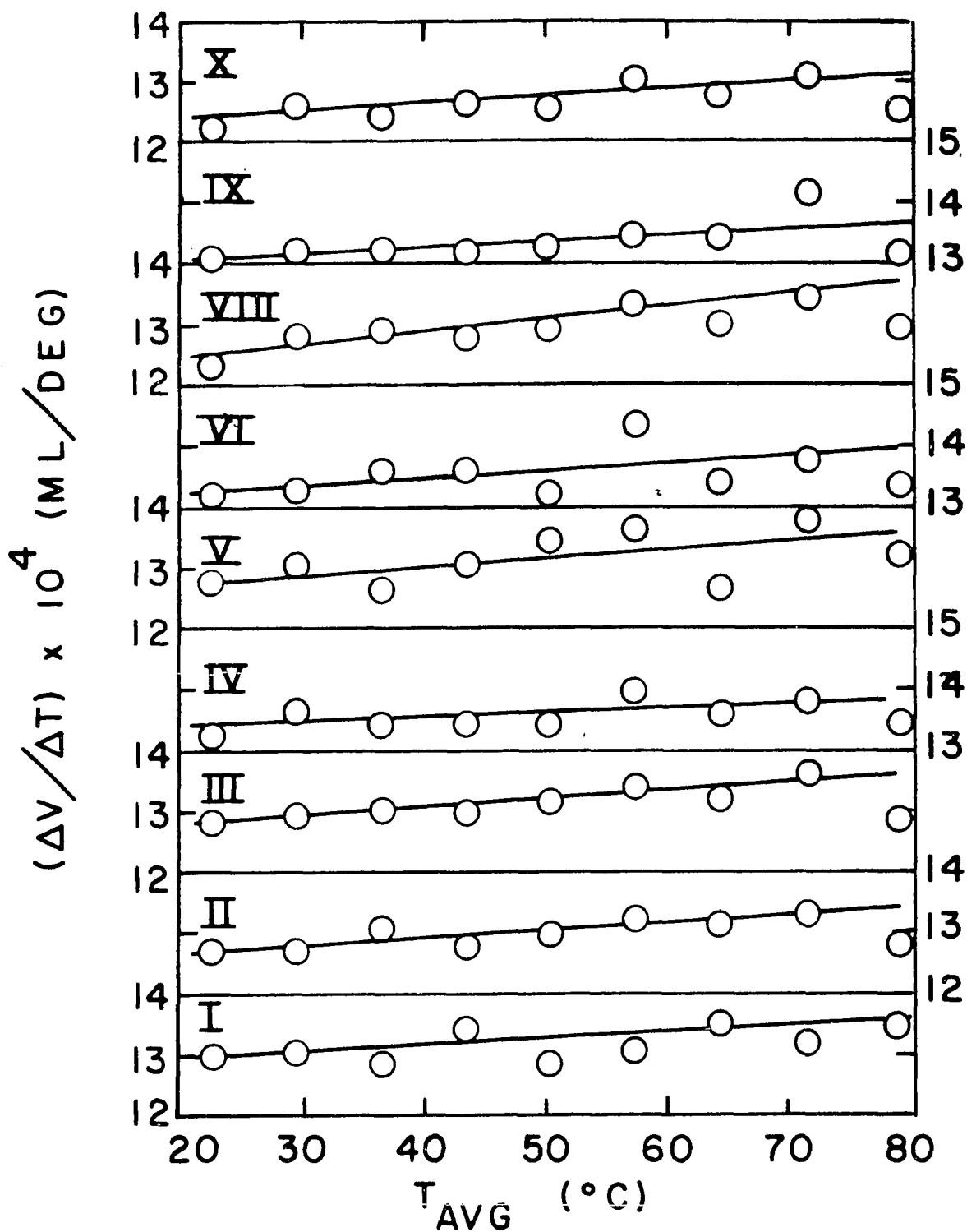
Figure 4. Calibration of dilatometers according to the second run with mercury

integration

$$\int_{V_{25}}^{V} dV = \int_{25}^{t} (a + bt) \, dt, \tag{4.6}$$

the equation

$$V = V_{25} + a \, (t-25) + (1/2)b(t^2-25^2) \tag{4.7}$$

is obtained. Equation 4.7 can be rearranged to give the relationship

$$V = V_{25} + A \, (t-25) + B \, (t-25)^2 \tag{4.8}$$

where $A = a + 25 \, b$ and $B = (1/2)b$. The values of a, b, A, and B for each dilatometer obtained from the calibration of the dilatometers with mercury are given in Table 6. In addition, the volumes of the dilatometers at 25° C were calculated from the experimental data.

D. Calibration of Dilatometers with Water

Two runs were made on water, the first run covering the temperature range of 20 to 60° C and the second run covering the temperature range of 20 to 80° C. The volume of water in each dilatometer was calculated for each withdrawal temperature. This calculation was possible since the volumes of the dilatometers as a function of temperature were known from the calibration of the dilatometers with mercury, and since the weights of mercury in the dilatometers and corresponding densities of mercury were known at each withdrawal temperature.

Due to variations of the atmospheric pressure from one withdrawal to the next, and due to the fact that water is compressible, the above volume

Table 6. Calibration parameters for the dilatometers from the calibration
with mercury

Dilatometer number	$a \times 10^4$ (ml/deg)	$b \times 10^7$ (ml/deg^2)	$A \times 10^4$ (ml/deg)	$B \times 10^7$ (ml/deg^2)
I	12.816	5.86	12.963	2.93
II	12.794	3.97	12.894	1.98
III	13.006	1.79	13.051	0.90
IV	13.182	6.61	13.347	3.30
V	12.630	10.70	12.898	5.35
VI	13.167	7.93	13.365	3.96
VIII	12.492	9.53	12.731	4.77
IX	12.956	6.62	13.122	3.31
X	12.197	10.60	12.462	5.30

changes of water in the dilatometers are affected by the atmospheric pressure
as well as by the temperature. Therefore, a barometric pressure reading
was made at the time of each withdrawal, and the volume changes of the
water in the dilatometers were corrected to what they would have been had
the atmospheric pressure been that of the first withdrawal. In making these
corrections, the definition of the isothermal coefficient of water, β_0,
given by

$$\beta_0 = (-1/V) \cdot (\partial V/\partial P)_T \qquad (4.9)$$

was approximated by

$$\beta_0 = (-1/V) \cdot (\Delta V/\Delta P)_T \qquad (4.10)$$

which is a good approximation since ΔP is small. Values of β_o at 25, 45, 65, and 85° C were computed from the Tait equation (43) given by

$$\beta_o \ V = 0.4343 \ C/(B + P) \tag{4.11}$$

in which the parameters C and B were obtained from Table (8-7-1) given by Harned and Owen (44). Using the above values of β_o, a plot of β_o versus temperature was made, and the values of β_o used in making the pressure corrections were interpolated from this plot for the corresponding withdrawal temperature. In all cases, the pressure corrections of the volumes of water in the dilatometers were no larger than a few one hundred thousandths of a milliliter.

Then, from the volume of water in each dilatometer and the density of water calculated from the Tilton and Taylor equation, the weight of water in each dilatometer was calculated at each withdrawal temperature up to and including 40° C. For each dilatometer, the mean of these calculated weights of water was used as the weight of water in the dilatometer. These mean calculated weights of water were used in preference to the weights obtained by weighing the dilatometers since the latter weights were capable of an accuracy in density of only a few parts in the fifth decimal place, whereas the Tilton and Taylor equation gives densities of water in agreement with the data of Chappuis to one part in the sixth decimal place. The use of the mean calculated weights of water forces the experimental data to agree with the Chappuis data from 20 to 40° C which were assumed to be correct.

Values of $\delta = d - d'$ where d is the experimentally determined density and d' is the Tilton and Taylor density are given in Table 7 for run number

Table 7. First calculation of $\delta \times 10^6$ in units of grams per milliliter for run number two on water

Temperature	Dilatometer number								
(°C)	I	II	III	IV	V	VI	VIII	IX	X
44.798	0.5	1.4	0.3	3.8	2.7	0.5	2.8	3.6	1.4
49.819	1.4	4.7	4.1	7.0	5.8	3.4	6.2	7.1	4.1
54.959	10.8	11.8	11.2	16.5	10.8	11.6	12.4	16.4	11.2
60.043	18.6	21.3	20.9	27.8	21.0	21.8	23.2	27.4	19.7
64.887	32.1	35.2	35.9	41.9	33.0	34.1	37.0	42.7	34.2
69.798	54.7	55.2	56.0	61.8	53.0	53.4	57.0	62.6	52.4
74.829	80.9	79.7	81.1	85.7	73.4	78.5	80.8	87.5	76.1
79.656	107.3	109.6	110.9	114.6	99.7	110.0	109.4	115.8	104.1

two on water. The mean value of δ was computed at each withdrawal temperature for both runs on water. It was found that from 40 to 80° C, the mean δ values could be expressed as a function of temperature by the equation

$$\delta \times 10^6 = 69.4 - 2.317t - 0.004856t^2 + 0.0005047t^3 \qquad (4.12)$$

which was obtained using the method of least squares.

It will be noticed in Table 7 that the δ values obtained from dilatometers IV, V, and IX deviate somewhat from the mean, expecially at the higher temperatures. Small errors in the calibration parameters A and B would cause deviations from the mean which would increase with increasing temperature. Although such deviations do not seriously affect the determination of the density of water, it is desirable that all of the dilatometers be consistent with one another when measurements are made on solutions.

Therefore, values of $\Delta V/\Delta t$ and t_{avg} were calculated for each dilatometer from the water data as was done with the mercury data. For these calculations, densities of water at withdrawal temperatures less than or equal to 40° C were calculated from the Tilton and Taylor equation alone. When the withdrawal temperatures were greater than 40° C, the δ values obtained from Equation 4.9 were added to the densities calculated from the Tilton and Taylor equation.

In addition to the two major runs on water, a run on water was made with dilatometer number IX during one of the solution runs. Values of $\Delta V/\Delta t$ and t_{avg} from this run were included with the corresponding values

for dilatometer number IX obtained from the two major runs on water. From these calibration data on water, new calibration parameters A and B for Equation 4.8 were calculated. These new values of A and B plus the mean values of the parameters A and B and the mean volumes of the dilatometers at 25° C, V_{25}, obtained from the mercury and water data are given in Table 8. These mean values of A, B, and V_{25} were used throughout the remainder of this research.

Table 8. Final calibration parameters for the dilatometers

Dilatometer number	Mean values of V_{25} (ml)	Calibration with water		Mean values of parameters	
		$A \times 10^4$ (ml/deg)	$B \times 10^7$ (ml/deg^2)	$A \times 10^4$ (ml/deg)	$B \times 10^7$ (ml/deg^2)
I	134.375	12.870	4.96	12.916	3.95
II	132.609	12.879	2.86	12.886	2.42
III	133.656	12.992	2.86	13.022	1.88
IV	138.021	13.088	8.72	13.217	6.01
V	134.404	13.051	-0.67	12.974	2.34
VI	138.396	13.251	6.02	13.308	5.00
VIII	132.410	12.851	2.18	12.791	3.47
IX	136.595	13.466	1.26	13.294	2.28
X	128.757	12.624	1.65	12.543	3.48

V. DENSITIES AND COEFFICIENTS OF THERMAL EXPANSION

A. Introduction

A knowledge of the densities of water and solutions at various

temperatures, together with the concentrations of the solutions, is

sufficient for the calculation of several thermodynamic properties. One

such property is the thermal coefficient of cubical expansion or as it

is sometimes called, the coefficient of thermal expansion or the coefficient

of expansibility.

The coefficient of thermal expansion, α, of a liquid or solution may

be defined by

$$\alpha = (1/V) \cdot (\partial V / \partial T)_{P, n_i} \tag{5.1}$$

which is simply the change in volume per degree per unit volume when the

pressure and the number of moles of components are held constant. Making

use of the relationships between density, d, and specific volume, $\bar{v}$, and

between density and the molar concentration, c; Equation 5.1 can also be

written as

$$\alpha = (1/\bar{v}) \cdot (\partial \bar{v} / \partial T)_{P, n_i}, \tag{5.2}$$

$$\alpha = -(1/d) \cdot (\partial d / \partial T)_{P, n_i}, \text{ and} \tag{5.3}$$

$$\alpha = -(1/c) \cdot (\partial c / \partial T)_{P, n_i}. \tag{5.4}$$

B. Water

Using the final calibration parameters for the dilatometers as given in Table 8, densities of water were again calculated from the data of the two runs on water. The differences, δ, between the experimentally determined densities and the densities calculated from the Tilton and Taylor equation are given in Table 9 for the second run on water. The values of δ x 10^6 given in Table 9 can be compared with the results of the first density calculation which were given in Table 7 of the previous chapter. The mean δ values, $\bar{\delta}$, and the mean absolute deviations from these mean values, $|\Delta\delta|$, are given in Table 10 for the first and second density calculations for the second run on water. It is seen in Table 10 that the values of $\bar{\delta}$ are about the same for the second density calculation as they were for the first. However, the mean absolute deviations of the second density calculation are somewhat less than those of the first calculation.

From the results of the second density calculation at temperatures above 40° C, the following empirical equation for δ as a function of temperature was calculated using the method of least squares.

$$\delta \times 10^6 = 67.0 - 2.188\ t - 0.00721\ t^2 + 0.0005182\ t^3. \tag{5.5}$$

The densities of water used in the remainder of this research were calculated from the equation

$$d = d' + \delta \tag{5.6}$$

in which d' is the Tilton and Taylor density as given by Equation 4.1, $\delta = 0$ if $t \le 40°$ C, and δ is calculated from equation 5.5 if $40°$ C $< t \le 80°$ C.

Table 9. Values of $\delta \times 10^6$ for the second run on water

Temperature (°C)	Dilatometer number								
	I	II	III	IV	V	VI	VIII	IX	X
20.040	-2.0	-0.2	-0.6	-2.3	-1.4	0.4	-1.2	-0.2	-1.6
25.032	-4.2	0.2	-0.2	-1.1	0.6	-1.9	-0.1	-0.7	0.2
30.016	3.5	0.6	0.5	0.0	0.9	0.1	0.2	0.1	0.2
34.888	2.0	-0.8	0.1	0.7	-1.2	0.6	-0.1	-0.6	0.5
39.970	0.1	-0.3	-0.1	2.2	0.4	0.3	0.8	0.8	0.4
44.798	0.8	1.4	0.5	4.7	2.5	0.9	2.4	1.6	0.8
49.819	1.7	4.6	4.2	7.9	5.9	3.9	5.7	4.6	3.5
54.959	11.0	11.7	11.3	17.4	11.3	12.1	12.0	13.3	10.9
60.043	18.7	21.1	20.7	28.4	22.0	22.4	22.9	23.9	19.4
64.887	32.2	34.9	35.5	42.2	34.6	34.4	36.8	38.5	34.1
69.798	54.6	54.6	55.4	61.7	55.4	53.6	57.0	58.4	52.6
74.829	80.6	79.0	80.3	85.0	76.7	78.5	81.1	83.1	76.8
79.656	106.8	108.8	109.8	113.4	104.0	109.5	110.0	111.1	105.3

Table 10. Comparison of first and second density calculations for the
second run on water

Temperature	First density calculation		Second density calculations	
(°C)	$\delta \times 10^6$ (g/ml)	$|\Delta\delta| \times 10^6$ (g/ml)	$\delta \times 10^6$ (g/ml)	$|\Delta\delta| \times 10^6$ (g/ml)
20.040	-1.1	0.9	-1.0	0.8
25.032	-0.8	1.0	-0.8	1.1
30.016	0.7	0.8	0.7	0.7
34.88	0.2	0.5	0.1	0.7
39.970	0.6	0.8	0.5	0.5
44.798	1.9	1.2	1.7	1.0
49.819	4.9	1.5	4.7	1.2
54.959	12.5	1.7	12.3	1.3
60.043	22.4	2.5	22.2	2.0
64.887	36.2	2.8	36.0	2.2
69.798	56.2	2.8	55.9	2.1
74.829	80.4	3.1	80.1	2.1
79.656	109.0	3.6	108.8	2.3

The densities calculated from Equation 5.6 agree with the mean experimental

densities to one part per million or better over the temperature range of

20 to 80° C.

Densities of water calculated from Equation 5.6 are compared with

literature values in Table 11. A further comparison of various measurements

of the densities of water at different temperatures, and some empirical

equations which have been derived to describe the change in density of

water with temperature are given by Dorsey (45). The density values

determined in this research and those given in Jones, et al. (34)

Table 11. Comparison of density values for water

Temperature (°C)	d^a (g/ml)	d^b (g/ml)	d^c (g/ml)	d^d (g/ml)	d^e (g/ml)	d^f (g/ml)
20.0		0.998234	0.998228			
30.0		0.995678	0.995671			
40.0		0.992247	0.992243			
45.0	0.990245		0.990243			0.990244
50.0	0.988068		0.988069	0.988073	0.988070	0.988065
55.0	0.985727		0.985730			0.985722
60.0	0.983232		0.983236	0.983239	0.983235	0.983223
65.0	0.980590		0.980592			0.980578
70.0	0.977805		0.977807	0.977813		0.977791
75.0	0.974885		0.974884			0.974870
80.0	0.971834		0.971830	0.971843		0.971816

[a]This research (Equation 5.6).

[b]Tilton and Taylor equation, (Equation 4.1).

[c]Thiesen's equation (46).

[d]Taylor (34) from Jones, et al. (34)

[e]Vogel from Jones, et al. (34).

[f]Owen, et al. (35).

and Owen, et al. (35), are based on the values of Chappuis (38) as
represented by the Tilton and Taylor (40) equation, and are therefore
given only above 40° C where the Tilton and Taylor equation does not hold.
It is seen from Table 11 that there is considerable disagreement between
the values above 40° C. Furthermore, with all of the values except those
by Thiesen, the differences can not be explained by ordinary experimental
errors.

The dilatometers used in this research as well as those used by
Taylor (Jones (34)) and Vogel (Jones (34)) were calibrated with mercury.
Vogel and this laboratory used the densities of mercury given by Beattie,
et al. (41), whereas Taylor (Vogel (47)) used the mercury density data of
Scheel and Blankenstein (48). This would perhaps account for some of the
discrepancies between these values. Also, Taylor and Vogel used a linear
equation in temperature to represent the volumes of their dilatometers as
a function of temperature, whereas in this laboratory it was found that a
quadratic equation was necessary.

Owen, et al. (35) calibrated their dilatometers with water plus
mercury. They assumed the Tilton and Taylor (40) equation to be correct
up to 45° C, and used ten degree temperature intervals from 5 to 45° C.
The calibration analysis which they used was identical to that used in
this laboratory. They then extrapolated the above calibration data to
85° C, and in this manner calculated densities of water above 45° C. In
order to check for convergence of their data, they then used the Tilton
and Taylor densities up to 45° C and their first approximation densities

from 45 to 85° C to recalibrate the dilatometers, and then they recalcu-
lated the densities. The densities which they obtained from the second
calculation were essentially

the same as the first approximation densities. This method of calibration could certainly lead to some discrepancy, but rather than the error exhibiting itself in a general shift towards lower densities, it would be expected that there would be considerable scatter in the densities as determined with the various dilatometers, especially for the first density calculation. The data of Owen, et al., however, had very little scatter. Although they used the tabulation of densities of mercury given by Fowle (49, p. 169), the amount of mercury present in their dilatometers, about seven milliliters, was so small that the mercury density data which they used had very little effect on their calibrations.

Of the various mercury density data available in the literature, the data tabulated in the Smithsonian Tables are probably as consistent as any with the density scale used by Chappuis in his measurements on water. On the other hand, it is felt that the expansion data of mercury given by Beattie, et al. are probably the most accurate data available. It was found in this laboratory that when calibrating the dilatometers with mercury, the use of the mercury density data of Beattie, et al. gave less scatter in the calibration data as well as lower values for the calibration parameter A and higher values for the calibration parameter B than when the mercury density data tabulated in the Smithsonian Tables were used. Furthermore, the A and B calibration parameters were changed in such a manner that if the mercury density values tabulated in the Smithsonian Tables were used, the calculated densities of water were indeed lower than when the mercury density data of Beattie, et al. were used. In fact, at 80° C the difference

in the density of water is of the order of 1×10^{-5} g/ml which would bring the water density values obtained in this research within possible experimental error of the water density values obtained by Owen, et al. (35). It can therefore be concluded that the mercury density data of Beattie, et al. (41) are probably less consistent with the density scale of Chappuis (38) than are the mercury density data found in the Smithsonian Tables (49). In summary, it is suggested that the discrepancies observed in Table 11 are due to the following:

1. differences in the densities of mercury used in calibrating the dilatometers with mercury;

2. failure to include the quadratic term when expressing the volume of a dilatometer as a function of temperature; and

3. the density data of water of Chappuis are not consistent with the density data of mercury of Beattie, et al.

It is interesting to note that the densities calculated from the equation of Thiesen (46) agree quite well with the results of this research, but it is doubtful that much emphasis should be placed on this fact since the water density data above 40° C which Thiesen used were significant only to the fifth decimal place.

It would seem that the density data for water obtained in this laboratory and that obtained by Owen, et al. (35) have the most to offer at the present time, and that a choice between the two is probably a matter of opinion as to whether the density scale of Chappuis (38) or the density scale of Beattie, et al. (41) is correct.

From the definition of the coefficient of thermal expansion, α, given by Equation 5.3, and the relationship $T = t + 273.16$, the coefficient of thermal expansion of water can be written as

$$\alpha = (-1/d) \cdot (\partial d/\partial t)_p. \tag{5.7}$$

Applying Equation 5.7 to Equation 5.6, the relationship

$$\alpha = (1/d) \cdot \left[-(\partial d'/\partial t)_p - (\partial \delta/\partial t)_p \right] \tag{5.8}$$

is obtained in which

$$-(\partial d'/\partial t)_p = (1 - d') \cdot \left[\frac{2}{t - 3.9863} + \frac{1}{t + 288.9414} \right. \tag{5.9}$$

$$\left. - \frac{1}{t + 68.12963} \right],$$

$$-(\partial \delta/\partial t)_p = 0 \text{ if } t \leq 40^\circ \text{ C, and} \tag{5.10}$$

$$-(\partial \delta/\partial t)_p = (2.188 \times 10^{-6}) + (1.44 \times 10^{-8}) t \tag{5.11}$$

$$- (1.555 \times 10^{-9}) t^2 \text{ if } 40 \leq t \leq 80^\circ \text{ C.}$$

The values of α for water above 40° C which were determined in this laboratory and the values of α for water above 40° C reported by Owen, et al. (35) are tabulated in Table 12. At temperatures less than or equal to 40° C, the values of α are merely those given by the Tilton and Taylor equation.

From Table 12, it is seen that although the densities determined in this research differed considerably from those of Owen, et al. at the higher temperatures, the two sets of coefficients of thermal expansion agree quite

well. This is due to the fact that the deviations in density between the two sets of data increase only slowly with temperature.

Table 12. Coefficients of thermal expansion of water

Temperature (°C)	$(\alpha \times 10^4)^a$ (1/deg)	$(\alpha \times 10^4)^b$ (1/deg)
20.0	2.066	
25.0	2.570	
30.0	3.031	
35.0	3.456	
40.0	3.854	
45.0	4.226	4.227
50.0	4.575	4.580
55.0	4.908	4.915
60.0	5.228	5.234
65.0	5.536	5.542
70.0	5.836	5.839
75.0	6.127	6.130
80.0	6.412	6.417

[a]This research plus Tilton and Taylor equation.

[b]Owen, et al. (35).

C. Lanthanum and Neodymium Chloride Solutions

The calculation of densities of solutions from the experimental data is complicated by the fact that there is a concentration variable. The weight of water in a dilatometer could be calculated from known densities

of water at the lower temperatures. This is possible with solutions only if the concentration of the solution in the dilatometer as well as the density of the solution at such a concentration for at least one temperature is known. Fortunately, the weights of mercury and solution in the dilatometers and the volumes of the dilatometers were known well enough to permit the determination of the absolute density of the solution with an accuracy of a few parts in the fifth decimal place. Using the withdrawal data at the temperatures near 20, 25, and 30° C, linear interpolation was used to determine the absolute densities of the solutions at exactly 25° C.

Saeger (50, 51) has determined the densities of both lanthanum chloride and neodymium chloride solutions at 25° C over the entire concentration range using the pycnometric method, and Ayers (52) has determined the densities of the more dilute concentrations of these rare-earth chloride solutions at 25° C using a magnetic float method. From these two sets of density data, the following polynomial equations representing the molalities of aqueous lanthanum and neodymium chloride solutions as a function of density at 25° C were computed by the method of least squares. For a 0.05 to 0.39 molal $LaCl_3$ solution,

$$m = -1.644727 - 1.391345\ d + 2.269667\ d^2 \tag{5.12}$$
$$+\ 1.806654\ d^3 - 1.027552\ d^4;$$

for a 0.39 to 3.9047 molal $LaCl_3$ solution,

$$m = -3.41568 + 2.41769\ d + 1.173498\ d^2 \tag{5.13}$$
$$-\ 0.351911\ d^3 + 0.189178\ d^4;$$

for a 0.03718 to 0.3522 molal $NdCl_3$ solution,

$$m = -2.877333 + 1.531003 \ d + 1.358717 \ d^2; \qquad (5.14)$$

and for a 0.3522 to 3.9292 molal $NdCl_3$ solution,

$$m = -2.97154 + 0.107537 \ d + 2.942257 \ d^2 \qquad (5.15)$$

$$- 1.437463 \ d^3 + 0.404410 \ d^4.$$

From Equations 5.12 through 5.15 and the experimentally determined densities of the solutions at 25° C, the molalities of the solutions were calculated. In this manner, the concentrations could be determined with about the same accuracy as if actual analyses had been made.

Densities of the solutions at the withdrawal temperatures were calculated according to the same method used with water, with the following two exceptions:

1. With solutions, the experimentally determined weights of the solutions were used as opposed to the calculated weights used with water.

2. In order to correct the volumes of the solutions for changes in pressure, a constant value of 1.4×10^{-6} (inch of mercury)$^{-1}$ was used for the isothermal coefficient of compressibility, β. The unit used for β was reciprocal inches of mercury since the scale of the barometer which was used was calibrated in inches of mercury. Although the above value for β was only approximate, it was sufficiently accurate since the pressure correction of the volume was never larger than a few one hundred thousandths of a milliliter.

It was found that the specific volumes, reciprocals of the densities, of the solutions could be represented as functions of temperature from 20 to 80° C by empirical equations of the form

$$\bar{v} = A + Bt + Ct^2 + Dt^3 + Et^4. \tag{5.16}$$

The parameters for these equations were computed using the method of least squares. Due to the large amount of round-off error associated with the computation, however, a sufficiently good fit with the data could not be obtained by directly computing the parameters of the fourth order polynominal. Instead, the parameters of a first order polynomial were first computed for the data. Then the deviations of the experimental data from the first order polynomial were fitted with a fourth order polynomial. The sum of these two polynomials was computed in order to obtain the parameters corresponding to Equation 5.16. The values of the parameters of Equation 5.16 are given in Tables 13 and 14 for the lanthanum and neodymium chloride solutions, respectively, and the differences between the experimental densities and those calculated from Equation 5.16 and the parameters of Tables 13 and 14 are given in Tables 15, 16, and 17 for the three solution runs.

Densities for the lanthanum and neodymium chloride solutions were calculated from the empirical specific volume equations given by Equation 5.16 together with the parameters given in Tables 13 and 14 at five degree temperature intervals from 20 to 80° C.

Also, coefficients of thermal expansion, α, of the rare-earth chloride solutions at the above temperatures were calculated according to Equation

Table 13. Parameters for lanthanum chloride corresponding to Equation 5.16

Molality	A	$B \times 10^4$	$C \times 10^7$	$D \times 10^{10}$	$E \times 10^{13}$
0.06362	0.9853241	0.02446	59.6542	-248.613	766.36
0.1167	0.9737923	0.13535	57.6884	-251.335	811.11
0.3121	0.9340256	0.64128	45.8462	-184.605	596.91
0.6532	0.8739245	1.26877	30.4363	- 99.656	329.70
0.9154	0.8341902	1.65970	18.9883	- 10.613	- 28.37
1.2368	0.7918335	1.82219	14.4110	- 11.520	41.71
1.5618	0.7545998	1.93585	10.0837	1.935	26.22
1.7911	0.7312401	1.94365	8.8329	- 2.648	61.81
1.9867	0.7128715	1.94114	7.8664	- 4.673	83.68
2.3370	0.6831310	1.93975	5.5756	8.682	33.84
3.0681	0.6316053	1.83293	3.6415	19.774	- 9.80
3.3907	0.6124241	1.77364	3.2685	25.841	48.77

Table 14. Parameters for neodymium chloride corresponding to Equation 5.16

Molality	A	$B \times 10^4$	$C \times 10^7$	$D \times 10^{10}$	$E \times 10^{13}$
0.1050	0.9753234	0.02167	61.5978	−302.413	1063.51
0.2992	0.9336823	0.71418	44.0215	−155.142	451.20
0.6152	0.8748732	1.32918	29.9082	− 82.711	242.55
0.9007	0.8293282	1.63491	22.9442	− 64.876	238.96
1.3170	0.7730058	1.93647	14.6728	− 27.844	137.25
1.6809	0.7315164	2.11112	8.7543	10.970	− 8.91
2.0853	0.6921011	2.20088	4.9297	34.735	− 103.79
2.2679	0.6762978	2.17208	4.9328	28.915	− 77.51
2.7090	0.6421498	2.10238	5.4194	13.154	− 17.01
2.7553	0.6389356	2.01288	8.4511	− 29.590	187.08
3.4160	0.5970546	2.01027	5.7154	9.027	− 53.43

Table 15. Values of $\Delta d^a \times 10^6$ for run number one with solutions

Temperature	Molality of $LaCl_3$					
(°C)	0.1167	0.3121	0.6532	1.7911	2.3370	3.0681
20.091	-2.0	-1.6	-1.1	-0.8	-0.2	-0.9
25.042	2.2	2.1	1.3	1.0	0.2	2.1
30.043	1.0	0.3	0.6	-0.1	-0.4	-2.1
34.954	0.5	0.3	-0.5	0.5	0.1	1.8
39.976	-1.1	-0.5	-0.9	-0.7	-0.5	1.3
44.909	-2.1	-0.5	-0.9	-0.7	-0.5	1.3
50.118	0.8	-0.6	-0.2	-0.4	-0.7	0.0
55.017	-0.6	-0.6	-0.4	0.0	-0.7	-2.1
60.044	0.6	0.4	0.4	0.8	1.0	1.1
64.960	0.9	0.2	0.2	0.7	-0.1	0.5
69.719	0.0	1.2	0.6	-0.9	0.3	1.0
74.790	-0.6	-0.8	-0.1	0.0	-0.3	-1.8
79.386	0.0	0.0	-0.3	0.1	0.0	0.6

$^a\Delta d$ = experimental density − calculated density.

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Table 16. Values of Δd^a x 10^6 for run number two on solutions

Temperature (°C)	Molality of LaCl$_3$				Molality of NdCl$_3$			
	0.06362	1.2368	1.5618	3.3907	0.2992	0.6152	1.6809	2.2679
20.127	-3.5	-1.3	-1.1	-0.2	-2.4	-2.3	-1.4	-1.2
25.051	3.9	1.2	1.2	-0.9	2.3	2.3	1.8	1.4
30.034	2.0	0.9	0.5	2.3	1.8	1.3	0.5	0.9
34.999	0.5	0.9	0.3	-1.9	0.6	0.4	0.0	-0.1
39.979	-3.3	-2.7	-2.0	0.1	-2.5	-2.2	-2.2	-2.1
45.069	0.0	0.9	1.0	1.3	0.2	0.4	2.1	1.7
49.931	-0.3	0.1	1.0	0.9	0.1	-0.3	-2.0	-1.0
54.997	-0.6	-0.2	-0.7	-2.6	-1.1	-0.3	1.4	-0.5
60.316	0.2	-0.5	-1.1	-0.6	-0.6	0.1	-1.3	-0.1
65.456	0.5	-0.4	-0.9	0.6	0.3	-0.8	0.5	1.8
70.330	0.9	1.1	1.8	1.6	2.1	1.8	0.6	-0.2
74.816	0.1	0.5	0.6	-0.5	-0.2	0.3	-0.1	-1.3
79.571	-0.7	-0.7	-0.9	-0.3	-0.8	-0.8	-0.2	0.5

$^a\Delta d$ = experimental density - calculated density.

Table 17. Values of $\Delta d^a \times 10^6$ for run number three on solutions

Temperature (°C)	Molality of LaCl$_3$		Molality of NdCl$_3$						
	0.9154	1.9867	0.1050	0.9007	1.3170	2.0853	2.7090	2.7553	3.4160
20.107	-0.3	0.7	0.0	0.5	1.0	3.5	0.1	0.5	0.3
20.089	2.4	-0.5	0.4	-0.4	-1.0	-6.2	0.7	-3.5	0.0
30.073	0.3	-1.2	0.5	-0.1	-0.6	0.1	-0.9	2.4	-0.9
35.051	-4.5	0.9	-0.7	0.1	0.1	1.8	-1.3	10.9	0.7
40.002	-6.9	0.2	-0.1	-0.8	0.5	2.1	1.4	-11.8	0.2
44.960	8.9	-0.4	-0.8	-0.5	-0.4	0.2	-1.1	-5.2	-2.8
49.848	6.9	-1.0	-0.2	0.8	0.4	-0.9	-0.1	2.3	1.0
54.998	-4.1	1.1	-1.4	0.9	0.7	-0.2	0.9	4.4	1.9
60.157	-3.8	1.5	3.7	-0.3	-0.7	-1.5	2.0	2.4	-0.4
65.201	-2.3	-2.0	0.6	-0.3	-0.3	-0.5	-2.1	0.8	0.4
70.185	1.5	-0.2	-1.6	0.7	0.2	1.6	-0.5	-3.2	-2.5
74.860	3.6	0.6	-1.3	-1.4	-0.1	0.2	0.2	-2.5	-2.5
79.741	-2.0	-0.1	0.8	0.6	0.0	-0.5	0.2	2.1	1.3

$^a\Delta d$ = experimental density - calculated density.

5.2 from the above empirical equations representing the specific volumes of the solutions as functions of temperature.

These values of d and α calculated at five degree intervals from 20 to 80° C are tabulated for the lanthanum chloride and neodymium chloride solutions in Tables 18 and 19, respectively.

As a concentration variable, molality, m = moles of salt per 1000 grams of solvent, has an advantage over molarity, c = moles of salt per 1000 milliters of solution, since the molality of a solution is independent of the temperature of the solution, whereas the molarity is temperature dependent. Consequently, the use of molality in this research simplified the mathematical analysis of the data. On the other hand, molarity is more consistent with electrolytic solution theory than is molality, and in plotting apparent and partial molal solution properties versus concentration at a single temperature, molarity has been the favorite concentration variable of past researchers. For these reasons, the corresponding values of molality and molarity, together with the square roots of their values, for the various lanthanum chloride and neodymium chloride solutions are tabulated in Tables 20 and 21, respectively. The molarities of the solutions were calculated from the relationship

$$c = 1000 \ m \ / \ \overline{v}(1000 + mM_2) \tag{5.18}$$

in which m is the molality, $\overline{v}$ is the specific volume, and M_2 is the molecular weight of the salt.

Table 18. Densities and coefficients of thermal expansion of aqueous
lanthanum chloride solutions

Temperature (°C)	d (g/ml)	$\alpha \times 10^4$ (1/deg)	d (g/ml)	$\alpha \times 10^4$ (1/deg)
	m = 0.06362		m = 0.1167	
20.0	1.012584	2.164	1.024399	2.220
25.0	1.011373	2.618	1.023148	2.659
30.0	1.009941	3.045	1.021683	3.071
35.0	1.008302	3.446	1.020016	3.457
40.0	1.006470	3.824	1.018161	3.820
45.0	1.004457	4.181	1.016130	4.162
50.0	1.002274	4.519	1.013935	4.486
55.0	0.999931	4.840	1.011584	4.795
60.0	0.997437	5.147	1.009087	5.090
65.0	0.994800	5.442	1.006450	5.375
70.0	0.992026	5.727	1.003680	5.651
75.0	0.989120	6.004	1.000780	5.921
80.0	0.986088	6.277	0.997755	6.187
	m = 0.3121		m = 0.6532	
20.0	1.067232	2.426	1.139465	2.709
25.0	1.065838	2.798	1.137843	2.986
30.0	1.064254	3.148	1.136070	3.251
35.0	1.062491	3.479	1.134152	3.504
40.0	1.060561	3.792	1.132098	3.747
45.0	1.058472	4.089	1.129912	3.980
50.0	1.056235	4.373	1.127602	4.206
55.0	1.053856	4.644	1.125172	4.424
60.0	1.051343	4.904	1.122626	4.636
65.0	1.048702	5.157	1.119968	4.843
70.0	1.117202	5.402	1.117202	5.047
75.0	1.043053	5.643	1.114331	5.247
80.0	1.040052	5.881	1.111356	5.446

Table 18 (Continued)

Temperature (°C)	d (g/ml)	$\alpha \times 10^4$ (1/deg)	d (g/ml)	$\alpha \times 10^4$ (1/deg)
	m = 0.9154		m = 1.2368	
20.0	1.192947	2.870	1.256209	2.997
25.0	1.191173	3.082	1.154275	3.165
30.0	1.189276	3.291	1.252239	3.331
35.0	1.187260	3.496	1.250104	3.495
40.0	1.185126	3.698	1.247871	3.657
45.0	1.182878	3.896	1.245541	3.817
50.0	1.180518	4.090	1.243117	3.975
55.0	1.178050	4.280	1.240600	4.132
60.0	1.175477	4.466	1.237992	4.287
65.0	1.172802	4.647	1.235293	4.441
70.0	1.170028	4.824	1.232506	4.594
75.0	1.167159	4.996	1.229631	4.746
80.0	1.164197	5.164	1.226670	4.897
	m = 1.5619		m = 1.7911	
20.0	1.317737	3.087	1.359657	3.121
25.0	1.315662	3.217	1.357498	3.236
30.0	1.313504	3.348	1.355264	3.352
35.0	1.311264	3.479	1.352955	3.467
40.0	1.308942	3.611	1.350572	3.585
45.0	1.306538	3.743	1.348115	3.701
50.0	1.304052	3.875	1.345583	3.819
55.0	1.301484	4.009	1.342977	3.938
60.0	1.298835	4.142	1.340294	4.059
65.0	1.296104	4.277	1.337536	4.181
70.0	1.293291	4.413	1.334701	4.306
75.0	1.290397	4.549	1.331789	4.432
80.0	1.287421	4.686	1.328798	4.561

Table 18 (Continued)

Temperature (°C)	d (g/ml)	$\alpha \times 10^4$ (1/deg)	d (g/ml)	$\alpha \times 10^4$ (1/deg)
	m = 1.9867		m = 2.3370	
20.0	1.394572	3.142	1.455094	3.164
25.0	1.392347	3.245	1.452762	3.250
30.0	1.390053	3.349	1.450372	3.338
35.0	1.387691	3.454	1.447921	3.428
40.0	1.385260	3.559	1.445408	3.521
45.0	1.382760	3.666	1.442831	3.617
50.0	1.380190	3.774	1.440189	3.715
55.0	1.377550	3.884	1.437480	3.816
60.0	1.374839	3.996	1.434704	3.919
65.0	1.272056	4.111	1.431857	4.026
70.0	1.369198	4.229	1.428938	4.136
75.0	1.366265	4.349	1.425946	4.249
80.0	1.363255	4.473	1.422879	4.365
	m = 3.0681		m = 3.3907	
20.0	1.573731	3.151	1.623055	3.139
25.0	1.571266	3.223	1.620480	3.212
30.0	1.568666	3.300	1.617848	3.291
35.0	1.566048	3.381	1.615155	3.374
40.0	1.563370	3.465	1.612397	3.461
45.0	1.560630	3.554	1.609573	3.552
50.0	1.557823	3.646	1.606679	3.647
55.0	1.554949	3.742	1.603712	3.745
60.0	1.552004	3.841	1.600672	3.846
65.0	1.548986	3.944	1.597555	3.950
70.0	1.545894	4.050	1.594361	4.056
75.0	1.542725	4.160	1.591088	4.165
80.0	1.539476	4.272	1.587734	4.276

Table 19. Densities and coefficients of thermal expansion of aqueous
neodymium chloride solutions

Temperature (°C)	d (g/ml)	$\alpha \times 10^4$ (1/deg)	d (g/ml)	$\alpha \times 10^4$ (1/deg)
	m = 0.1050		m = 0.2992	
20.0	1.022907	2.206	1.067515	2.459
25.0	1.021663	2.657	1.066104	2.828
30.0	1.020198	3.077	1.064504	3.178
35.0	1.018529	3.468	1.062725	3.510
40.0	1.016671	3.833	1.060777	3.826
45.0	1.014636	4.176	1.058670	4.127
50.0	1.012437	4.500	1.056411	4.414
55.0	1.010083	4.809	1.054009	4.689
60.0	1.007582	5.105	1.051471	4.954
65.0	1.004942	5.391	1.048802	5.208
70.0	1.002166	5.671	1.046010	5.456
75.0	0.999259	5.948	1.043097	5.696
80.0	0.996222	6.225	1.040069	5.931
	m = 0.6152		m = 0.9007	
20.0	1.138089	2.770	1.199806	2.978
25.0	1.136434	3.051	1.197953	3.205
30.0	1.134624	3.320	1.195969	3.423
35.0	1.132669	3.580	1.193861	3.634
40.0	1.130572	3.829	1.191632	3.837
45.0	1.128341	4.070	1.189289	4.035
50.0	1.125982	4.302	1.186835	4.228
55.0	1.123499	4.528	1.184273	4.416
60.0	1.120896	4.746	1.181606	4.601
65.0	1.118180	4.959	1.178837	4.784
70.0	1.115342	5.168	1.175967	4.964
75.0	1.112417	5.372	1.173000	5.144
80.0	1.109377	5.573	1.169934	5.323

Table 19 (Continued)

Temperature (°C)	d (g/ml)	$\alpha \times 10^4$ (1/deg)	d (g/ml)	$\alpha \times 10^4$ (1/deg)
	m = 1.3170		m = 1.6809	
20.0	1.286264	3.208	1.358516	3.361
25.0	1.284149	3.373	1.356193	3.484
30.0	1.281933	3.534	1.353791	3.608
35.0	1.279620	3.691	1.351309	3.733
40.0	1.277210	3.847	1.348746	3.860
45.0	1.274707	4.000	1.346102	3.988
50.0	1.272112	4.152	1.343378	4.117
55.0	1.269426	4.302	1.340572	4.246
60.0	1.266651	4.452	1.337685	4.377
65.0	1.263787	4.602	1.334716	4.509
70.0	1.260835	4.753	1.331666	4.642
75.0	1.257794	4.904	1.328535	4.775
80.0	1.254666	5.057	1.325322	4.909
	m = 2.0853		m = 2.2679	
20.0	1.435284	3.497	1.468728	3.527
25.0	1.432744	3.590	1.466107	3.618
30.0	1.430139	3.689	1.463422	3.714
35.0	1.427467	3.791	1.460671	3.813
40.0	1.424726	3.897	1.457852	3.915
45.0	1.421914	4.006	1.454963	4.021
50.0	1.419029	4.119	1.452002	4.129
55.0	1.416069	4.233	1.448968	4.239
60.0	1.413034	4.349	1.445859	4.351
65.0	1.409924	4.467	1.442676	4.465
70.0	1.406737	4.585	1.439418	4.579
75.0	1.403474	4.704	1.436085	4.695
80.0	1.400136	4.822	1.432676	4.810

Table 19 (Continued)

Temperature (°C)	d (g/ml)	$\alpha \times 10^4$ (1/deg)	d (g/ml)	$\alpha \times 10^4$ (1/deg)
	m = 2.7090		m = 2.7553	
20.0	1.546595	3.610	1.554536	3.609
25.0	1.543771	3.700	1.551694	3.711
30.0	1.540882	3.792	1.548779	3.810
35.0	1.537927	3.886	1.545793	3.907
40.0	1.534905	3.983	1.542739	4.003
45.0	1.531814	4.080	1.539618	4.098
50.0	1.528654	4.180	1.536429	4.194
55.0	1.525424	4.281	1.533174	4.290
60.0	1.522123	4.384	1.529851	4.389
65.0	1.518751	4.488	1.526458	4.491
70.0	1.515307	4.593	1.522995	4.596
75.0	1.511791	4.700	1.519458	4.706
80.0	1.508202	4.807	1.515844	4.820
	m = 3.4160			
20.0	1.663035	3.738		
25.0	1.659890	3.834		
30.0	1.656672	3.929		
35.0	1.653380	4.025		
40.0	1.650017	4.120		
45.0	1.646582	4.215		
50.0	1.643077	4.309		
55.0	1.639502	4.403		
60.0	1.635859	4.494		
65.0	1.632150	4.585		
70.0	1.628377	4.673		
75.0	1.624541	4.760		
80.0	1.620646	4.844		

Table 20. Molalities and molarities of aqueous lanthanum chloride
solutions

Temperature (°C)	c	$c^{1/2}$	c	$c^{1/2}$
	$m = 0.06362$		$m = 0.1167$	
	$m^{1/2} = 0.25223$		$m^{1/2} = 0.34161$	
20.0	0.06343	0.25185	0.1162	0.34091
25.0	0.06336	0.25170	0.1161	0.34070
30.0	0.06326	0.25153	0.1159	0.34046
35.0	0.06316	0.25132	0.1157	0.34018
40.0	0.06305	0.25109	0.1155	0.33987
45.0	0.06292	0.25084	0.1153	0.33953
50.0	0.06278	0.25057	0.1150	0.33917
55.0	0.06264	0.25028	0.1148	0.33877
60.0	0.06248	0.24996	0.1145	0.33835
65.0	0.06232	0.24963	0.1142	0.33791
70.0	0.06214	0.24928	0.1139	0.33745
75.0	0.06196	0.24892	0.1135	0.33696
80.0	0.06177	0.24854	0.1132	0.33645
	$m = 0.3121$		$m = 0.6532$	
	$m^{1/2} = 0.55867$		$m^{1/2} = 0.8024$	
20.0	0.3094	0.55624	0.6416	0.80098
25.0	0.3090	0.55588	0.6406	0.80041
30.0	0.3085	0.55547	0.6396	0.79978
35.0	0.3080	0.55501	0.6386	0.79911
40.0	0.3075	0.55450	0.6374	0.79838
45.0	0.3069	0.55396	0.6362	0.79761
50.0	0.3062	0.55337	0.6349	0.79680
55.0	0.3055	0.55275	0.6335	0.79594
60.0	0.3048	0.55209	0.6321	0.79504
65.0	0.3040	0.55140	0.6306	0.79409
70.0	0.3032	0.55067	0.6290	0.79311
75.0	0.3024	0.54991	0.6274	0.79209
80.0	0.3015	0.54912	0.6257	0.79104

Table 20 (Continued)

Temperature (°C)	c	$c^{1/2}$	c	$c^{1/2}$
	$m = 0.9154$		$m = 1.2368$	
	$m^{1/2} = 0.95676$		$m^{1/2} = 1.11210$	
20.0	0.8918	0.94435	1.1920	1.09180
25.0	0.8905	0.94364	1.1902	1.09096
30.0	0.8890	0.94289	1.1883	1.09008
35.0	0.8875	0.94209	1.1862	1.08915
40.0	0.8859	0.94125	1.1841	1.08818
45.0	0.8843	0.94035	1.1819	1.08716
50.0	0.8825	0.93941	1.1796	1.08610
55.0	0.8806	0.93843	1.1772	1.08500
60.0	0.8787	0.93741	1.1748	1.08386
65.0	0.8767	0.93634	1.1722	1.08268
70.0	0.8746	0.93523	1.1695	1.08146
75.0	0.8725	0.93408	1.1668	1.08019
80.0	0.8703	0.93290	1.1640	1.07889
	$m = 1.5618$		$m = 1.7911$	
	$m^{1/2} = 1.24974$		$m^{1/2} = 1.33833$	
20.0	1.4881	1.21987	1.6920	1.30077
25.0	1.4857	1.21891	1.6893	1.29974
30.0	1.4833	1.21791	1.6865	1.29867
35.0	1.4808	1.21688	1.6837	1.29756
40.0	1.4782	1.21581	1.6807	1.29642
45.0	1.4755	1.21470	1.6776	1.29524
50.0	1.4727	1.21355	1.6745	1.29402
55.0	1.4698	1.21237	1.6712	1.29277
60.0	1.4669	1.21115	1.6679	1.29148
65.0	1.4638	1.20989	1.6645	1.29014
70.0	1.4607	1.20860	1.6609	1.28878
75.0	1.4575	1.20727	1.6573	1.28737
80.0	1.4542	1.20590	1.6536	1.28592

Table 20 (Continued)

Temperature (°C)	c	c$^{1/2}$	c	c$^{1/2}$
	m = 1.9867		m = 2.3370	
	m$^{1/2}$ = 1.40949		m$^{1/2}$ = 1.52872	
20.0	1.8628	1.36486	2.1616	1.47022
25.0	1.8599	1.36377	2.1581	1.46904
30.0	1.8568	1.36265	2.1545	1.46784
35.0	1.8536	1.36149	2.1509	1.46660
40.0	1.8504	1.36030	2.1472	1.46532
45.0	1.8471	1.35907	2.1433	1.46402
50.0	1.8436	1.35781	2.1394	1.46267
55.0	1.8401	1.35651	2.1354	1.46130
60.0	1.8365	1.35517	2.1313	1.45988
65.0	1.8328	1.35380	2.1270	1.45844
70.0	1.8290	1.35239	2.1227	1.45695
75.0	1.8250	1.35094	2.1182	1.45542
80.0	1.8210	1.34945	2.1137	1.45386
	m = 3.0681		m = 3.3907	
	m$^{1/2}$ = 1.75160		m$^{1/2}$ = 1.84139	
20.0	2.7551	1.65985	3.0046	1.73337
25.0	2.7507	1.65853	2.9998	1.73200
30.0	2.7462	1.65718	2.9949	1.73059
35.0	2.7416	1.65580	2.9900	1.72915
40.0	2.7370	1.65438	2.9848	1.72767
45.0	2.7322	1.65293	2.9796	1.72616
50.0	2.7272	1.65144	2.9743	1.72461
55.0	2.7222	1.64992	2.9688	1.72302
60.0	2.7171	1.64835	2.9632	1.72138
65.0	2.7118	1.64675	2.9574	1.71970
70.0	2.7064	1.64511	2.9515	1.71798
75.0	2.7008	1.64342	2.9541	1.71622
80.0	2.6951	1.64169	2.9392	1.71441

Table 21. Molalities and molarities of aqueous neodymium chloride solutions

Temperature (°C)	c	$c^{1/2}$	c	$c^{1/2}$
	$m = 0.1050$		$m = 0.2992$	
	$m^{1/2} = 0.32411$		$m^{1/2} = 0.54695$	
20.0	0.1047	0.32357	0.2971	0.54505
25.0	0.1046	0.32338	0.2967	0.54469
30.0	0.1004	0.32314	0.2962	0.54428
35.0	0.1042	0.32288	0.2956	0.54382
40.0	0.1041	0.32259	0.2952	0.54332
45.0	0.1038	0.32226	0.2946	0.54278
50.0	0.1036	0.32191	0.2940	0.54220
55.0	0.1034	0.32154	0.2933	0.54159
60.0	0.1031	0.32114	0.2926	0.54094
65.0	0.1029	0.32072	0.2919	0.54025
70.0	0.1026	0.32028	0.2911	0.53953
75.0	0.1023	0.31981	0.2903	0.53878
80.0	0.1020	0.31933	0.2894	0.53800
	$m = 0.6152$		$m = 0.9007$	
	$m^{1/2} = 0.78437$		$m^{1/2} = 0.94907$	
20.0	0.6067	0.77889	0.8817	0.93898
25.0	0.6058	0.77832	0.8803	0.93826
30.0	0.6048	0.77770	0.8789	0.93748
35.0	0.6038	0.77703	0.8773	0.93665
40.0	0.6026	0.77631	0.8757	0.93578
45.0	0.6015	0.77554	0.8740	0.93486
50.0	0.6002	0.77473	0.8722	0.93389
55.0	0.5989	0.77388	0.8703	0.93288
60.0	0.5975	0.77298	0.8683	0.93183
65.0	0.5960	0.77204	0.8663	0.93074
70.0	0.5945	0.77107	0.8642	0.92961
75.0	0.5930	0.77005	0.8620	0.93843
80.0	0.5914	0.76900	0.8597	0.92722

Table 21 (Continued)

Temperature (°C)	c	$c^{1/2}$	c	$c^{1/2}$
	$m = 1.3170$		$m = 1.6809$	
	$m^{1/2} = 1.14762$		$m^{1/2} = 1.29650$	
20.0	1.2737	1.12858	1.6067	1.26757
25.0	1.2716	1.12765	1.6040	1.26648
30.0	1.2694	1.12667	1.6011	1.26536
35.0	1.2671	1.12566	1.5982	1.26420
40.0	1.2647	1.12460	1.5952	1.26300
45.0	1.2622	1.12350	1.5920	1.26176
50.0	1.2597	1.12235	1.5888	1.26049
55.0	1.2570	1.12116	1.5855	1.25917
60.0	1.2543	1.11994	1.5821	1.25781
65.0	1.2514	1.11867	1.5786	1.25642
70.0	1.2485	1.11736	1.5750	1.25498
75.0	1.2455	1.11602	1.5713	1.25350
80.0	1.2424	1.11463	1.5675	1.25199
	$m = 2.0853$		$m = 2.2679$	
	$m^{1/2} = 1.44406$		$m^{1/2} = 1.50595$	
20.0	1.9658	1.40206	2.1238	1.45735
25.0	1.9623	1.40082	2.1201	1.45605
30.0	1.9587	1.39954	2.1162	1.45471
35.0	1.9550	1.39823	2.1122	1.45334
40.0	1.9513	1.39689	2.1081	1.45194
45.0	1.9474	1.39551	2.1040	1.45050
50.0	1.9435	1.39409	2.0997	1.44902
55.0	1.9394	1.39264	2.0953	1.44751
60.0	1.9353	1.39115	2.0908	1.44596
65.0	1.9310	1.38961	2.0862	1.44436
70.0	1.9267	1.38804	2.0815	1.44273
75.0	1.9222	1.38643	2.0766	1.44106
80.0	1.9176	1.38478	2.0717	1.43935

Table 21 (Continued)

Temperature (°C)	c	$c^{1/2}$	c	$c^{1/2}$
	$m = 2.7090$		$m = 2.7553$	
	$m^{1/2} = 1.64589$		$m^{1/2} = 1.65991$	
20.0	2.4955	1.57972	2.5337	1.59177
25.0	2.4910	1.57828	2.5291	1.59031
30.0	2.4863	1.57680	2.5243	1.58882
35.0	2.4815	1.57529	2.5195	1.58729
40.0	2.4767	1.57374	2.5145	1.58572
45.0	2.4717	1.57216	2.5094	1.58411
50.0	2.4666	1.57054	2.5042	1.58247
55.0	2.4614	1.56888	2.4989	1.58079
60.0	2.4560	1.56718	2.4935	1.57908
65.0	2.4506	1.56544	2.4880	1.57733
70.0	2.4450	1.56366	2.4823	1.57554
75.0	2.4394	1.56185	2.4766	1.57371
80.0	2.4336	1.55999	2.4707	1.57183
	$m = 3.4160$			
	$m^{1/2} = 1.84824$			
20.0	3.0608	1.74950		
25.0	3.0550	1.74785		
30.0	3.0490	1.74616		
35.0	3.0430	1.74442		
40.0	3.0368	1.74264		
45.0	3.0305	1.74083		
50.0	3.0240	1.73898		
55.0	3.0174	1.73708		
60.0	3.0108	1.73515		
65.0	3.0039	1.73318		
70.0	2.9970	1.73118		
75.0	2.9899	1.72914		
80.0	2.9828	1.72706		

In Figures 5 and 6, coefficients of thermal expansion of the lanthanum chloride and neodymium chloride solutions are plotted versus molality at 25, 35, 50, and 75° C, and in Figures 7 and 8, coefficients of thermal expansion of selected lanthanum chloride and neodymium chloride solutions are plotted versus temperature from 20 to 80° C.

From Figures 5, 6, 7, and 8, the following observations can be made:

1. At 25° C, the coefficients of thermal expansion of neodymium chloride increase with increasing concentration. With lanthanum chloride, however, a maximum is reached somewhere between 2.0 and 2.5 molal.

2. At 50 and 75° C, the coefficients of thermal expansion of lanthanum chloride decrease with increasing concentration up to about 3.2 molal, at which the coefficients of thermal expansion begin to increase with concentration. With neodymium chloride, the minima are much more noticeable, and at 50 and 75° C, the minima occur at about 1.9 molal and 2.5 molal, respectively.

3. The plots of the coefficients of thermal expansion of lanthanum chloride versus temperature at constant molality show a general increase in the coefficients of thermal expansion with temperature. For the solutions of concentration 1.2368 molal or less, the curves have negative curvature. The 1.9867 molal curve is almost linear, and the 2.3370 molal and 3.3907 molal curves have positive curvature. With one exception, the coefficients of thermal expansion at 20° C increase with increasing concentration, whereas at 80° C, the opposite is true. This means that the curves must cross one another between 20 and 80° C. The solutions of concentration less than
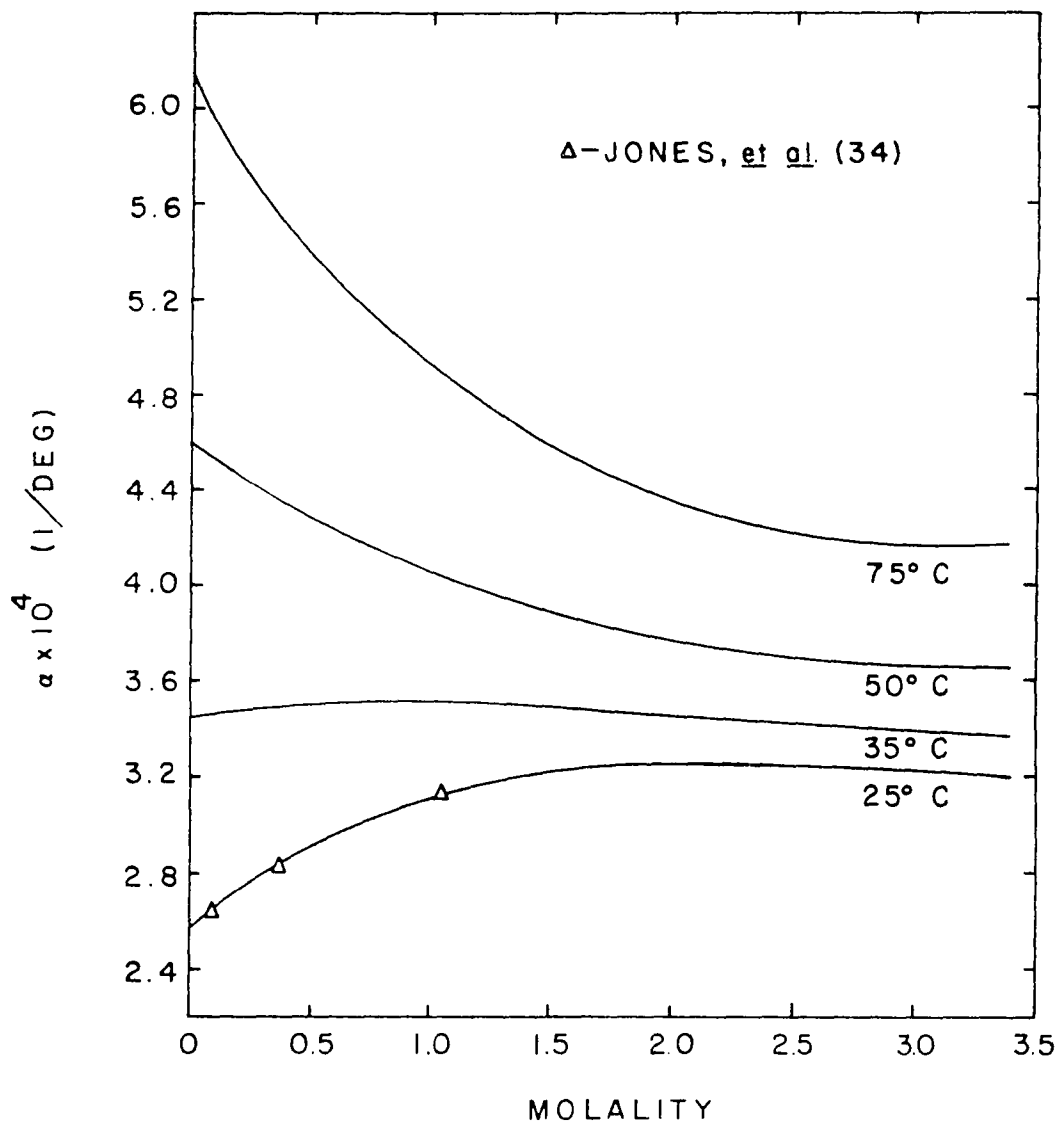
Figure 5. Coefficients of thermal expansion of aqueous lanthanum chloride
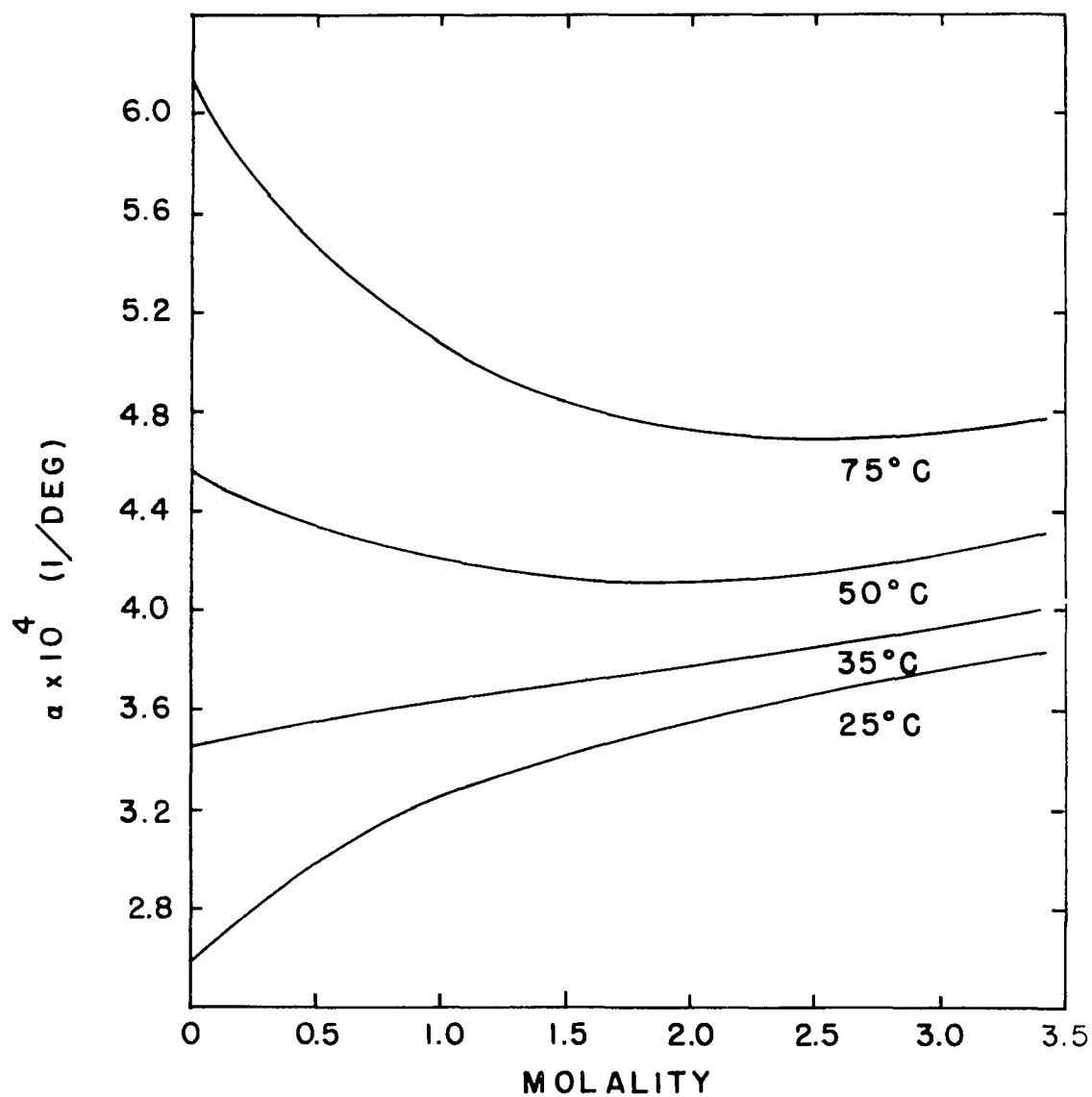solutions at 25, 50, and 75° C

Figure 6. Coefficients of thermal expansion of aqueous neodymium chloride solutions at 25, 50, and 75° C
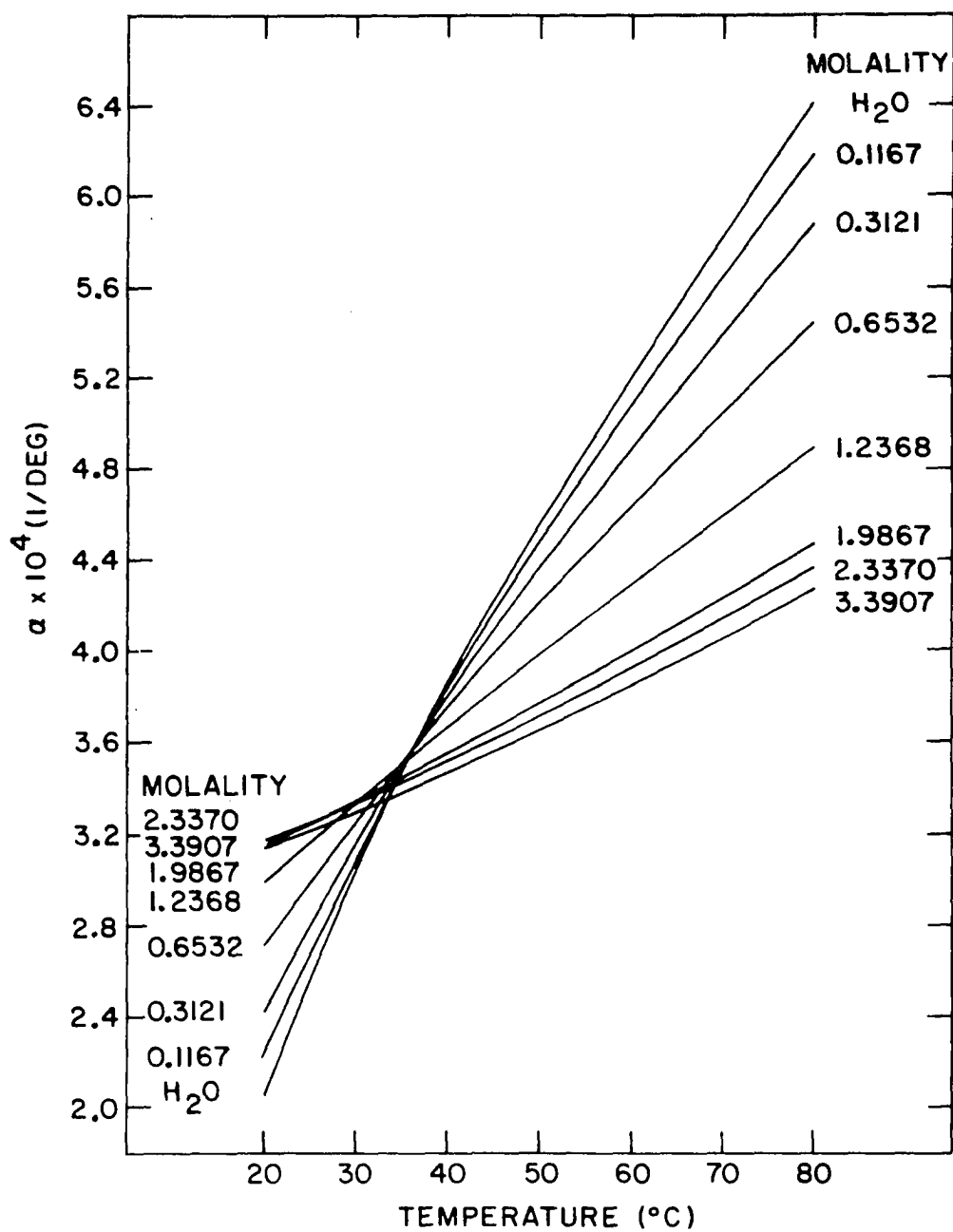
Figure 7. Coefficients of thermal expansion of some aqueous lanthanum chloride solutions
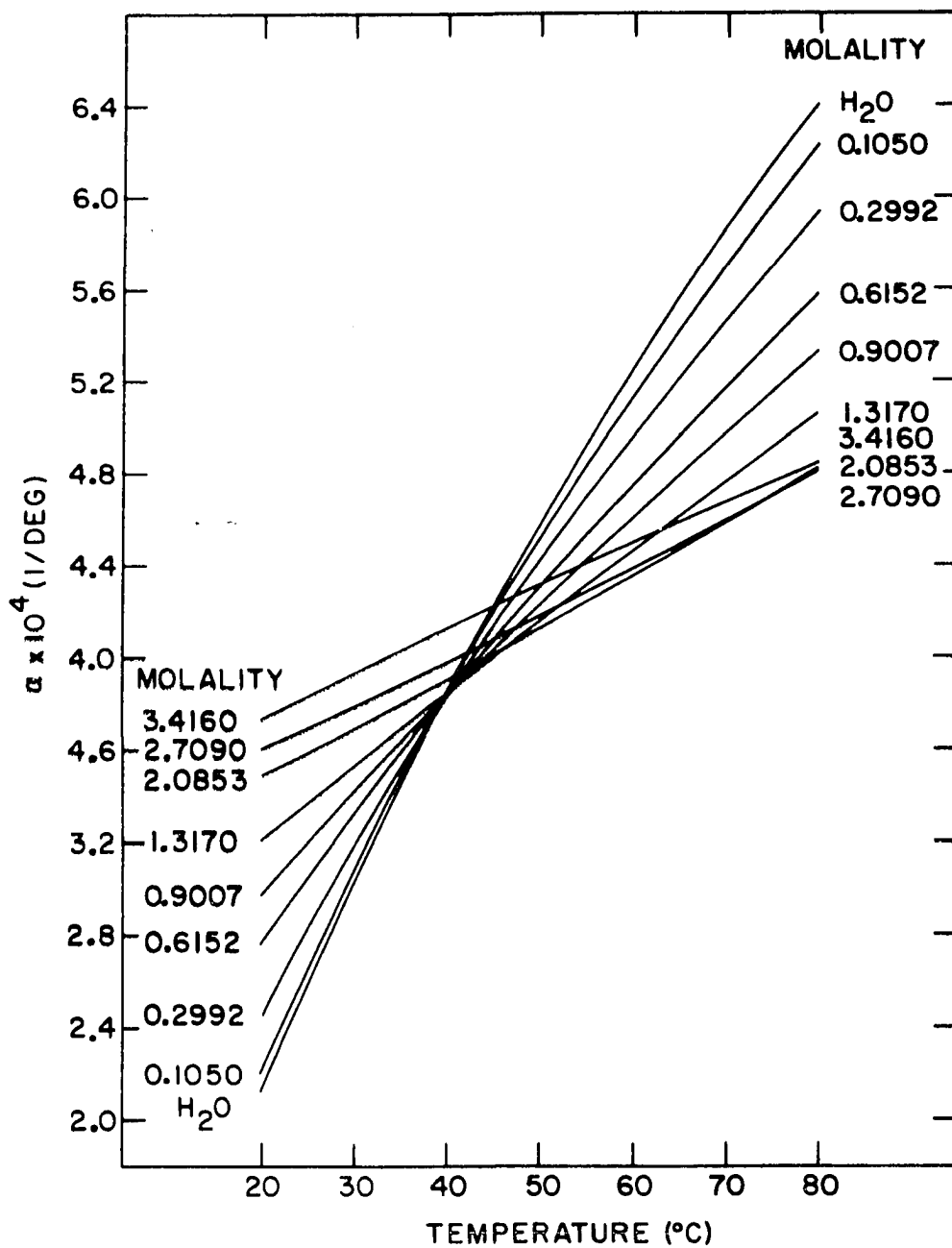
Figure 8. Coefficients of thermal expansion of some aqueous neodymium chloride solutions

or equal to 0.6532 molal cross one another at about 36.5° C. The situation with the more concentrated solutions is not quite this simple, but in general the temperature at which the curves cross decreases with increasing concentration.

4. The plots of the coefficients of thermal expansion of neodymium chloride at constant molality differ from those of lanthanum chloride in several aspects. As with lanthanum chloride, the more dilute solutions have curves of negative curvature. However, with neodymium chloride, the situation does not reverse itself nicely as with lanthanum chloride. Instead, the 3.4160 molal solution of neodymium chloride has negative curvature, whereas the 2.0853 and 2.7090 molal solutions have positive curvature. Also, at 20° C the coefficients of thermal expansion of neo-dymium chloride increase regularly with increasing concentration, and at 80° C they decrease, except that the coefficient of thermal expansion of the 3.4160 molal solution is greater than for the 2.0853 and 2.7090 molal solutions. With neodymium chloride, the curves of the solutions of concentration 0.9007 molal and less cross one another at about 39.5° C, and contrary to the situation with lanthanum chloride, the temperatures at which the curves cross one another increase for the solutions more concentrated than 0.9007 molal. In general, the coefficients of thermal expansion of neodymium chloride are larger than those of lanthanum chloride at the same concentrations and temperatures.

Jones, et al. have also determined the coefficients of thermal expansion for lanthanum chloride up to a concentration of 1.04 molal and over

a temperature range of 20 to 60° C (34). Their results agree very well with those obtained in this research. The agreement at 25° C is shown in Figure 5. From their data on potassium chloride, barium chloride, and lanthanum chloride, they made the following generalizations concerning coefficients of thermal expansion:

1. At 25° C, solutions of all three salts which they studied had larger coefficients of thermal expansion than did water. The opposite was found to be true at higher temperatures.

2. For each salt, there was a particular temperature at which the coefficient of thermal expansion became independent of the concentration. In the case of lanthanum chloride, this temperature was 37° C.

The results of this research indicate that, at least for lanthanum chloride and neodymium chloride, the situation is not quite as simple for the more concentrated solutions as the observations which Jones, et al. made on the less concentrated solutions would lead one to believe.

Although one might expect complexities of solution properties to occur at higher concentrations when viewed over a large temperature range, it is somewhat surprising that the results for the lanthanum and neodymium chloride solutions differed as much as they did.

VI. APPARENT AND PARTIAL MOLAL PROPERTIES

A. Introduction

The use of apparent and partial molal properties makes it possible to examine the contribution of each of the components of a solution to the property being studied. Since the volume of a solution reflects the structure of the solution, the apparent and partial molal volumes reflect the structures of the various components in the solution, and the apparent and partial molal expansibilities reflect the changes in structure of these components with temperature. An examination of the apparent and partial molal volumes and expansibilities of lanthanum and neodymium chloride solutions should, therefore, give some insight into the structures of these solutions.

The apparent molal quantity of the solute may be defined for any extensive property, G, of the solution according to the equation

$$\emptyset_G = (G - n_1 \bar{G}_1^\circ)/n_2 \tag{6.1}$$

in which $\emptyset_G$ is the apparent molal G, G is the value of this extensive property for a solution containing n_1 moles of solvent and n_2 moles of solute, and $\bar{G}_1^\circ$ is the partial molal quantity of the pure solvent, i.e., the value of G for one mole of the pure solvent. In other words, the apparent molal quantity of a solute is merely the change in the value of the extensive property, G, accompanying the addition of one mole of the

solute to a sufficient quantity of solvent necessary to prepare the desired concentration.

The partial molal quantity of an extensive property as defined in Chapter II, may be written as

$$\bar{G}_1 = (\partial G/\partial n_1)_{T,P,n_j}. \tag{6.2}$$

Differentiating Equation 6.1 with respect to temperature at constant temperature, pressure, and n_1 and rearranging the result gives

$$\bar{G}_2 = (\partial G/\partial n_2)_{T,P,n_1} = \emptyset_G + n_2(\partial \emptyset_G/\partial n_2)_{T,P,n_1}. \tag{6.3}$$

Using the relationship, $n_2 = mn_1M_1/1000$ in which M_1 is the molecular weight of the solvent, and the rules of partial differentiation, Equation 6.3 becomes

$$\bar{G}_2 = \emptyset_G + m(\partial \emptyset_G/\partial m)_{T,P,n_1}. \tag{6.4}$$

Substitution of Equations 6.1 and 6.3 into Equation 2.8 and rearranging gives

$$\bar{G}_1 = \bar{G}_1^\circ - (n_2^2/n_1) \cdot (\partial \emptyset_G/\partial n_2)_{T,P,n_1}. \tag{6.5}$$

Again making use of the relationship, $n_2 = mn_1M_1/1000$, and the rules of partial differentiation, Equation 6.3 becomes

$$\bar{G}_1 = \bar{G}_1^\circ - (M_1m^2/1000) \cdot (\partial \emptyset_G/\partial m)_{T,P,n_1}. \tag{6.6}$$

B. Apparent and Partial Molal Volumes

The volume of a solution is an extensive property, and therefore, an apparent molal volume can be defined. According to the general definition of an apparent molal property given by Equation 6.1, the apparent molal volume of a salt may be defined as

$$\phi_V = (V - n_1 \bar{V}_1^\circ)/n_2. \tag{6.7}$$

Substitution of $V = (1000 + mM_2)/d$, $n_1\bar{V}_1^\circ = 1000/d_o$, and $n_2 = m$ into Equation 6.7 gives

$$\phi_V = \left[1000(d_o - d)/mdd_o\right] + M_2/d \tag{6.8}$$

in which d is the density of the solution, d_o is the density of water, m is the molality of the solution, and M_2 is the molecular weight of the solute.

The experimental apparent molal volumes of the lanthanum and neodymium chloride solutions were calculated from the experimental solution densities and from the densities of water given by Equation 5.6. Empirical equations of the form

$$\phi_V = A + Bt + Ct^2 + Dt^3 + Et^4 \tag{6.9}$$

were computed for each of the rare-earth chloride solutions over the temperature range of 20 to 80° C by the same method that was used with the specific volume equations corresponding to Equation 5.17. The parameters

of Equation 6.9 which were computed for the lanthanum chloride and neodymium chloride solutions are given in Tables 22 and 23, respectively.

The differences between the experimental apparent molal volumes and those calculated from Equation 6.9 and the parameters given in Tables 22 and 23 are tabulated in Tables 24, 25, and 26 for the three runs on solutions.

In addition to calculating apparent molal volumes from the apparent molal volume equations corresponding to Equation 6.9, apparent molal volumes can also be calculated from the specific volumes corresponding to Equation 5.7, the relationship between density and specific volume, and Equation 6.8. It was found that for the 0.06362, 0.1167, and 0.3121 molal solutions of lanthanum chloride and for the 0.1050, 0.2992, 0.6152, and 2.7553 molal solutions of neodymium chloride, the empirical equations for the apparent molal volumes as functions of temperature represented by Equation 6.9 gave the better agreement with the experimental results. For the other lanthanum and neodymium chloride solutions, better agreement with the experimental apparent molal volumes was obtained by calculating $\emptyset_V$ from the empirical equations for the specific volumes as functions of temperature represented by Equation 5.17.

Using those equations giving the best fit with the experimental data, apparent molal volumes were calculated for each lanthanum and neodymium chloride solution at each five degree interval from 20 to 80° C. From these calculated data, empirical equations of the form

$$\emptyset_V = A + Bm^{1/2} + Cm + Dm^{3/2} + Em^2 \tag{6.10}$$

Table 22. Parameters for lanthanum chloride corresponding to Equation 6.9

Molality	A	$B \times 10^1$	$C \times 10^3$	$D \times 10^5$	$E \times 10^7$
0.06362	13.9300	4.22953	-9.76564	8.67317	-3.59661
0.1167	15.5734	3.57732	-7.37416	5.58680	-2.16262
0.3121	18.1999	3.09703	-5.93409	3.97368	-1.40748
0.6532	21.5840	2.67770	-4.98918	3.17613	-1.07280
0.9154	23.5792	2.57423	-5.04654	3.61742	-1.33252
1.2368	26.0481	2.11720	-3.88053	2.36386	-0.76919
1.5618	28.0790	1.86995	-3.38176	1.98427	-0.62030
1.7911	29.3849	1.71661	-3.08154	1.78308	-0.55549
1.9867	30.3700	1.61643	-2.90701	1.69744	-0.53391
2.3370	32.0274	1.42498	-2.53246	1.44412	-0.44237
3.0681	34.8902	1.13724	-2.00501	1.16576	-0.35858
3.3907	35.9590	1.02973	-1.79215	1.04521	-0.32252

Table 23. Parameters for neodymium chloride corresponding to Equation 6.9

Molality	A	$B \times 10^1$	$C \times 10^3$	$D \times 10^5$	$E \times 10^7$
0.1050	10.4911	3.31032	-5.97544	3.28169	-0.92543
0.2992	12.9215	3.37959	-6.49954	4.69433	-1.73740
0.6152	16.1708	2.88756	-5.23692	3.43611	-1.17554
0.9007	18.4620	2.58543	-4.59062	2.94176	-0.99251
1.3170	21.4413	2.20220	-3.79293	2.33411	-0.76233
1.6809	23.7039	1.92978	-3.23201	1.92076	-0.60553
2.0853	25.8386	1.76284	-2.97180	1.90581	-0.64501
2.2679	26.8292	1.60986	-2.60470	1.55741	-0.49816
2.7090	28.8607	1.42324	-2.22991	1.35480	-0.44941
2.7553	29.1100	1.35295	-2.00312	1.06898	-0.31606
3.4160	31.6933	1.18742	-1.72336	1.05766	-0.37652

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Table 24. Values of $\Delta\emptyset_V{}^a \times 10^3$ for run number one on solutions

Temperature	Molality of $LaCl_3$					
(°C)	0.1167	0.3121	0.6532	1.7911	2.3370	3.0681
20.091	0.2	-1.4	-1.4	-0.8	-0.8	-0.4
25.042	-3.1	-0.3	1.1	0.6	0.7	0.1
30.043	4.4	4.1	1.5	0.9	0.8	1.0
34.954	-2.1	0.2	1.1	0.0	0.0	-0.3
39.976	1.5	-1.5	-2.0	-0.4	-0.8	0.1
44.909	7.5	-2.6	-0.6	-0.4	-0.4	-0.7
50.118	-15.5	-1.4	-1.2	-0.3	-0.2	-0.3
55.017	5.2	1.8	0.6	0.0	0.2	0.5
60.044	1.8	1.2	0.8	0.1	0.0	0.0
64.960	-0.3	2.3	1.2	0.2	0.4	0.2
69.719	1.1	-3.1	-0.5	0.5	0.0	-0.2
74.790	0.0	0.6	-0.8	-0.3	-0.2	0.2
79.386	-0.6	0.0	0.3	0.0	0.0	-0.2

$^a\Delta\emptyset_V$ = experimental $\emptyset_V$ - $\emptyset_V$ calculated from Equation 6.9.

Table 25. Values of $\Delta\phi_V{}^a \times 10^3$ for run number two on solutions

Temperature	Molality of LaCl$_3$				Molality of NdCl$_3$			
(°C)	0.06362	1.2368	1.5618	3.3907	0.2992	0.6152	1.6809	2.2679
20.127	8.8	-1.5	-1.4	-0.8	-2.1	-1.6	-1.1	-0.9
25.051	-24.1	1.1	0.9	0.9	0.8	0.4	0.6	0.6
30.034	6.4	1.3	1.3	0.2	2.3	2.0	1.2	0.8
34.999	4.9	0.1	0.4	0.6	0.7	0.8	0.5	0.4
39.979	37.6	1.1	0.5	-0.3	5.0	1.8	0.5	0.3
45.069	-26.1	-2.0	-1.6	-0.8	-6.5	-3.4	-2.0	-1.3
49.931	-20.2	-1.4	-1.4	-0.7	-5.9	-2.2	0.0	-0.4
54.997	0.0	-0.3	0.0	0.4	1.8	-0.4	-1.0	0.0
60.316	8.7	0.9	1.0	0.3	4.4	1.1	1.0	0.4
65.456	10.4	1.3	1.3	0.2	3.2	3.3	0.5	0.0
70.330	-3.3	-0.1	-0.5	-0.1	-4.2	-1.4	0.2	0.4
74.816	-3.4	-0.5	-0.4	0.0	0.3	-0.6	0.0	0.4
79.571	0.4	0.0	0.0	-0.1	0.2	0.0	-0.3	-0.4

$^a\Delta\phi_V$ = experimental ϕ_V - ϕ_V calculated from Equation 6.9.

Table 26. Values of $\Delta\phi_V{}^a \times 10^3$ for run number three on solutions

Temperature	Molality of LaCl$_3$		Molality of NdCl$_3$						
(°C)	0.9154	1.9867	0.1050	0.9007	1.3170	2.0853	2.7090	2.7553	3.4160
20.107	0.0	-0.4	- 1.7	-0.7	-0.8	-1.3	-0.1	-0.2	-0.1
20.089	-1.0	0.7	6.4	1.6	1.5	2.8	0.2	1.3	0.3
30.073	-0.2	0.5	- 4.4	0.2	0.4	0.0	0.2	-0.6	0.2
35.051	3.3	-0.8	- 1.8	-1.1	-0.8	-1.1	0.0	-3.1	-0.4
40.002	6.4	-0.2	- 0.5	0.5	-0.5	-0.9	-0.5	3.0	-0.1
44.960	-9.6	-0.4	- 1.2	-0.5	-0.5	-0.6	-0.1	1.0	0.3
49.848	-7.0	0.2	- 0.2	-1.1	-0.5	0.2	-0.1	-0.7	-0.3
54.998	4.8	-0.1	21.2	0.0	0.1	0.4	0.0	-0.9	-0.2
60.157	5.0	0.0	-24.5	1.6	1.3	1.1	-0.1	-0.2	0.4
65.201	2.9	1.1	- 0.7	0.9	0.6	0.5	0.8	0.0	0.1
70.185	-2.2	-0.2	9.5	-1.4	-0.6	-0.9	-0.1	0.6	-0.3
74.860	-4.9	-0.9	- 0.2	0.0	-0.9	-0.7	-0.5	0.2	0.2
79.741	2.6	0.4	- 1.8	0.2	0.5	0.5	0.2	-0.3	-0.1

$^a \Delta\phi_V$ = experimental ϕ_V − ϕ_V calculated from Equation 6.9.

were computed for each rare-earth salt at each of the above temperatures.
The parameters for these empirical equations representing apparent molal
volumes as functions of molality were calculated according to the method of
least squares and are tabulated in Tables 27 and 28 for the lanthanum and
neodymium chloride solutions, respectively.

Substituting Equation 6.10 into Equations 6.4 and 6.6 gives

$$\bar{V}_2 = A + (3/2)Bm^{1/2} + 2Cm + (5/2)Dm^{3/2} + 3Em^2 \tag{6.11}$$

and

$$\bar{V}_1 = \bar{V}_1^{\circ} - (M_1/1000)\left[(1/2)Bm^{3/2} + Cm^2 \tag{6.12} \right.$$
$$\left. + (3/2)Dm^{5/2} + 2Em^3\right],$$

respectively, from which partial molal volumes of the salt, $\bar{V}_2$, and partial
molal volumes of water, $\bar{V}_1$, can be calculated using the parameters given in
Tables 27 and 28.

The apparent molal volumes calculated from the empirical specific
volume equations and the empirical apparent molal volume equations giving
the best agreement with the experimental apparent molal volumes and the
experimental apparent molal volumes, the partial molal volumes of the salt,
and the partial molal volumes of water calculated from Equations 6.10,
6.11, and 6.12, respectively, are tabulated in Table 29 for lanthanum
chloride and in Table 30 for neodymium chloride. In addition, the differ-
ences, $\Delta\phi_V$, between the apparent molal volumes calculated from the specific

Table 27. Parameters for lanthanum chloride corresponding to Equation 6.10

Temperature (°C)	A	B	C	D	E
20.0	16.787	9.243	0.7488	1.3978	-0.6710
25.0	17.228	9.622	0.0764	1.6677	-0.7021
30.0	17.326	10.646	- 1.5022	2.5412	-0.8727
35.0	17.176	11.960	- 3.4084	3.6312	-1.0936
40.0	16.830	13.431	- 5.5462	4.8261	-1.3402
45.0	16.348	14.842	- 7.3194	5.8995	-1.5603
50.0	15.750	16.183	- 8.9973	6.8686	-1.7599
55.0	15.053	17.441	-10.4851	7.7294	-1.9372
60.0	14.289	18.481	-11.5576	8.3285	-2.0569
65.0	13.436	19.451	-12.4659	8.8334	-2.1574
70.0	12.477	20.430	-13.3244	9.3120	-2.2533
75.0	11.384	21.546	-14.3176	9.8778	-2.3694
80.0	10.127	22.899	-15.5522	10.5773	-2.5129

Table 28. Parameters for neodymium chloride corresponding to Equation 6.10

Temperature (°C)	A	B	C	D	E
20.0	11.298	11.984	- 2.9339	3.1736	-0.8581
25.0	11.698	12.756	- 4.1711	3.7948	-0.9648
30.0	11.922	13.384	- 5.0709	4.2260	-1.0343
35.0	11.940	14.109	- 6.0097	4.6980	-1.1161
40.0	11.780	14.874	- 6.8932	5.1415	-1.1937
45.0	11.423	15.860	- 8.0185	5.7435	-1.3078
50.0	10.894	17.001	- 9.2841	6.4355	-1.4426
55.0	10.202	18.317	-10.7315	7.2430	-1.6035
60.0	9.359	19.802	-12.3631	8.1706	-1.7921
65.0	8.382	21.416	-14.1327	9.1932	-2.0036
70.0	7.288	23.118	-15.9894	10.2852	-2.2335
75.0	6.119	24.710	-17.6269	11.2553	-2.4405
80.0	4.919	25.988	-18.7296	11.9099	-2.5834

Table 29. Values of ϕ_V, $\bar{V}_2$, and $\bar{V}_1$ in units of ml/mole for aqueous
solutions of lanthanum chloride

Molality	$\phi_V{}^a$	$\phi_V{}^b$	$\Delta\phi_V$	$\bar{V}_2$	$\bar{V}_1$
		$\begin{array}{c} t = 20.0^\circ \text{ C} \\ \bar{V}_1^\circ = 18.05 \text{ ml/mole} \end{array}$			
0.06362	19.12	19.18	-0.06	20.43	18.04
0.1167	20.19	20.08	0.11	21.81	18.04
0.3121	22.32	22.36	-0.04	25.41	18.03
0.6532	25.18	25.20	-0.02	29.96	17.99
0.9154	26.98	26.98	0.00	32.80	17.95
1.2368	28.90	28.89	0.01	35.79	17.89
1.5618	30.61	30.60	0.01	38.36	17.83
1.7911	31.72	31.70	0.02	39.94	17.78
1.9867	32.57	32.57	0.00	41.14	17.74
2.3370	33.97	34.00	-0.03	42.97	17.67
3.0681	36.45	36.47	-0.02	45.50	17.55
3.3907	37.38	37.36	0.02	46.07	17.52
		$\begin{array}{c} t = 25.0^\circ \text{ C} \\ \bar{V}_1^\circ = 18.07 \text{ ml/mole} \end{array}$			
0.06362	19.61	19.68	-0.07	20.94	18.07
0.1167	20.70	20.58	0.12	22.31	18.06
0.3121	22.80	22.85	-0.05	25.86	18.05
0.6532	25.62	25.64	-0.02	30.30	18.01
0.9154	27.38	27.38	0.00	33.06	17.97
1.2368	29.26	29.24	0.02	35.98	17.92
1.5618	30.93	30.91	0.02	38.50	17.85
1.7911	32.01	31.99	0.02	40.06	17.81
1.9867	32.84	32.84	0.00	41.24	17.77

^{a}Calculated from Equation 5.17 together with parameters from Table 13 and Equation 6.9 together with parameters from Table 22, whichever gave the best agreement with the experimental data.

^{b}Calculated from Equation 6.10 and parameters from Table 27.

Table 29 (Continued)

Molality	$\phi_V{}^a$	$\phi_V{}^b$	$\Delta\phi_V$	$\bar{V}_2$	$\bar{V}_1$
		$t = 25.0°$ C			
		$\bar{V}_1^\circ = 18.07$ ml/mole			
2.3370	34.22	34.24	-0.02	43.04	17.70
3.0681	36.65	36.67	-0.02	45.56	17.58
3.3907	37.56	37.54	0.02	46.14	17.54
		$t = 30.0°$ C			
		$\bar{V}_1^\circ = 18.09$ ml/mole			
0.06362	19.88	19.95	-0.07	21.25	18.09
0.1167	21.00	20.88	0.12	22.65	18.09
0.3121	23.11	23.16	-0.05	26.16	18.08
0.6532	25.90	25.92	-0.02	30.51	18.04
0.9154	27.63	27.63	0.00	33.23	18.00
1.2368	29.48	29.47	0.01	36.10	17.94
1.5618	31.13	31.12	0.01	38.61	17.88
1.7911	32.20	32.18	0.02	40.15	17.84
1.9867	33.02	33.02	0.00	41.23	17.80
2.3370	34.38	34.40	-0.02	43.12	17.73
3.0681	36.78	36.81	-0.03	45.58	17.61
3.3907	37.69	37.67	0.02	46.11	17.58
		$t = 35.0°$ C			
		$\bar{V}_1^\circ = 18.12$ ml/mole			
0.06362	19.95	20.03	-0.08	21.40	18.12
0.1167	21.13	20.99	0.14	22.83	18.12
0.3121	23.26	23.32	-0.06	26.32	18.10
0.6532	26.04	26.07	-0.03	30.62	18.07
0.9154	27.76	27.76	0.00	33.30	18.03
1.2368	29.60	29.58	0.02	36.16	17.98
1.5618	31.24	31.22	0.02	38.67	17.91
1.7911	32.30	32.27	0.03	40.21	17.87
1.9867	33.11	33.11	0.00	41.39	17.83

Table 29 (Continued)

Molality	$\phi_V{}^a$	$\phi_V{}^b$	$\Delta\phi_V$	$\bar{V}_2$	$\bar{V}_1$
		$t = 35.0°$ C $\bar{V}_1^o = 18.12$ ml/mole			
2.3370	34.46	34.50	−0.04	43.19	17.76
3.0681	36.86	36.89	−0.03	45.59	17.64
3.3907	37.77	37.74	0.03	46.06	17.61
		$t = 40.0°$ C $\bar{V}_1^o = 18.16$ ml/mole			
0.06362	19.85	19.94	−0.09	21.39	18.15
0.1167	21.11	20.95	0.15	22.86	18.15
0.3121	23.28	23.34	−0.06	26.39	18.14
0.6532	26.07	26.09	−0.02	30.63	18.10
0.9154	27.77	27.78	−0.01	33.30	18.06
1.2368	29.62	29.60	0.02	36.17	18.01
1.5618	31.26	31.24	0.02	38.69	17.95
1.7911	32.32	32.29	0.03	40.25	17.90
1.9867	33.13	33.13	0.00	41.44	17.86
2.3370	34.48	34.52	−0.04	43.25	17.79
3.0681	36.88	36.92	−0.04	45.60	17.68
3.3907	37.80	37.77	0.03	46.00	17.65
		$t = 45.0°$ C $\bar{V}_1^o = 18.19$ ml/mole			
0.06362	19.62	19.71	−0.09	21.25	18.19
0.1167	20.94	20.77	0.17	22.77	18.19
0.3121	23.16	23.23	−0.07	26.33	18.17
0.6532	25.98	26.01	−0.03	30.57	18.14
0.9154	27.69	27.71	−0.02	33.24	18.10
1.2368	29.55	29.53	0.02	36.12	18.04
1.5618	31.20	31.17	0.03	38.67	17.98
1.7911	32.26	32.24	0.02	40.26	17.93
1.9867	33.08	33.08	0.00	41.46	17.89

Table 29 (Continued)

Molality	$\phi_V{}^a$	$\phi_V{}^b$	$\Delta\phi_V$	$\bar{V}_2$	$\bar{V}_1$
		$t = 45.0°$ C $\bar{V}_1^° = 18.19$ ml/mole			
2.3370	34.44	34.48	-0.04	43.29	17.82
3.0681	36.86	36.90	-0.04	45.62	17.71
3.3907	37.78	37.75	0.03	45.96	17.69
		$t = 50.0°$ C $\bar{V}_1^° = 18.23$ ml/mole			
0.06362	19.26	19.36	-0.10	20.98	18.23
0.1167	20.66	20.48	0.18	22.56	18.23
0.3121	22.94	23.01	-0.07	26.18	18.22
0.6532	25.80	25.83	-0.03	30.43	18.18
0.9154	27.52	27.54	-0.02	33.12	18.14
1.2368	29.40	29.38	0.02	36.03	18.08
1.5618	31.07	31.04	0.03	38.62	18.02
1.7911	32.14	32.11	0.03	40.23	17.97
1.9867	32.97	32.97	0.00	41.46	17.93
2.3370	34.35	34.39	-0.04	43.32	17.86
3.0681	36.80	36.84	-0.04	45.64	17.75
3.3907	37.73	37.69	0.04	45.95	17.73
		$t = 55.0°$ C $\bar{V}_1^° = 18.28$ ml/mole			
0.06362	18.79	18.90	-0.11	20.60	18.27
0.1167	20.26	20.07	0.19	22.23	18.27
0.3121	22.61	22.68	-0.07	25.93	18.26
0.6532	25.52	25.55	-0.03	30.22	18.22
0.9154	27.27	27.29	-0.02	32.94	18.18
1.2368	29.18	29.15	0.03	35.90	18.12
1.5618	30.87	30.84	0.03	38.54	18.06
1.7911	31.96	31.93	0.03	40.18	18.01
1.9867	32.80	32.80	0.00	41.44	17.97

Table 29 (Continued)

Molality	$\phi_V{}^a$	$\phi_V{}^b$	$\Delta\phi_V$	$\bar{V}_2$	$\bar{V}_1$
		$t = 55.0°$ C $\bar{V}_1^° = 18.28$ ml/mole			
2.3370	34.20	34.25	-0.05	43.34	17.89
3.0681	36.69	36.74	-0.05	45.68	17.78
3.3907	37.64	37.60	0.04	45.96	17.76
		$t = 60.0°$ C $\bar{V}_1^° = 18.32$ ml/mole			
0.06362	18.22	18.34	-0.12	20.12	18.32
0.1167	19.76	19.56	0.20	21.81	18.32
0.3121	22.18	22.26	-0.08	25.60	18.30
0.6532	25.16	25.20	-0.04	29.96	18.27
0.9154	26.94	26.96	-0.02	32.72	18.23
1.2368	28.89	28.86	0.03	35.73	18.17
1.5618	30.61	30.57	0.04	38.42	18.10
1.7911	31.72	31.69	0.03	40.10	18.05
1.9867	32.58	32.58	0.00	41.39	18.01
2.3370	34.01	34.05	-0.04	43.33	17.93
3.0681	36.55	36.60	-0.05	45.74	17.82
3.3907	37.52	37.48	0.04	46.02	17.80
		$t = 65.0°$ C $\bar{V}_1^° = 18.37$ ml/mole			
0.06362	17.56	17.68	-0.12	19.54	18.37
0.1167	19.15	18.95	0.20	21.28	18.37
0.3121	21.66	21.74	-0.08	25.17	18.35
0.6532	24.72	24.76	-0.04	29.63	18.31
0.9154	26.55	26.56	-0.01	32.44	18.27
1.2368	28.53	28.50	0.03	35.52	18.22
1.5618	30.29	30.25	0.04	38.28	18.15
1.7911	31.43	31.39	0.04	40.00	18.09
1.9867	32.30	32.30	0.00	41.32	18.05

Table 29 (Continued)

Molality	$\phi_V{}^a$	$\phi_V{}^b$	$\Delta\phi_V$	$\bar{V}_2$	$\bar{V}_1$
		$t = 65.0°$ C $\bar{V}_1^\circ = 18.37$ ml/mole			
2.3370	33.77	33.81	-0.04	43.32	17.97
3.0681	36.37	36.42	-0.05	45.80	17.85
3.3907	37.38	37.33	0.05	46.09	17.84
		$t = 70.0°$ C $\bar{V}_1^\circ = 18.42$ ml/mole			
0.06362	16.80	16.92	-0.12	18.86	18.42
0.1167	18.45	18.24	0.21	20.67	18.42
0.3121	21.05	21.14	-0.09	24.68	18.40
0.6532	24.20	24.24	-0.04	29.24	18.36
0.9154	26.08	26.09	-0.01	32.13	18.32
1.2368	28.12	28.08	0.04	35.28	18.26
1.5618	29.92	29.88	0.04	38.10	18.19
1.7911	31.08	31.05	0.03	39.88	18.14
1.9867	31.98	31.98	0.00	41.24	18.09
2.3370	33.48	33.53	-0.05	43.30	18.01
3.0681	36.16	36.21	-0.05	45.87	17.89
3.3907	37.20	37.15	0.05	46.18	17.87
		$t = 75.0°$ C $\bar{V}_1^\circ = 18.48$ ml/mole			
0.06362	15.93	16.06	-0.13	18.08	18.48
0.1167	17.65	17.44	0.21	19.97	18.47
0.3121	20.36	20.44	-0.08	24.12	18.46
0.6532	23.61	23.65	-0.04	28.80	18.42
0.9154	25.54	25.56	-0.02	31.76	18.38
1.2368	27.64	27.60	0.04	35.00	18.31
1.6518	29.49	29.45	0.04	37.91	18.24
1.7911	30.69	30.65	0.04	39.74	18.19
1.9867	31.61	31.62	-0.01	41.14	18.14

Table 29 (Continued)

Molality	$\phi_V{}^a$	$\phi_V{}^b$	$\Delta\phi_V$	$\bar{V}_2$	$\bar{V}_1$
		$t = 75.0°$ C $\bar{V}_1^\circ = 18.48$ ml/mole			
2.3370	33.16	33.21	-0.05	43.27	18.06
3.0681	35.92	35.98	-0.06	45.94	17.93
3.3907	36.99	36.94	0.05	46.26	17.91
		$t = 80.0°$ C $\bar{V}_1^\circ = 18.54$ ml/mole			
0.06362	14.94	15.07	-0.13	17.21	18.53
0.1167	16.74	16.52	0.22	19.19	18.53
0.3121	19.58	19.66	-0.08	23.48	18.52
0.6532	22.94	22.99	-0.05	28.31	18.47
0.9154	24.94	24.96	-0.02	31.36	18.43
1.2368	27.10	27.06	0.04	34.70	18.37
1.5618	29.01	28.97	0.04	37.70	18.29
1.7911	30.25	30.21	0.04	39.59	18.23
1.9867	31.20	31.21	-0.01	41.04	18.18
2.3370	32.80	32.85	-0.05	43.24	18.10
3.0681	35.66	35.71	-0.05	46.00	17.97
3.3907	36.76	36.71	0.05	46.34	17.95

Table 30. Values of ϕ_V, $\bar{V}_2$, and $\bar{V}_1$ in units of ml/mole for aqueous solutions of neodymium chloride

Molality	$\phi_V{}^a$	$\phi_V{}^b$	$\Delta\phi_V$	$\bar{V}_2$	$\bar{V}_1$
		$t = 20.0°$ C $\bar{V}_1^° = 18.05$ ml/mole			
0.1050	14.97	14.97	0.00	16.75	18.04
0.2992	17.43	17.42	0.01	20.44	18.03
0.6152	20.11	20.10	0.01	24.64	18.00
0.9007	22.02	22.05	-0.03	27.77	17.95
1.3170	24.50	24.50	0.00	31.73	17.88
1.6809	26.41	26.40	0.01	34.76	17.79
2.0853	28.32	28.31	0.01	37.72	17.69
2.2679	29.12	29.12	0.00	38.92	17.65
2.7090	30.92	30.93	-0.01	41.47	17.53
2.7553	31.10	31.11	-0.01	41.71	17.52
3.4160	33.46	33.45	0.01	44.53	17.36
		$t = 25.0°$ C $\bar{V}_1^° = 18.07$ ml/mole			
0.1050	15.51	15.51	0.00	17.32	18.06
0.2992	17.97	17.96	0.01	20.96	18.05
0.6152	20.61	20.60	0.01	25.06	18.02
0.9007	22.48	22.51	-0.03	28.10	17.98
1.3170	24.91	24.90	0.01	31.99	17.90
1.6809	26.79	26.77	0.02	34.98	17.82
2.0853	28.66	28.65	0.01	37.91	17.72
2.2679	29.45	29.45	0.00	39.11	17.67
2.7090	31.22	31.23	-0.01	41.65	17.56
2.7553	31.40	31.41	-0.01	41.89	17.55
3.4160	33.74	33.72	0.02	44.69	17.39

[a]Calculated from Equation 5.17 together with parameters from Table 14 and Equation 6.9 together with parameters from Table 23, whichever gave the best agreement with the experimental data.

[b]Calculated from Equation 6.10 and parameters from Table 28.

Table 30 (Continued)

Molality	$\phi_V{}^a$	$\phi_V{}^b$	$\Delta\phi_V$	$\bar{V}_2$	$\bar{V}_1$
		$t = 30.0°$ C $\bar{V}_1^° = 18.09$ ml/mole			
0.1050	15.86	15.86	0.00	17.69	18.09
0.2992	18.34	18.32	0.02	21.32	18.08
0.6152	20.95	20.95	0.00	25.35	18.04
0.9007	22.80	22.83	−0.03	28.36	18.00
1.3170	25.20	25.20	0.00	32.19	17.93
1.6809	27.06	27.04	0.02	35.16	17.85
2.0853	28.91	28.90	0.01	38.09	17.75
2.2679	29.70	29.69	0.01	39.28	17.70
2.7090	31.45	31.47	−0.02	41.83	17.59
2.7553	31.63	31.64	−0.01	42.07	17.58
3.4160	33.96	33.95	0.01	44.88	17.42
		$t = 35.0°$ C $\bar{V}_1^° = 18.12$ ml/mole			
0.1050	16.02	16.03	−0.01	17.90	18.12
0.2992	18.54	18.53	0.01	21.54	18.11
0.6152	21.16	21.15	0.01	25.55	18.07
0.9007	23.00	23.03	−0.03	28.52	18.03
1.3170	25.39	25.38	0.01	32.34	17.96
1.6809	27.23	27.22	0.01	35.31	17.88
2.0853	29.09	29.08	0.01	38.24	17.78
2.2679	29.87	29.86	0.01	39.44	17.73
2.7090	31.62	31.64	−0.02	42.01	17.62
2.7553	31.80	31.82	−0.02	42.25	17.60
3.4160	34.13	34.12	0.01	45.08	17.45
		$t = 40.0°$ C $\bar{V}_1^° = 18.16$ ml/mole			
0.1050	16.04	16.04	0.00	17.96	18.15
0.2992	18.60	18.59	0.01	21.64	18.14
0.6152	21.24	21.24	0.00	25.65	18.11

Table 30 (Continued)

Molality	$\emptyset_V{}^a$	$\emptyset_V{}^b$	$\Delta\emptyset_V$	$\bar{V}_2$	$\bar{V}_1$
		$t = 40.0°$ C $\bar{V}_1^\circ = 18.16$ ml/mole			
0.9007	23.08	23.12	-0.04	28.62	18.07
1.3170	25.48	25.47	0.01	32.44	17.99
1.6809	27.32	27.31	0.01	35.43	17.91
2.0853	29.19	29.18	0.01	38.38	17.81
2.2679	29.97	29.97	0.00	29.60	17.76
2.7079	31.74	31.75	-0.01	42.19	17.65
2.7553	31.92	31.93	-0.01	42.43	17.63
3.4160	34.26	34.26	0.00	45.29	17.48
		$t = 45.0°$ C $\bar{V}_1^\circ = 18.19$ ml/mole			
0.1050	15.90	15.90	0.00	17.90	18.19
0.2992	18.53	18.52	0.01	21.64	18.18
0.6152	21.21	21.21	0.00	25.66	18.14
0.9007	23.07	23.10	-0.03	28.65	18.10
1.3170	25.48	25.48	0.00	32.50	18.03
1.6809	27.34	27.33	0.01	35.52	17.94
2.0853	29.22	29.21	0.01	38.51	17.84
2.2679	30.01	30.01	0.00	39.74	17.80
2.7090	31.80	31.82	-0.02	42.36	17.68
2.7553	31.99	32.00	-0.01	42.61	17.66
3.4160	34.36	34.35	0.01	45.48	17.51
		$t = 50.0°$ C $\bar{V}_1^\circ = 18.23$ ml/mole			
0.1050	15.63	15.63	0.00	17.71	18.23
0.2992	18.35	18.34	0.01	21.53	18.22
0.6152	21.08	21.08	0.00	25.60	18.18

Table 30 (Continued)

Molality	$\phi_V{}^a$	$\phi_V{}^b$	$\Delta\phi_V$	$\bar{V}_2$	$\bar{V}_1$
		$t = 50.0°$ C $\bar{V}_1^\circ = 18.23$ ml/mole			
0.9007	22.97	23.00	-0.03	28.61	18.14
1.3170	25.41	25.40	0.01	32.52	18.06
1.6809	27.29	27.28	0.01	35.58	17.98
2.0853	29.20	29.19	0.01	38.63	17.88
2.2679	30.00	30.00	0.00	39.88	17.83
2.7090	31.81	31.83	-0.02	42.54	17.71
2.7553	32.00	32.01	-0.01	42.79	17.70
3.4160	34.41	34.40	0.01	45.68	17.54
		$t = 55.0°$ C $\bar{V}_1^\circ = 18.28$ ml/mole			
0.1050	15.24	15.24	0.00	17.42	18.27
0.2992	18.07	18.05	0.02	21.34	18.26
0.6152	20.85	20.86	-0.01	25.47	18.22
0.9007	22.78	22.81	-0.03	28.52	18.18
1.3170	25.27	25.26	0.01	32.49	18.10
1.6809	27.18	27.16	0.02	35.62	18.02
2.0853	29.12	29.11	0.01	38.73	17.91
2.2679	29.94	29.94	0.00	40.00	17.86
2.7090	31.79	31.80	-0.01	42.72	17.74
2.7553	31.98	31.99	-0.01	42.97	17.73
3.4160	34.43	34.42	0.01	45.86	17.57
		$t = 60.0°$ C $\bar{V}_1^\circ = 18.32$ ml/mole			
0.1050	14.73	14.74	-0.01	17.02	18.32
0.2992	17.69	17.67	0.02	21.07	18.30
0.6152	20.54	20.55	-0.01	25.27	18.27

Table 30 (Continued)

Molality	$\phi_V{}^a$	$\phi_V{}^b$	$\Delta\phi_V$	$\bar{V}_2$	$\bar{V}_1$

$$t = 60.0° \text{ C}$$
$$\bar{V}_1^° = 18.32 \text{ ml/mole}$$

Molality	$\phi_V{}^a$	$\phi_V{}^b$	$\Delta\phi_V$	$\bar{V}_2$	$\bar{V}_1$
0.9007	22.52	22.55	−0.03	28.38	18.23
1.3170	25.05	25.04	0.01	32.43	18.15
1.6809	27.01	26.99	0.02	35.63	18.06
2.0853	29.00	28.98	0.02	38.82	17.95
2.2679	29.83	29.83	0.00	40.12	17.90
2.7090	31.72	31.74	−0.02	42.88	17.78
2.7553	31.92	31.93	−0.01	43.14	17.76
3.4160	34.41	34.40	0.01	46.02	17.61

$$t = 65.0° \text{ C}$$
$$\bar{V}_1^° = 18.37 \text{ ml/mole}$$

Molality	$\phi_V{}^a$	$\phi_V{}^b$	$\Delta\phi_V$	$\bar{V}_2$	$\bar{V}_1$
0.1050	14.12	14.13	−0.01	16.54	18.37
0.2992	17.22	17.19	0.03	20.72	18.35
0.6152	20.15	20.16	−0.01	25.01	18.32
0.9007	22.18	22.21	−0.03	28.18	18.28
1.3170	24.78	24.77	0.01	32.33	18.19
1.6809	26.79	26.77	0.02	35.62	18.10
2.0853	28.82	28.81	0.01	38.90	17.99
2.2679	29.68	29.68	0.00	40.24	17.94
2.7090	31.61	31.63	−0.02	43.05	17.81
2.7553	31.81	31.83	−0.02	43.31	17.80
3.4160	34.36	34.35	0.01	46.17	17.64

$$t = 70.0° \text{ C}$$
$$\bar{V}_1^° = 18.42 \text{ ml/mole}$$

Molality	$\phi_V{}^a$	$\phi_V{}^b$	$\Delta\phi_V$	$\bar{V}_2$	$\bar{V}_1$
0.1050	13.42	13.43	−0.01	15.97	18.42
0.2992	16.66	16.63	0.03	20.30	18.40
0.6152	19.69	19.70	−0.01	24.68	18.37
0.9007	21.77	21.81	−0.02	27.94	18.32
1.3170	24.45	24.43	0.02	32.21	18.24
1.6809	26.51	26.49	0.02	35.60	18.15

Table 30 (Continued)

Molality	$\phi_V{}^a$	$\phi_V{}^b$	$\Delta\phi_V$	$\bar{V}_2$	$\bar{V}_1$
		$t = 70.0°$ C $\bar{V}_1^\circ = 18.42$ ml/mole			
2.0853	28.60	28.59	0.01	38.97	18.03
2.2679	29.48	29.48	0.00	40.34	17.98
2.7090	31.46	31.49	−0.03	43.21	17.85
2.7553	31.67	31.69	−0.02	43.47	17.84
3.4160	34.28	34.27	0.01	46.29	17.68
		$t = 75.0°$ C $\bar{V}_1^\circ = 18.48$ ml/mole			
0.1050	12.62	12.63	−0.01	15.31	18.47
0.2992	16.02	15.98	0.04	19.79	18.46
0.6152	19.15	19.16	−0.01	24.31	18.42
0.9007	21.30	21.34	−0.04	27.66	18.38
1.3170	24.06	24.04	0.02	32.06	18.29
1.6809	26.18	26.16	0.02	25.55	18.20
2.0853	28.34	28.32	0.02	39.02	18.08
2.2679	29.24	29.24	0.00	40.43	18.02
2.7090	31.28	31.31	−0.03	43.35	17.89
2.7553	31.50	31.52	−0.02	43.62	17.88
3.4160	34.18	34.16	0.02	46.42	17.72
		$t = 80.0°$ C $\bar{V}_1^\circ = 18.54$ ml/mole			
0.1050	11.74	11.75	−0.01	14.55	18.53
0.2992	15.28	15.25	0.03	19.21	18.52
0.6152	18.53	18.55	−0.02	23.88	18.48
0.9007	20.76	20.80	−0.04	27.34	18.43
1.3170	23.61	23.60	0.01	31.88	18.34
1.6809	25.81	25.79	0.02	35.48	18.24

Table 30 (Continued)

Molality	$\emptyset_V{}^a$	$\emptyset_V{}^b$	$\Delta\emptyset_V$	$\bar{V}_2$	$\bar{V}_1$
		$t = 80.0°$ C $\bar{V}_1^\circ = 18.54$ ml/mole			
2.0853	28.04	28.02	0.02	39.06	18.12
2.2679	28.97	28.97	0.00	40.50	18.07
2.7090	31.07	31.10	-0.03	43.49	17.93
2.7553	31.29	31.31	-0.02	43.76	17.92
3.4160	34.04	34.02	0.02	46.56	17.76

volume and apparent molal volume empirical equations, Equations 5.17 and 6.9, and the apparent molal volumes calculated from Equation 6.10 are given in Tables 29 and 30.

Although apparent molal volumes had been calculated since the early 1900's, it was not until 1929 that Masson (53) observed that the apparent molal volumes of dilute electrolytic solutions varied linearly with the square root of the molar concentration. Furthermore, Masson noted that this linear relationship often extended to concentrated solutions.

From the Debye-Hückel limiting law, Equation 2.27, and the relationship between the partial molal volume of a component and the partial molal free energy of that component given by

$$\bar{V}_i = (\partial \bar{F}_i / \partial P)_T, \tag{6.13}$$

Redlich and Rosenfeld (54) showed in 1931 that

$$\bar{V}_2 = \bar{V}_2^\circ + S_V c^{1/2}. \tag{6.14}$$

In Equation 6.14, $\bar{V}_2^\circ$ is the partial molal volume of the solute at infinite dilution, and

$$S_V = (3/2)RT\sigma(\partial \ln D/\partial P) - (1/2)RT\sigma\beta_\circ \tag{6.15}$$

in which $\beta_\circ$ is the isothermal coefficient of compressibility of the solvent, and

$$\sigma = (\pi N\epsilon^6/1000)^{1/2} \cdot \left[D \sum_{i=1}^{s} \nu_i z_i^2 \right]^{3/2} \tag{6.16}$$

For a particular solute, solvent, temperature, and pressure, it is seen that S_V is a constant, and therefore for very dilute solutions the partial molal volume of the solute should become linear with the square root of concentration. Also, from Equations 6.4 and 6.14 and from the fact that

$$\lim_{c \to 0} (c/m) = 1 \, , \tag{6.17}$$

it can be shown that the apparent molal volume should be linear with concentration for very dilute solutions.

It is emphasized, however, that the limiting laws for the partial molal volume and apparent molal volume of the solute as derived by Redlich and Rosenfeld from the Debye-Hückel limiting law do not constitute a theoretical verification of the empirical observations of Masson. The limiting law applies only to very dilute solutions, whereas the observations of Masson were concerned with electrolytic solutions of intermediate concentrations.

Experimental verification of Masson's observations over the temperature range of 0 to 70° C was also obtained by Scott (55) from the data of Baxter and Wallace (56) and by Geffcken (57) who combined his data with that from

several other sources (58, 59, 60, 61). The work of Masson, Scott, and Geffcken indicates that as a general rule the apparent molal volumes of aqueous electrolytic solutions are linear with respect to the square root of molarity over wide ranges of concentration and temperature. Masson found that magnesium nitrate and sodium acetate did not conform to this rule. Furthermore, Masson found that the plotted points for sulfuric acid, lithium chloride, nitric acid, and ammonium nitrate exhibited abrupt changes from a linear relationship at relatively high concentrations. The data of Gibson and Kincaid (62), Scott, et al. (63, 64), Baxter and Wallace (56), and Hüttig and Kükenthal (58) show that a plot of the apparent molal volume of lithium bromide versus $c^{1/2}$ exhibits a sharp transition from a straight line when the concentration is about 0.6 molar. In addition, the above investigations have shown that the ϕ_V versus $c^{1/2}$ plots of salts of the same valence type, such as the alkali halides, exhibit different slopes for the intermediate to high concentrations. This is in direct conflict with the limiting law derived by Redlich and Rosenfeld which would predict a common slope for salts of the same valence type. No satisfactory reason has yet been given for the linearity of ϕ_V with $c^{1/2}$ at higher concentrations, but some attempts have been made to explain the differences between the slopes of the curves at the higher concentrations (55, 65, 66, 67, 68).

Measurements for very dilute solutions by Geffcken, Beckmann, and Kruis (69); Kruis (70); and Geffcken, Kruis, and Solana (71) indicate that at the more dilute solutions, salts of the same valence type converge towards an identical slope as predicted by the limiting law. The differences

between the limiting slope and the slopes of the curves at higher concentrations causes the ϕ_V versus $c^{1/2}$ plots to exhibit somewhat sigmoid shapes.

The data obtained in this research is concerned with higher concentrations, and therefore, can not be expected to obey the limiting law. However, the apparent and partial molal volumes are plotted versus $c^{1/2}$ in order to examine the agreement with Masson's rule.

Plots of ϕ_V versus $c^{1/2}$ for lanthanum chloride and neodymium chloride at 25 and 75° C are given in Figures 9 and 10, respectively. Apparent molal volumes of several concentrations each of aqueous lanthanum chloride and neodymium chloride solutions are plotted versus temperature in Figures 11 and 12, respectively.

In Figures 13 and 14, $\bar{V}_2$ is plotted versus $c^{1/2}$ for lanthanum chloride and neodymium chloride at 25° C and 75° C, respectively. Plots of $\bar{V}_2$ versus temperature are given in Figures 15 and 16 for several concentrations each of the aqueous lanthanum chloride and neodymium chloride solutions.

In Figure 17, the partial molal volumes of water associated with the lanthanum chloride and neodymium chloride solutions are plotted versus molality for the temperatures 25, 50, and 75° C. Plots of the partial molal volumes of water in several concentrations each of the aqueous lanthanum chloride and neodymium chloride solutions versus temperature are given in Figure 18.

Apparent molal volumes are simply the change in volume accompanying the dissolution of one mole of the solute in enough solvent necessary for that particular concentration. For dilute solutions, in which the total
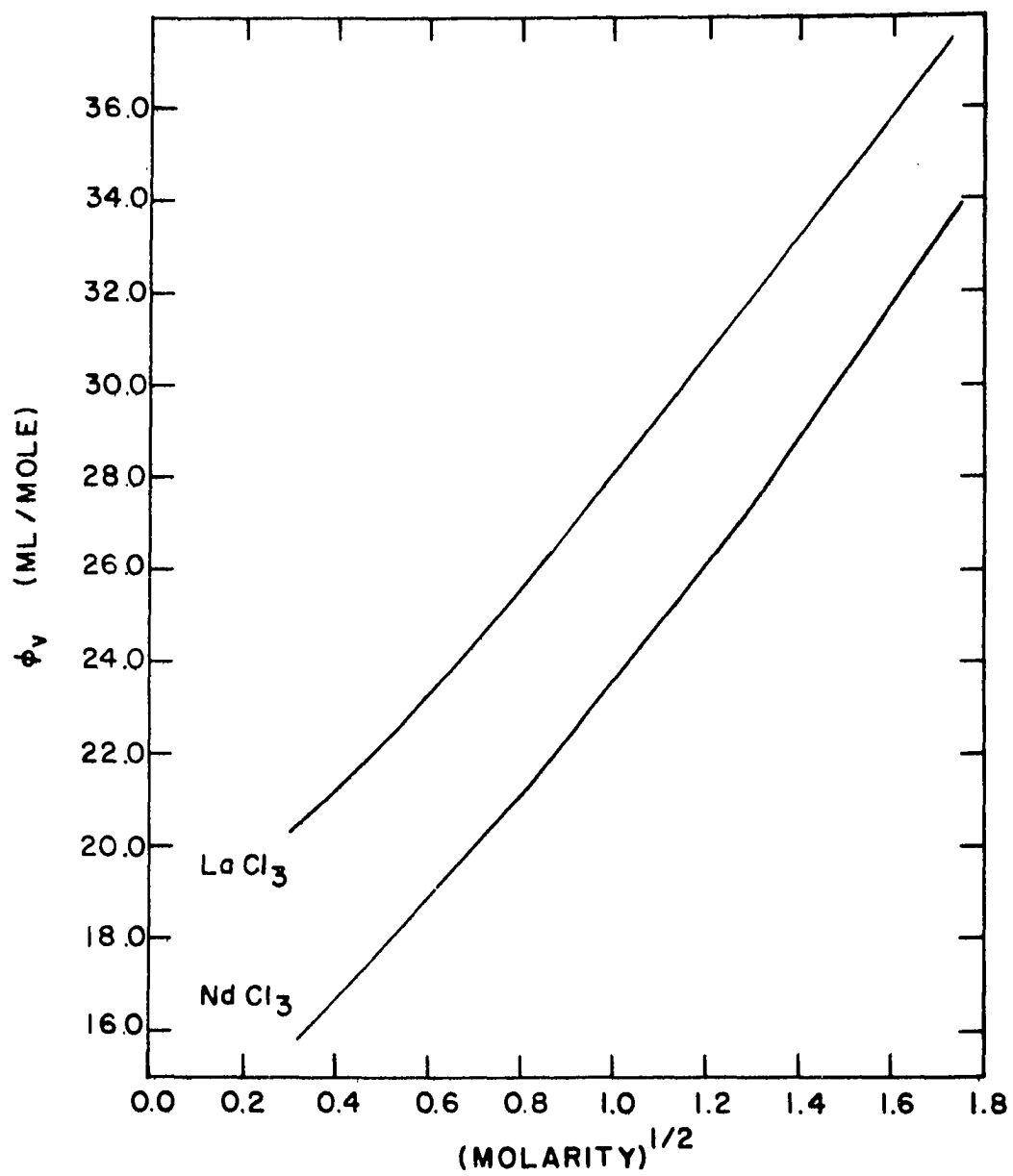
Figure 9. Apparent molal volumes of aqueous lanthanum chloride neodymium chloride solutions at 25° C
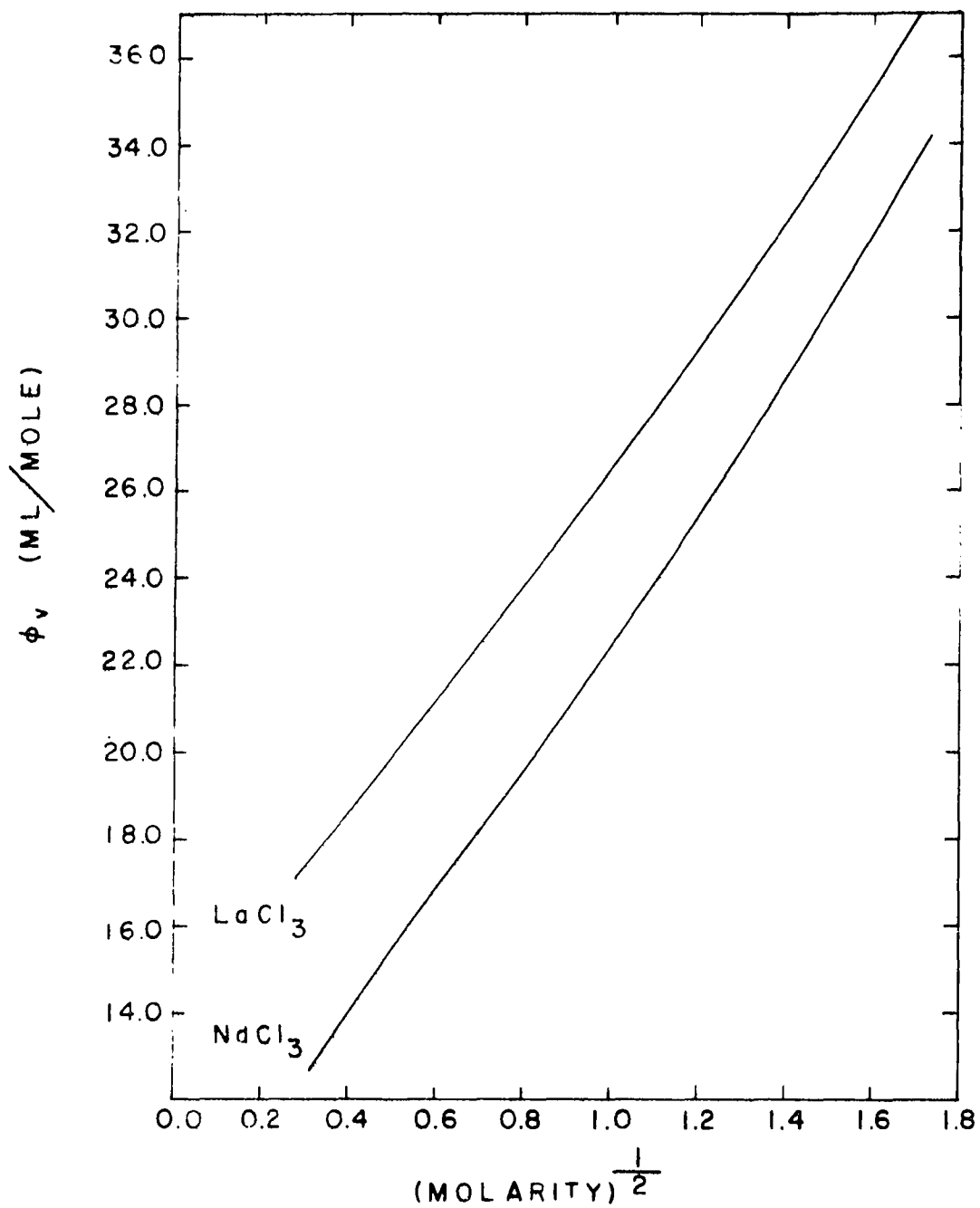
Figure 10. Apparent molal volumes of aqueous lanthanum chloride and
neodymium chloride solutions at 75° C
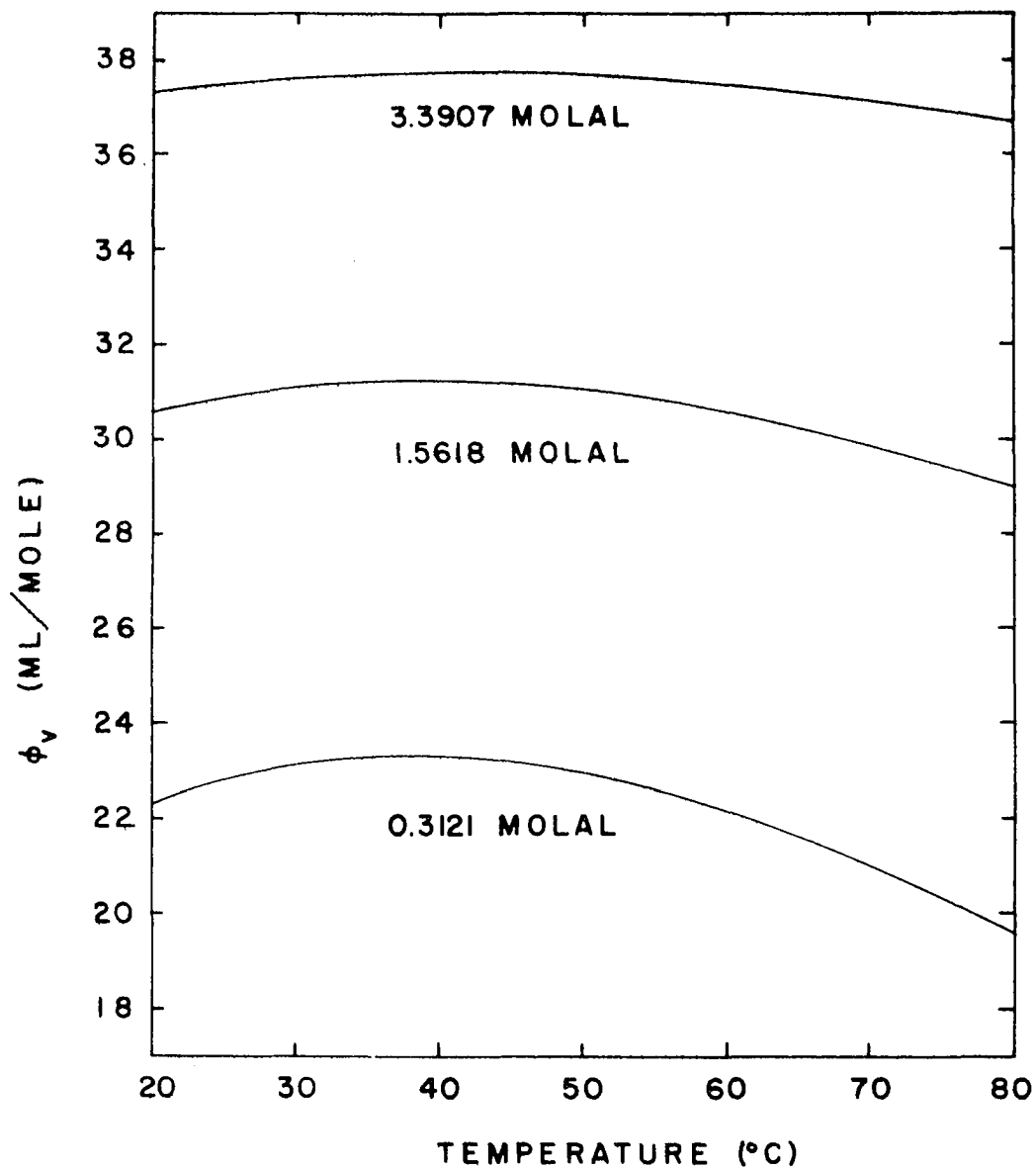
Figure 11. Apparent molal volumes of some aqueous lanthanum chloride
solutions
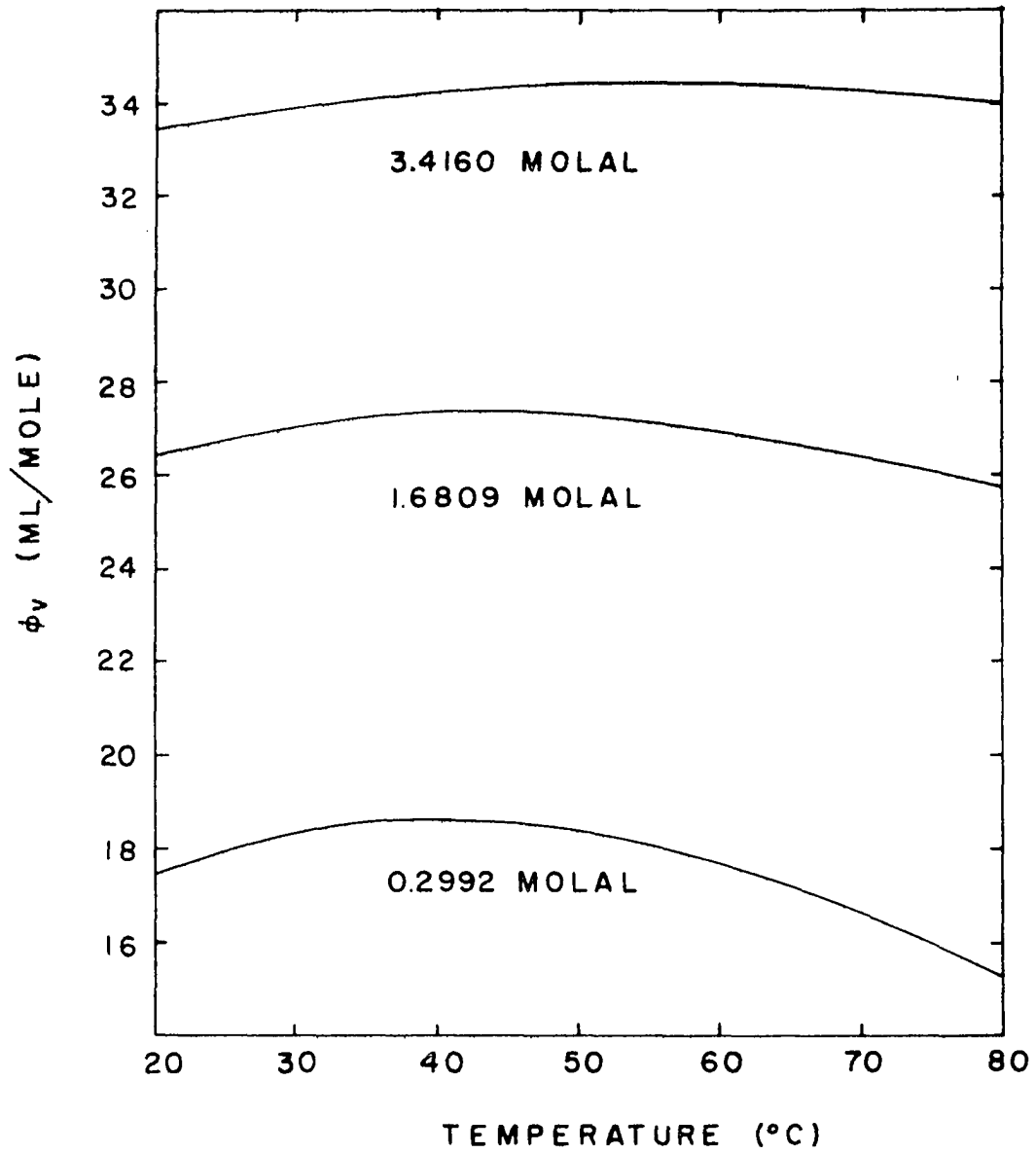
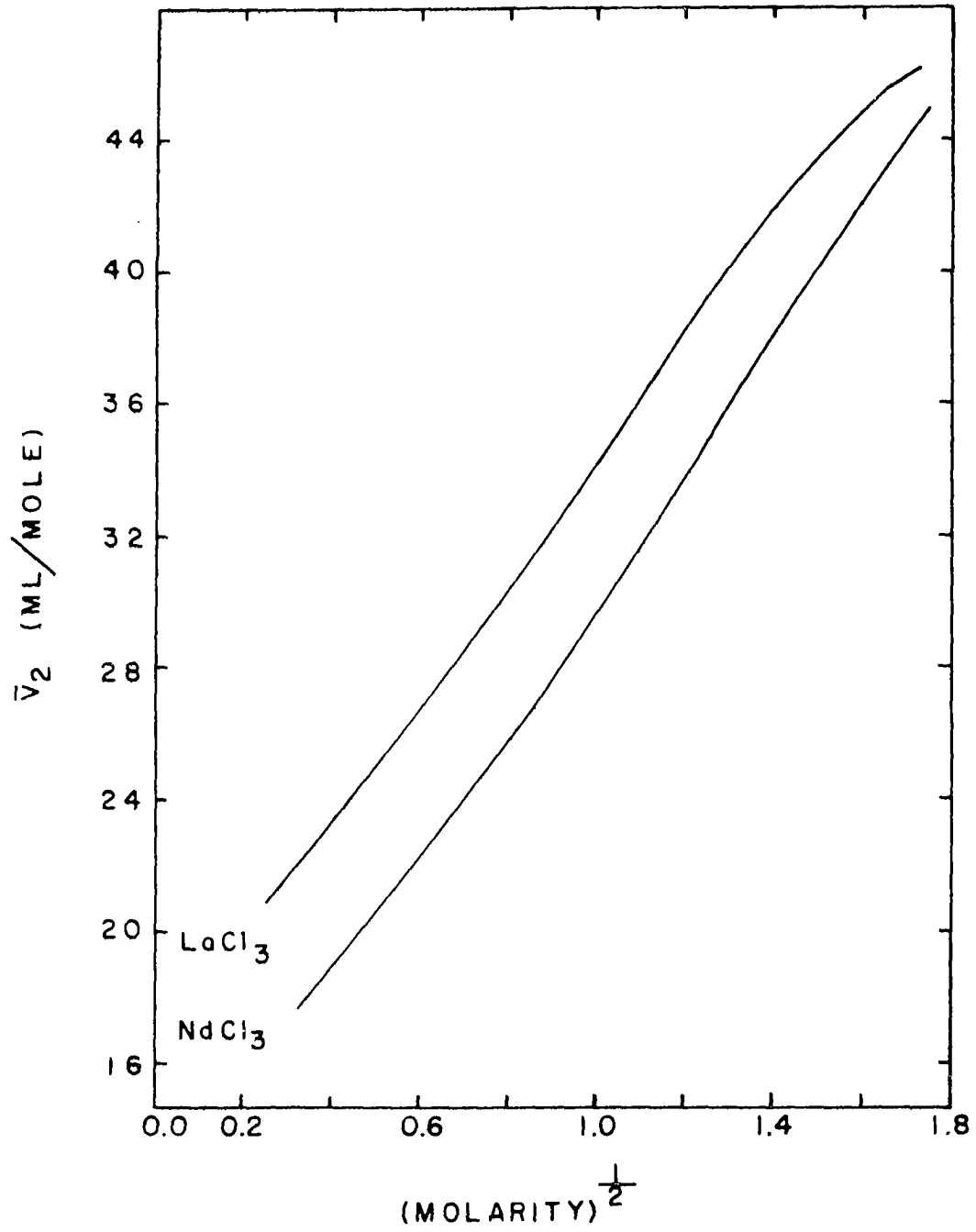Figure 12. Apparent molal volumes of some aqueous neodymium chloride solutions

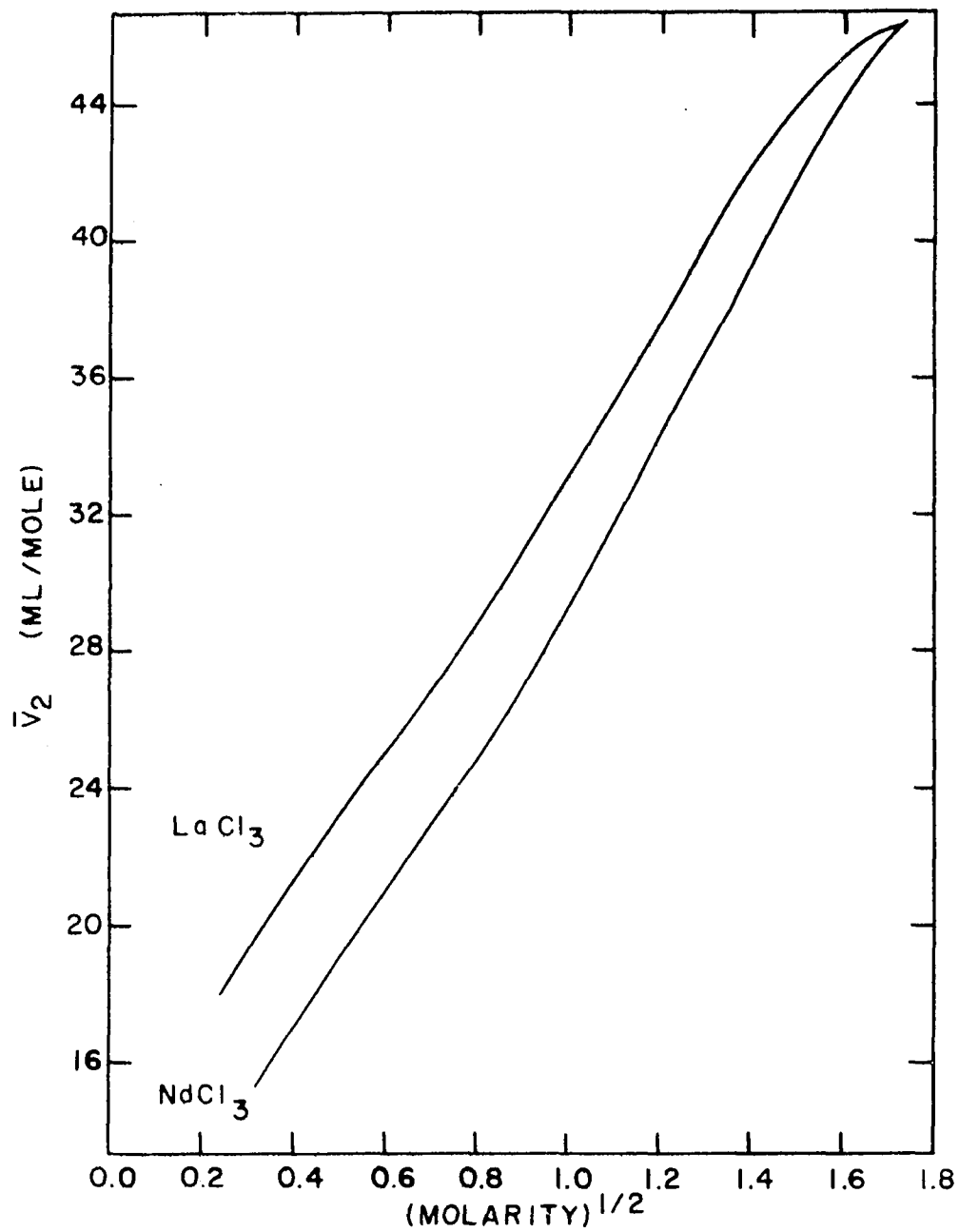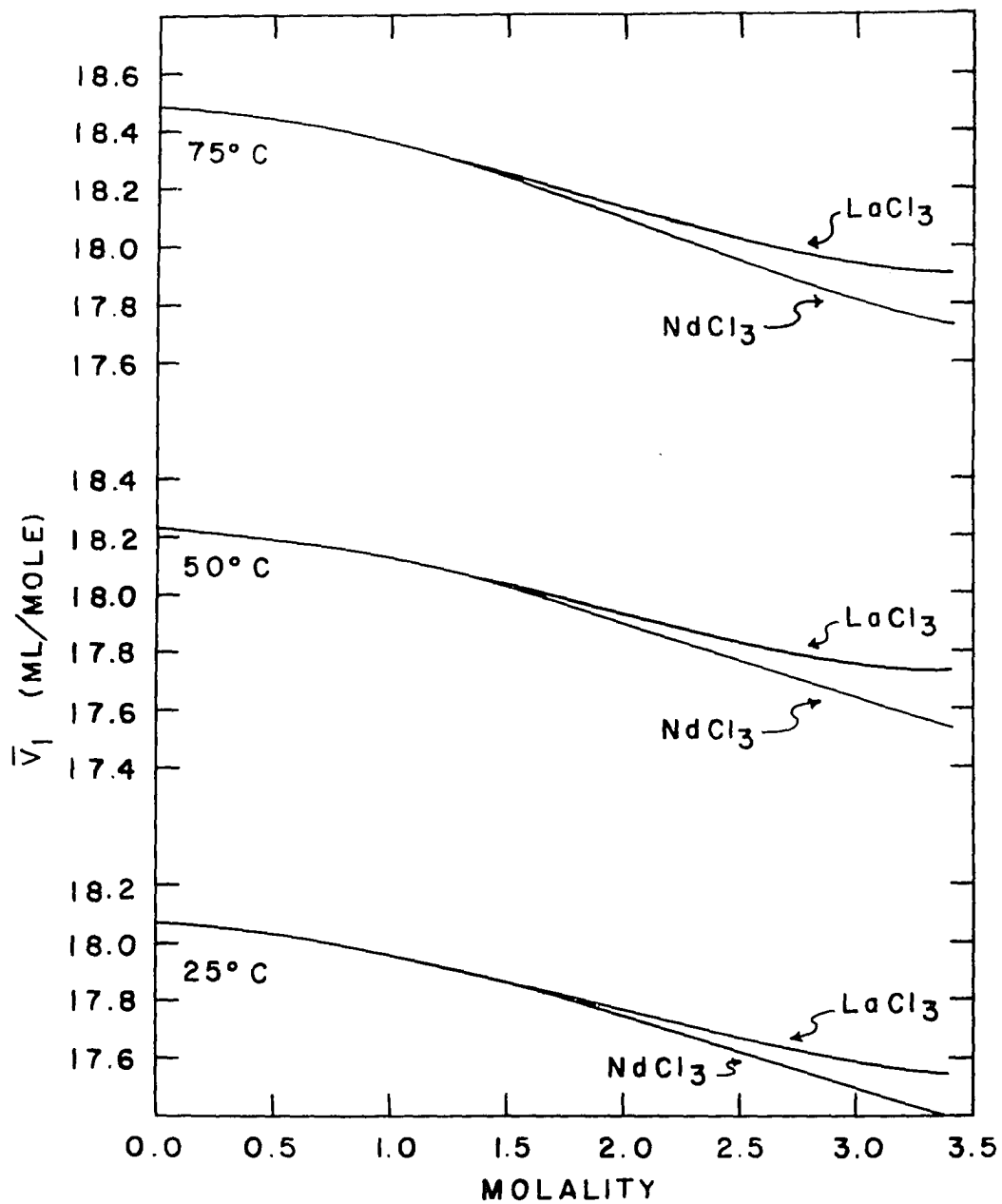Figure 13. Partial molal volumes of lanthanum chloride and neodymium chloride in aqueous solutions of these salts at 25° C

Figure 14. Partial molal volumes of lanthanum chloride and neodymium
chloride in aqueous solutions of these salts at 75° C
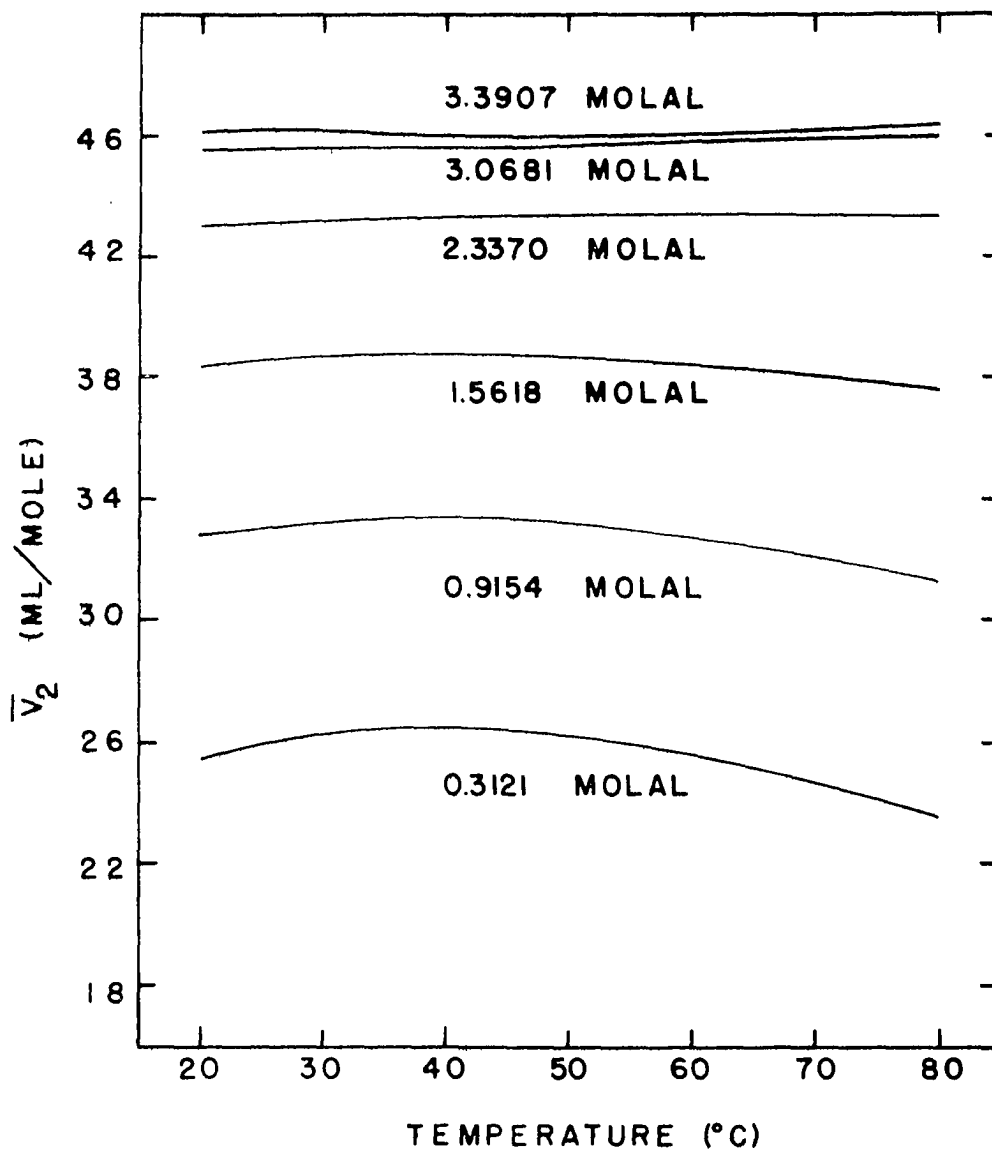
Figure 15. Partial molal volumes of lanthanum chloride in some aqueous solutions of this salt
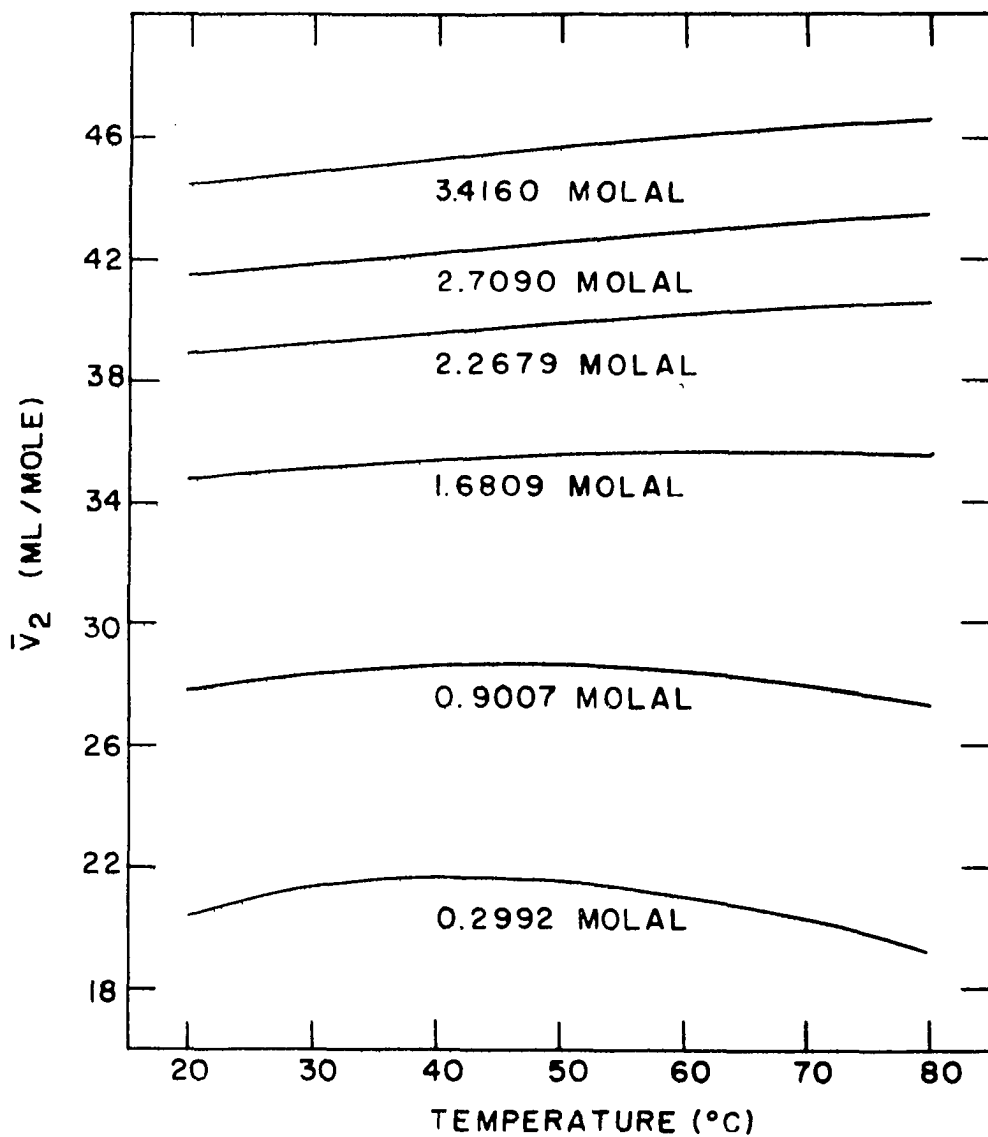
Figure 16. Partial molal volumes of neodymium chloride in some aqueous solutions of this salt

Figure 17. Partial molal volumes of water in aqueous lanthanum chloride and neodymium chloride solutions at 25, 50, and 75° C
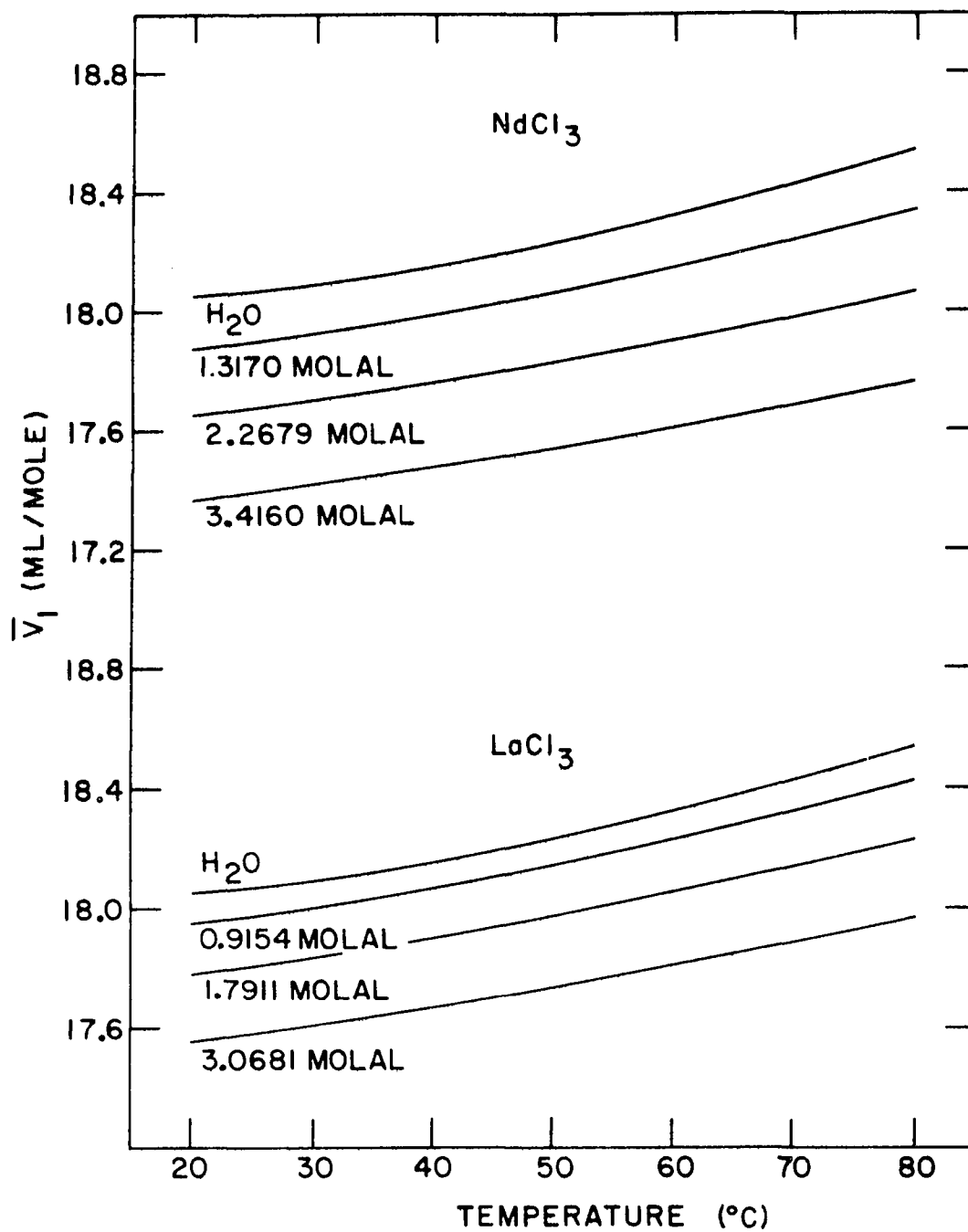
Figure 18. Partial molal volumes of water in some aqueous lanthanum chloride and neodymium chloride solutions

solvent structure is only slightly changed upon addition of the solute, apparent molal volumes give a good approximation of the volume due to the solute. On the other hand, the partial molal volume of a solution component is the volume change occuring when one mole of that component is added to a sufficient quantity of solution such that the change in concentration is negligible upon addition of the solute. Hence, the partial molal volume gives a much more realistic picture of the volume of the solution component than does the apparent molal volume, especially at higher concentrations.

From the plots of apparent and partial molal volumes given in Tables 9 through 18, the following observations were made:

1. The ϕ_V versus $c^{1/2}$ plots given in Figures 9 and 10 are not exactly linear, but the curvature is not excessive, and hence, these ϕ_V data obey Masson's rule to the first approximation.

2. The $\bar{V}_2$ versus $c^{1/2}$ plots given in Figures 13 and 14 are not linear, but exhibit a sigmoid shape. The values of $\bar{V}_2$ for lanthanum chloride are larger than for neodymium chloride. However, the differences in $\bar{V}_2$ between the lanthanum and neodymium chlorides decreases with both increasing temperature and increasing concentration until at 75° C they are approximately equal for the most concentrated solutions.

3. Past investigations (72, 73, 74, 75, 76) have shown that plots of ϕ_V versus temperature exhibit maxima. The temperatures at which these maxima occur have been shown to increase slightly with increasing concentration, and furthermore, there is a considerable decrease in the curvature of the plot with an increase in concentration. These generalizations are

verified with the data of the aqueous lanthanum chloride and neodymium chloride solutions given in Figures 11 and 12, respectively.

4. The above past investigations (72, 73, 74, 75, 76) also indicate that the situation with $\bar{V}_2$ as a function of temperature is similar to that of ϕ_V. The results with lanthanum chloride and neodymium chloride obtained in this research and shown in Figures 15 and 16, respectively, deviate somewhat from this. It is observed that as the concentration increases, the maxima in the $\bar{V}_2$ versus t plots disappear. Also, it is noticed that for the most concentrated solutions, $\bar{V}_2$ for lanthanum chloride remains practically constant with a change in temperature, whereas with neodymium chloride, $\bar{V}_2$ increases steadily with temperature for the most concentrated solutions.

5. From Figure 17, it is observed that the values of $\bar{V}_1$ for the aqueous lanthanum and neodymium chloride solutions of concentrations 1.5 molal and less are equal. However, above 1.5 molal the values of $\bar{V}_1$ for lanthanum chloride are greater than those for neodymium chloride, the difference increasing with increasing concentration.

6. The plots of $\bar{V}_1$ versus temperature for the lanthanum and neodymium solutions given in Figure 18 indicate that for all concentrations, $\bar{V}_1$ increases with temperature. Furthermore, the various constant molality curves exhibit very little curvature, and parallel the other curves for the same salt very closely over the entire temperature range.

C. Apparent and Partial Molal Expansibilities

The coefficient of thermal expansion of a solution as defined by Equation 5.1 is an intensive property rather than an extensive property, and therefore, α can not be used in defining an apparent molal property. The expansibility, E, of a solution defined as

$$E = \alpha V = (\partial V/\partial T)_{P,n_1} \qquad (6.18)$$

is, however, an extensive property. Using this property, Gucker (77) defined the apparent molal expansibility as

$$\phi_E = (E - n_1 \bar{E}_1^\circ)/n_2. \qquad (6.19)$$

However, as was pointed out by Vogel (47), Gucker did not define the coefficient of thermal expansion correctly.

Substituting $E = \alpha V$, $V = (1000 + mM_2)/d$, $\bar{E}_1^\circ = \alpha_o \bar{V}_1^\circ$, $n_1 \bar{V}_1^\circ = 1000/d_o$, and $n_2 = m$ into Equation 6.19 gives

$$\phi_E = \left[1000(\alpha d_o - \alpha_o d)/mdd_o\right] + \alpha M_2/d \qquad (6.20)$$

in which d is the density of the solution, d_o is the density of water, α is the coefficient of thermal expansion of the solution, α_o is the coefficient of thermal expansion of water, m is the molality of the solution, and M_2 is the molecular weight of the salt.

Upon differentiation of Equation 6.7 with respect to temperature and upon substitution of Equations 6.18 and 6.19 into the result, it is found that

$$\emptyset_E = (\partial \emptyset_V / \partial T)_{P,n_i} . \tag{6.21}$$

It was found when calculating values of $\emptyset_V$ at five degree temperature intervals from 20 to 80° C, that empirical equations representing $\bar{v}$ as a function of temperature gave better agreement with experimental values of $\emptyset_V$ for certain lanthanum and neodymium chloride solutions. For the remaining lanthanum and neodymium chloride solutions, empirical equations representing $\emptyset_V$ as a function of temperature gave better agreement with the experimental values of $\emptyset_V$. Those empirical equations giving the best agreement with the experimental apparent molal volumes were also used to calculate the values of $\emptyset_E$ at five degree intervals from 20 to 80° C.

Apparent molal expansibilities were computed from the empirical specific volume versus temperature equations through the use of Equation 6.20. The densities and coefficients of thermal expansion needed were obtained from the values given in Tables 18 and 19.

Then the empirical equations representing the apparent molal volume as a function of temperature were used, the apparent molal expansibilities were obtained by differentiating the empirical equation with respect to temperature in accordance with Equation 6.21. Empirical equations of the form

$$\emptyset_E = A + Bm^{1/2} + Cm + Dm^{3/2} + Em^2 \tag{6.22}$$

were computed according to the method of least squares from the calculated apparent molal expansibilities of the lanthanum chloride and neodymium chloride solutions at five degree intervals from 20 to 80° C. The parameters

obtained at each of these temperatures are given in Tables 31 and 32 for

lanthanum chloride and neodymium chloride, respectively.

Values of the partial molal expansibilities of both the salt, $\bar{E}_2$, and

water, $\bar{E}_1$, for the lanthanum and neodymium chloride solutions were

calculated from the empirical equations of the form given in Equation 6.22

together with the parameters given in Tables 31 and 32 in accordance with

relationships for $\bar{E}_2$ and $\bar{E}_1$ generalized in Equations 6.4 and 6.6,

respectively. These calculated values of $\bar{E}_2$ and $\bar{E}_1$ plus the values of ϕ_E

calculated from the empirical specific volume and apparent molal equations,

the values of ϕ_E calculated from Equation 6.22 and the parameters given in

Tables 31 and 32, and the differences between these two sets of ϕ_E values

are tabulated in Tables 33 and 34 for the aqueous lanthanum chloride and

neodymium chloride solutions, respectively.

In addition to defining the apparent molal expansibility, Gucker (77)

used the density data for LiCl, NaCl, and KCl obtained by Geffcken (57) and

Baxter and Wallace (56) to show that apparent molal expansibilities, of

these electrolytes were linear functions of $c^{1/2}$ over a wide ranges of

concentration and temperature. In the same paper, Gucker (77) used the

density data for sodium sulfate obtained by Gibson (78) and density data

for HCl, LiOH, and NaOH tabulated in the International Critical Tables (79)

to show that the apparent molal expansibilities of these salts were also

linear functions of $c^{1/2}$ over a considerable concentration range. These

observations are similar to those which Masson (53) made concerning apparent

molal volumes.

Table 31. Parameters for lanthanum chloride corresponding to Equation 6.22

Temperature (°C)	A	B	C	D	E
20.0	0.12520	0.00874	-0.04253	-0.00688	0.00780
25.0	0.05092	0.15117	-0.24266	0.12614	-0.02290
30.0	-0.00679	0.23761	-0.35346	0.19940	-0.03982
35.0	-0.05096	0.28115	-0.39908	0.23022	-0.04710
40.0	-0.08441	0.29317	-0.39929	0.23235	-0.04799
45.0	-0.10961	0.28173	-0.36470	0.21195	-0.04377
50.0	-0.12914	0.25588	-0.30885	0.17760	-0.03638
55.0	-0.14584	0.22702	-0.25110	0.14263	-0.02892
60.0	-0.16220	0.20340	-0.20285	0.11389	-0.02287
65.0	-0.18064	0.19266	-0.17410	0.09714	-0.01944
70.0	-0.20363	0.20293	-0.17542	0.09842	-0.01988
75.0	-0.23359	0.24157	-0.21583	0.12263	-0.02517
80.0	-0.27296	0.31629	-0.30481	0.17491	-0.03632

Table 32. Parameters for neodymium chloride corresponding to Equation 6.22

Temperature (°C)	A	B	C	D	E
20.0	0.10172	0.15301	-0.25382	0.12414	-0.02057
25.0	0.06191	0.13920	-0.21295	0.10522	-0.01767
30.0	0.02359	0.13555	-0.18448	0.09112	-0.01538
35.0	-0.01430	0.14710	-0.17925	0.08991	-0.01563
40.0	-0.05201	0.17420	-0.19967	0.10402	-0.01907
45.0	-0.08827	0.20857	-0.23236	0.12511	-0.02393
50.0	-0.12237	0.24506	-0.26965	0.14876	-0.02929
55.0	-0.15443	0.28321	-0.31244	0.17632	-0.03557
60.0	-0.18338	0.31587	-0.34942	0.20090	-0.04130
65.0	-0.20797	0.33479	-0.36729	0.21425	-0.04472
70.0	-0.22692	0.33148	-0.35229	0.20778	-0.04398
75.0	-0.23873	0.29623	-0.28846	0.17144	-0.03692
80.0	-0.24187	0.21912	-0.15951	0.09497	-0.02129

Table 33. Values of ϕ_E, $\bar{E}_2$, and $\bar{E}_1$ in units of ml/deg/mole for aqueous solutions of lanthanum chloride

Molality	$\phi_E{}^a \times 10^2$	$\phi_E{}^b \times 10^2$	$\Delta\phi_E \times 10^2$	$\bar{E}_2 \times 10^2$	$\bar{E}_1 \times 10^3$
		$t = 20.0°$ C			
		$\bar{E}_1^\circ = 3.729 \times 10^{-3}$ ml/deg/mole			
0.06362	12.49	12.46	0.03	12.29	3.73
0.1167	12.29	12.30	-0.01	11.94	3.74
0.3121	11.55	11.64	-0.09	10.52	3.79
0.6532	10.53	10.42	0.09	8.11	4.00
0.9154	9.56	9.51	0.05	6.44	4.24
1.2368	8.41	8.48	-0.07	4.67	4.58
1.5618	7.49	7.53	-0.04	3.22	4.94
1.7911	6.89	6.92	-0.03	2.42	5.18
1.9867	6.44	6.45	-0.01	1.89	5.36
2.3370	5.78	5.72	0.06	1.28	5.60
3.0681	4.69	4.65	0.04	1.50	5.47
3.3907	4.34	4.38	-0.04	2.26	5.03
		$t = 25.0°$ C			
		$\bar{E}_1^\circ = 4.644 \times 10^{-3}$ ml/deg/mole			
0.06362	7.48	7.55	-0.07	8.20	4.64
0.1167	8.03	7.90	0.13	8.34	4.63
0.3121	7.87	7.94	-0.07	7.44	4.67
0.6532	7.15	7.14	0.01	5.43	4.84
0.9154	6.45	6.47	-0.02	4.22	5.01
1.2368	5.75	5.74	0.01	3.15	5.22

[a]Calculated from Equation 5.17 together with parameters from Table 13 and from Equation 6.9 together with parameters from Table 22, whichever gave the best agreement with the experimental apparent molal volumes.

[b]Calculated from Equation 6.22 together with parameters from Table 31.

Table 33 (Continued)

Molality	$\phi_E{}^a \times 10^2$	$\phi_E{}^b \times 10^2$	$\Delta\phi_E \times 10^2$	$\bar{E}_2 \times 10^2$	$\bar{E}_1 \times 10^3$
		$t = 25.0°$ C			
		$\bar{E}_1^\circ = 4.644 \times 10^{-3}$ ml/deg/mole			
1.5618	5.15	5.12	0.03	2.42	5.40
1.7911	4.76	4.75	0.01	2.06	5.51
1.9867	4.47	4.47	0.00	1.82	5.59
2.3370	4.03	4.05	-0.02	1.48	5.73
3.0681	3.32	3.35	-0.03	0.71	6.10
3.3907	3.11	3.08	0.03	0.19	6.41
		$t = 30.0°$ C			
		$\bar{E}_1^\circ = 3.729 \times 10^{-3}$ ml/deg/mole			
0.06362	3.23	3.37	-0.14	4.56	5.47
0.1167	4.28	4.05	0.23	5.07	5.46
0.3121	4.57	4.65	-0.08	4.70	5.48
0.6532	4.22	4.26	-0.04	3.17	5.61
0.9154	3.76	3.83	-0.07	2.36	5.72
1.2368	3.42	3.36	0.06	1.82	5.83
1.5618	3.08	3.02	0.06	1.62	5.88
1.7911	2.88	2.84	0.04	1.58	5.89
1.9867	2.72	2.71	0.01	1.56	5.90
2.3370	2.47	2.53	-0.06	1.45	5.94
3.0681	2.10	2.17	-0.07	0.31	6.51
3.3907	2.01	1.94	0.07	-0.84	7.18
		$t = 35.0°$ C			
		$\bar{E}_1^\circ = 6.264 \times 10^{-3}$ ml/deg/mole			
0.06362	-0.36	-0.19	-0.17	1.33	6.25
0.1167	0.98	0.70	0.28	2.10	6.23
0.3121	1.62	1.71	0.09	2.21	6.24
0.6532	1.65	1.70	-0.05	1.21	6.32
0.9154	1.41	1.49	-0.08	0.76	6.38
1.2368	1.35	1.27	0.08	0.64	6.40

Table 33 (Continued)

Molality	$\phi_E{}^a \times 10^2$	$\phi_E{}^b \times 10^2$	$\Delta\phi_E \times 10^2$	$\bar{E}_2 \times 10^2$	$\bar{E}_1 \times 10^3$
		t = 35.0° C			
		$\bar{E}_1^\circ$ = 6.264 x 10^{-3} ml/deg/mole			
1.5618	1.23	1.16	0.07	0.82	6.36
1.7911	1.18	1.13	0.05	1.02	6.30
1.9867	1.13	1.12	0.01	1.17	6.25
2.3370	1.06	1.14	-0.08	1.29	6.20
3.0681	1.00	1.09	-0.09	0.18	6.76
3.3907	1.03	0.95	0.08	-1.17	7.56
		t = 40.0° C			
		$\bar{E}_1^\circ$ = 6.997 x 10^{-3} ml/deg/mole			
0.06362	-3.40	-3.23	-0.17	-1.56	6.98
0.1167	-1.94	-2.22	0.28	-0.62	6.96
0.3121	-1.03	-0.94	-0.09	-0.07	6.95
0.6532	-0.67	-0.61	-0.06	-0.54	6.99
0.9154	-0.69	-0.61	-0.08	-0.66	7.00
1.2368	-0.52	-0.60	0.08	-0.43	6.96
1.5618	-0.44	-0.52	0.08	0.06	6.84
1.7911	-0.36	-0.42	0.06	0.44	6.72
1.9867	-0.32	-0.32	0.00	0.73	6.62
2.3370	-0.22	-0.14	-0.08	1.06	6.50
3.0681	0.00	0.10	-0.10	0.23	6.93
3.3907	0.14	0.06	0.08	-1.08	7.69
		t = 45.0° C			
		$\bar{E}_1^\circ$ = 7.687 x 10^{-3} ml/deg/mole			
0.06362	-6.02	-5.85	-0.17	-4.14	7.67
0.1167	-4.54	-4.81	0.27	-3.10	7.65
0.3121	-3.43	-3.34	-0.09	-2.16	7.62
0.6532	-2.75	-2.69	-0.06	-2.08	7.62
0.9154	-2.55	-2.50	-0.05	-1.90	7.59
1.2368	-2.21	-2.28	0.07	-1.38	7.49

Table 33 (Continued)

Molality	$\phi_E{}^a \times 10^2$	$\phi_E{}^b \times 10^2$	$\Delta\phi_E \times 10^2$	$\bar{E}_2 \times 10^2$	$\bar{E}_1 \times 10^3$
		t = 45.0° C			
		$\bar{E}_1^\circ = 7.687 \times 10^{-3}$ ml/deg/mole			
1.5618	-1.95	-2.02	0.07	-0.68	7.31
1.7911	-1.76	-1.82	0.06	-0.16	7.15
1.9867	-1.63	-1.63	0.00	0.24	7.02
2.3370	-1.38	-1.31	-0.07	0.76	6.82
3.0681	-0.90	-0.81	-0.09	0.41	7.01
3.3907	-0.66	-0.74	0.08	-0.62	7.61
		t = 50.0° C			
		$\bar{E}_1^\circ = 8.341 \times 10^{-3}$ ml/deg/mole			
0.06362	-8.30	-8.15	-0.15	-6.49	8.32
0.1167	-6.88	-7.12	0.24	-5.39	8.30
0.3121	-5.60	-5.52	-0.08	-4.07	8.26
0.6532	-4.63	-4.58	-0.05	-3.46	8.21
0.9154	-4.23	-4.20	-0.03	-2.99	8.14
1.2368	-3.74	-3.79	0.05	-2.25	8.00
1.5618	-3.33	-3.38	0.05	-1.38	7.78
1.7911	-3.04	-3.08	0.04	-0.76	7.59
1.9867	-2.83	-2.83	0.00	-0.27	7.43
2.3370	-2.45	-2.39	-0.06	0.43	7.15
3.0681	-1.72	-1.65	-0.07	0.68	7.05
3.3907	-1.39	-1.45	0.06	0.07	7.41
		t = 55.0° C			
		$\bar{E}_1^\circ = 8.970 \times 10^{-3}$ ml/deg/mole			
0.06362	-10.35	-10.24	-0.11	-8.65	8.95
0.1167	- 9.03	- 9.23	0.20	-7.51	8.93
0.3121	- 7.61	- 7.53	-0.08	-5.86	8.88
0.6532	- 6.39	- 6.34	-0.05	-4.74	8.78
0.9154	- 5.79	- 5.78	-0.01	-4.01	8.68
1.2368	- 5.16	- 5.20	0.04	-3.05	8.49

Table 33 (Continued)

Molality	$\phi_E^a \times 10^2$	$\phi_E^b \times 10^2$	$\Delta\phi_E \times 10^2$	$\bar{E}_2 \times 10^2$	$\bar{E}_1 \times 10^3$
		t = 55.0° C			
		$\bar{E}_1^\circ = 8.970 \times 10^{-3}$ ml/deg/mole			
1.5618	− 4.60	− 4.64	0.04	− 2.02	8.23
1.7911	− 4.23	− 4.26	0.03	− 1.32	8.02
1.9867	− 3.95	− 3.94	−0.01	− 0.75	7.83
2.3370	− 3.44	− 3.40	−0.04	0.12	7.49
3.0681	− 2.48	− 2.43	−0.05	0.95	7.10
3.3907	− 2.07	− 2.12	0.05	0.73	7.23
		t = 60.0° C			
		$\bar{E}_1^\circ = 9.578 \times 10^{-3}$ ml/deg/mole			
0.06362	−12.30	−12.21	−0.09	−10.68	9.56
0.1167	−11.06	−11.22	0.16	− 9.49	9.54
0.3121	− 9.48	− 9.42	−0.06	− 7.54	9.47
0.6532	− 8.04	− 8.00	−0.04	− 5.96	9.34
0.9154	− 7.26	− 7.27	0.01	− 4.98	9.20
1.2368	− 6.50	− 6.52	0.02	− 3.80	8.97
1.5618	− 5.80	− 5.83	0.03	− 2.62	8.67
1.7911	− 5.35	− 5.37	0.02	− 1.82	8.43
1.9867	− 5.00	− 4.99	−0.01	− 1.17	8.21
2.3370	− 4.36	− 4.34	−0.02	− 0.14	7.81
3.0681	− 3.19	− 3.15	−0.04	1.17	7.19
3.3907	− 2.70	− 2.73	0.03	1.28	7.12
		t = 65.0° C			
		$\bar{E}_1^\circ = 10.171 \times 10^{-3}$ ml/deg/mole			
0.06362	−14.23	−14.16	−0.07	−12.62	10.15
0.1167	−13.03	−13.15	0.12	−11.36	10.13
0.3121	−11.27	−11.23	−0.04	− 9.12	10.05
0.6532	− 9.62	− 9.57	−0.05	− 7.12	9.88
0.9154	− 8.67	− 8.69	0.02	− 5.91	9.71
1.2368	− 7.76	− 7.78	0.02	− 4.51	9.44

Table 33 (Continued)

Molality	$\phi_E{}^a \times 10^2$	$\phi_E{}^b \times 10^2$	$\Delta\phi_E \times 10^2$	$\bar{E}_2 \times 10^2$	$\bar{E}_1 \times 10^3$
		$t = 65.0°$ C			
		$\bar{E}_1^° = 10.171 \times 10^{-3}$ ml/deg/mole			
1.5618	-6.92	-6.96	0.04	-3.16	9.10
1.7911	-6.40	-6.41	0.01	-2.25	8.83
1.9867	-5.99	-5.97	-0.02	-1.52	8.58
2.3370	-5.23	-5.21	-0.02	-0.35	8.12
3.0681	-3.86	-3.83	-0.03	1.33	7.32
3.3907	-3.29	-3.32	0.04	1.66	7.13
		$t = 70.0°$ C			
		$\bar{E}_1^° = 10.752 \times 10^{-3}$ ml/deg/mole			
0.06362	-16.27	-16.21	-0.06	-14.55	10.73
0.1167	-15.01	-15.11	0.10	-13.16	10.71
0.3121	-13.00	-12.98	-0.02	-10.60	10.62
0.6532	-11.13	-11.07	-0.06	-8.23	10.42
0.9154	-10.04	-10.05	0.01	-6.80	10.22
1.2368	-8.97	-8.99	0.02	-5.18	9.90
1.5618	-8.00	-8.04	0.04	-3.64	9.51
1.7911	-7.40	-7.41	0.01	-2.62	9.20
1.9867	-6.92	-6.90	-0.02	-1.80	8.93
2.3370	-6.05	-6.03	-0.02	-0.49	8.42
3.0681	-4.49	-4.46	-0.03	1.40	7.51
3.3907	-3.86	-3.88	0.02	1.78	7.29
		$t = 75.0°$ C			
		$\bar{E}_1^° = 11.322 \times 10^{-3}$ ml/deg/mole			
0.06362	-18.52	-18.45	-0.07	-16.50	11.30
0.1167	-17.06	-17.17	0.11	-14.90	11.27
0.3121	-14.74	-14.71	-0.03	-11.98	11.17
0.6532	-12.58	-12.53	-0.05	-9.30	10.94
0.9154	-11.39	-11.37	-0.02	-7.68	10.71
1.2368	-10.14	-10.17	0.03	-5.83	10.36

Table 33 (Continued)

Molality	$\phi_E{}^a \times 10^2$	$\phi_E{}^b \times 10^2$	$\Delta\phi_E \times 10^2$	$\bar{E}_2 \times 10^2$	$\bar{E}_1 \times 10^3$
		t = 75.0° C			
		$\bar{E}_1^\bullet = 11.322 \times 10^{-3}$ ml/deg/mole			
1.5618	− 9.02	− 9.08	0.06	− 4.07	9.91
1.7911	− 8.34	− 8.36	0.02	− 2.91	9.56
1.9867	− 7.80	− 7.78	−0.02	− 1.99	9.25
2.3370	− 6.83	− 6.80	−0.03	− 0.55	8.69
3.0681	− 5.08	− 5.05	−0.03	1.36	7.78
3.3907	− 4.40	− 4.43	0.03	1.62	7.63
		t = 80.0° C			
		$\bar{E}_1^a = 11.886 \times 10^{-3}$ ml/deg/mole			
0.06362	−21.09	−20.99	−0.10	−18.55	11.86
0.1167	−19.24	−19.40	0.16	−16.61	11.83
0.3121	−16.50	−16.44	−0.06	−13.25	11.71
0.6532	−13.97	−13.96	−0.01	−10.34	11.46
0.9154	−12.74	−12.66	−0.08	− 8.54	11.21
1.2368	−11.28	−11.32	0.04	− 6.45	10.80
1.5618	−10.01	−10.09	0.08	− 4.44	10.30
1.7911	− 9.25	− 9.28	0.03	− 3.13	9.90
1.9867	− 8.64	− 8.63	−0.01	− 2.10	9.55
2.3370	− 7.58	− 7.53	−0.05	− 0.52	8.94
3.0681	− 5.65	− 5.60	−0.05	1.19	8.13
3.3907	− 4.91	− 4.96	0.05	1.10	8.18

Table 34. Values of ϕ_E, $\bar{E}_2$, and $\bar{E}_1$ in units of ml/deg/mole for aqueous solutions of neodymium chloride

Molality	$\phi_E^a \times 10^2$	$\phi_E^b \times 10^2$	$\Delta\phi_E \times 10^2$	$\bar{E}_2 \times 10^2$	$\bar{E}_1 \times 10^3$
		$t = 20.0°$			
		$\bar{E}_1^° = 3.729 \times 10^{-3}$ ml/deg/mole			
0.1050	12.84	12.86	-0.02	13.27	3.72
0.2992	12.88	12.80	0.08	12.06	3.77
0.6152	11.68	11.77	-0.09	9.58	3.97
0.9007	10.80	10.77	0.03	7.75	4.22
1.3170	9.47	9.50	-0.03	5.86	4.59
1.6809	8.60	8.58	0.02	4.79	4.88
2.0853	7.86	7.77	0.09	4.07	5.12
2.2679	7.48	7.47	0.01	3.86	5.20
2.7090	6.82	6.85	-0.03	3.51	5.36
2.7553	6.70	6.79	-0.09	3.48	5.37
3.4160	6.15	6.12	0.03	3.10	5.58
		$t = 25.0°$ C			
		$\bar{E}_1^° = 4.644 \times 10^{-3}$ ml/deg/mole			
0.1050	8.80	8.80	0.00	9.32	4.63
0.2992	9.01	9.00	0.01	8.70	4.66
0.6152	8.40	8.42	-0.02	7.05	4.80
0.9007	7.79	7.78	0.01	5.83	4.96
1.3170	6.95	6.96	-0.01	4.63	5.20
1.6809	6.38	6.38	0.00	4.02	5.36
2.0853	5.94	5.89	0.05	3.69	5.47
2.2679	5.70	5.71	-0.01	3.62	5.50
2.7090	5.34	5.36	-0.02	3.57	5.52

[a]Calculated from Equation 5.17 together with parameters from Table 14 and from Equation 6.9 together with parameters from Table 23, whichever gave the best agreement with the experimental apparent molal volumes.

[b]Calculated from Equation 6.22 together with parameters from Table 32.

Table 34 (Continued)

Molality	$\phi_E^a \times 10^2$	$\phi_E^b \times 10^2$	$\Delta\phi_E \times 10^2$	$\bar{E}_2 \times 10^2$	$\bar{E}_1 \times 10^3$
		t = 25.0° C			
		$\bar{E}_1^\circ = 4.644 \times 10^{-3}$ ml/deg/mole			
2.7553	5.32	5.33	-0.01	3.57	5.52
3.4160	5.00	4.99	0.01	3.52	5.55
		t = 30.0° C			
		$\bar{E}_1^\circ = 5.484 \times 10^{-3}$ ml/deg/mole			
0.1050	5.11	5.11	0.00	5.80	5.47
0.2992	5.60	5.61	-0.01	5.76	5.48
0.6152	5.46	5.46	0.00	4.85	5.55
0.9007	5.15	5.15	0.00	4.15	5.64
1.3170	4.72	4.72	0.00	3.53	4.77
1.6809	4.42	4.44	-0.02	3.31	5.82
2.0853	4.23	4.22	0.01	3.32	5.82
2.2679	4.13	4.14	-0.01	3.38	5.80
2.7090	4.02	4.04	-0.02	3.59	5.70
2.7553	4.06	4.03	0.03	3.61	5.69
3.4160	3.98	3.98	0.00	3.89	5.54
		t = 35.0° C			
		$\bar{E}_1^\circ = 6.264 \times 10^{-3}$ ml/deg/mole			
0.1050	1.75	1.74	0.01	2.67	6.25
0.2992	2.57	2.58	-0.01	3.17	6.23
0.6152	2.83	2.83	0.00	2.89	6.26
0.9007	2.81	2.80	0.01	2.63	6.29
1.3170	2.73	2.72	0.01	2.52	6.31
1.6809	2.67	2.69	-0.02	2.65	6.27
2.0853	2.72	2.71	0.01	2.97	6.16
2.2679	2.72	2.74	-0.02	3.15	6.10
2.7090	2.83	2.84	-0.01	3.58	5.90

Table 34 (Continued)

Molality	$\emptyset_E{}^a \times 10^2$	$\emptyset_E{}^b \times 10^2$	$\Delta\emptyset_E \times 10^2$	$\bar{E}_2 \times 10^2$	$\bar{E}_1 \times 10^3$
		$t = 35.0°$ C			
		$\bar{E}_1^\circ = 6.264 \times 10^{-3}$ ml/deg/mole			
2.7553	2.89	2.85	0.04	3.63	5.88
3.4160	3.05	3.05	0.00	4.09	5.63
		$t = 40.0°$ C			
		$\bar{E}_1^\circ = 6.997 \times 10^{-3}$ ml/deg/mole			
0.1050	-1.32	-1.32	0.00	-0.10	6.97
0.2992	-0.12	-0.11	-0.01	0.89	6.94
0.6152	0.46	0.48	0.02	1.11	6.93
0.9007	0.70	0.69	0.01	1.22	6.91
1.3170	0.92	0.91	0.01	1.57	6.84
1.6809	1.09	1.10	-0.01	2.05	6.71
2.0853	1.35	1.34	0.01	2.68	6.50
2.2679	1.44	1.46	-0.02	2.96	6.38
2.7090	1.74	1.76	-0.02	3.58	6.11
2.7553	1.83	1.79	0.04	3.63	6.08
3.4160	2.20	2.20	0.00	4.08	5.84
		$t = 45.0°$ C			
		$\bar{E}_1^\circ = 7.687 \times 10^{-3}$ ml/deg/mole			
0.1050	-4.11	-4.11	0.00	-2.58	7.66
0.2992	-2.51	-2.54	0.03	-1.14	7.61
0.6152	-1.67	-1.63	-0.04	-0.50	7.56
0.9007	-1.20	-1.21	0.01	-0.08	7.50
1.3170	-0.71	-0.73	0.02	0.69	7.35
1.6809	-0.34	-0.34	0.00	1.50	7.13
2.0853	0.11	0.11	0.00	2.41	6.82
2.2679	0.29	0.31	-0.02	2.80	6.67
2.7090	0.76	0.78	-0.02	3.55	6.33

Table 34 (Continued)

Molality	$\phi_E{}^a \times 10^2$	$\phi_E{}^b \times 10^2$	$\Delta\phi_E \times 10^2$	$\bar{E}_2 \times 10^2$	$\bar{E}_1 \times 10^3$
		$t = 45.0°$ C			
		$\bar{E}_1^° = 7.687 \times 10^{-3}$ ml/deg/mole			
2.7553	0.84	0.82	0.02	3.61	6.30
3.4160	1.42	1.41	0.01	3.95	6.12
		$t = 50.0°$ C			
		$\bar{E}_1^° = 8.341 \times 10^{-3}$ ml/deg/mole			
0.1050	−6.66	−6.65	−0.01	−4.82	8.31
0.2992	−4.68	−4.73	0.05	−2.97	8.25
0.6152	−3.60	−3.54	−0.06	−1.96	8.17
0.9007	−2.93	−2.93	0.00	−1.26	8.07
1.3170	−2.20	−2.22	0.02	−0.11	7.84
1.6809	−1.64	−1.65	0.01	0.99	7.54
2.0853	−1.01	−1.02	0.01	2.16	7.14
2.2679	−0.75	−0.75	0.00	2.63	6.96
2.7090	−0.14	−0.12	−0.02	3.50	6.57
2.7553	−0.06	−0.06	0.00	3.56	6.54
3.4160	0.70	0.68	0.02	3.74	6.46
		$t = 55.0°$ C			
		$\bar{E}_1^° = 8.970 \times 10^{-3}$ ml/deg/mole			
0.1050	−9.00	−8.98	−0.02	−6.86	8.93
0.2992	−6.66	−6.73	0.07	−4.64	8.86
0.6152	−5.37	−5.29	−0.08	−3.33	8.75
0.9007	−4.53	−4.52	−0.01	−2.38	8.62
1.3170	−3.58	−3.61	0.03	−0.87	8.32
1.6809	−2.84	−2.87	0.03	0.51	7.95
2.0853	−2.05	−2.07	0.02	1.94	7.46
2.2679	−1.72	−1.72	0.00	2.49	7.25
2.7090	−0.98	−0.95	−0.03	3.44	6.83

Table 34 (Continued)

Molality	$\phi_E^a \times 10^2$	$\phi_E^b \times 10^2$	$\Delta\phi_E \times 10^2$	$\bar{E}_2 \times 10^2$	$\bar{E}_1 \times 10^3$
		$t = 55.0°$ C			
		$\bar{E}_1^° = 8.970 \times 10^{-3}$ ml/deg/mole			
2.7553	− 0.91	− 0.88	−0.03	3.50	6.80
3.4160	0.01	0.00	0.01	3.41	6.86
		$t = 60.0°$ C			
		$\bar{E}_1^° = 9.578 \times 10^{-3}$ ml/deg/mole			
0.1050	−11.16	−11.13	−0.03	− 8.75	9.53
0.2992	− 8.51	− 8.60	0.09	− 6.22	9.45
0.6152	− 7.01	− 6.93	−0.08	− 4.62	9.32
0.9007	− 6.04	− 6.01	−0.03	− 3.43	9.16
1.3170	− 4.87	− 4.90	0.03	− 1.58	8.79
1.6809	− 3.96	− 4.00	0.04	0.07	8.34
2.0853	− 3.02	− 3.05	0.03	1.72	7.78
2.2679	− 2.63	− 2.64	0.01	2.34	7.54
2.7090	− 1.78	− 1.74	−0.04	3.35	7.10
2.7553	− 1.69	− 1.65	−0.04	3.41	7.07
3.4160	− 0.64	− 0.67	0.03	3.04	7.30
		$t = 65.0°$ C			
		$\bar{E}_1^° = 10.171 \times 10^{-3}$ ml/deg/mole			
0.1050	−13.15	−13.12	−0.03	−10.56	10.12
0.2992	−10.28	−10.37	0.09	− 7.74	10.03
0.6152	− 8.56	− 8.49	−0.07	− 5.83	9.88
0.9007	− 7.46	− 7.42	−0.04	− 4.40	9.68
1.3170	− 6.09	− 6.12	0.03	− 2.22	9.25
1.6809	− 5.02	− 5.07	0.04	− 0.34	8.74
2.0853	− 3.94	− 3.97	0.03	1.49	8.12
2.2679	− 3.49	− 3.50	0.01	2.17	7.85
2.7090	− 2.53	− 2.48	−0.05	3.23	7.38

Table 34 (Continued)

Molality	$\emptyset_E{}^a \times 10^2$	$\emptyset_E{}^b \times 10^2$	$\Delta\emptyset_E \times 10^2$	$\bar{E}_2 \times 10^2$	$\bar{E}_1 \times 10^3$
		$t = 65.0°$ C			
		$\bar{E}_1^° = 10.171 \times 10^{-3}$ ml/deg/mole			
2.7553	− 2.43	− 2.38	−0.05	3.28	7.36
3.4160	− 1.26	− 1.30	0.04	2.71	7.70
		$t = 70.0°$ C			
		$\bar{E}_1^° = 10.752 \times 10^{-3}$ ml/deg/mole			
0.1050	−15.01	−14.99	−0.02	−12.36	10.70
0.2992	−12.03	−12.09	0.06	− 9.26	10.60
0.6152	−10.06	−10.00	−0.06	− 6.97	10.42
0.9007	− 8.82	− 8.77	−0.05	− 5.26	10.18
1.3170	− 7.24	− 7.27	0.03	− 2.80	9.69
1.6809	− 6.03	− 6.08	0.05	− 0.74	9.13
2.0853	− 4.82	− 4.84	0.02	1.23	8.47
2.2679	− 4.32	− 4.33	0.01	1.94	8.19
2.7090	− 3.24	− 3.20	−0.04	3.05	7.70
2.7553	− 3.14	− 3.10	−0.04	3.11	7.67
3.4160	− 1.88	− 1.91	0.03	2.51	8.03
		$t = 75.0°$ C			
		$\bar{E}_1^° = 11.322 \times 10^{-3}$ ml/deg/mole			
0.1050	−16.77	−16.76	−0.01	−14.20	11.27
0.2992	−13.80	−13.82	0.02	−10.81	11.16
0.6152	−11.53	−11.51	−0.02	− 8.02	10.94
0.9007	−10.10	−10.08	−0.02	− 6.01	10.66
1.3170	− 8.34	− 8.36	0.02	− 3.29	10.12
1.6809	− 7.00	− 7.02	0.02	− 1.12	9.54
2.0853	− 5.67	− 5.67	0.00	0.90	8.85
2.2679	− 5.10	− 5.12	0.02	1.63	8.57
2.7090	3.94	− 3.91	−0.03	2.81	8.04

Table 34 (Continued)

Molality	$\phi_E{}^a$ x 10^2	$\phi_E{}^b$ x 10^2	$\Delta\phi_E$ x 10^2	$\bar{E}_2$ x 10^2	$\bar{E}_1$ x 10^3
		$t = 75.0°$ C			
		$\bar{E}_1^\circ = 11.322$ x 10^{-3} ml/deg/mole			
2.7553	− 3.82	− 3.80	−0.02	2.88	8.01
3.4160	− 2.48	− 2.50	0.02	2.55	8.22
		$t = 80.0°$ C			
		$\bar{E}_1^\circ = 11.886$ x 10^{-3} ml/deg/mole			
0.1050	−18.45	−18.46	0.01	−16.15	11.84
0.2992	−15.65	−15.61	−0.04	−12.44	11.72
0.6152	−13.02	−13.04	0.02	− 8.99	11.44
0.9007	−11.34	−11.37	0.03	− 6.61	11.12
1.3170	− 9.39	− 9.39	0.00	− 3.68	10.53
1.6809	− 7.93	− 7.91	−0.02	− 1.50	9.95
2.0853	− 6.49	− 6.47	−0.02	0.47	9.28
2.2679	− 5.87	− 5.88	0.01	1.19	9.00
2.7090	− 4.60	− 4.61	0.01	2.47	8.43
2.7553	− 4.47	− 4.49	0.02	2.56	8.38
3.4160	− 3.08	− 3.06	−0.02	2.94	8.19

This linear relationship of ϕ_E versus $c^{1/2}$ has been verified for aqueous solutions of LiBr, KBr, KNO_3, and NaI by Gibson and Kincaid (62), and for NaCl and NaBr over wide ranges of concentration and temperature by Gibson and Loeffler (67). Gibson and Kincaid (66) have also shown that the apparent molal expansibilities of LiBr and NaI in methanol and NaI, LiBr, NaBr, and KI in glycol are linear functions of $c^{1/2}$ over considerable concentration ranges. Jones, et al. (34) have determined apparent molal expansibilities of aqueous solutions of $BaCl_2$ and $LaCl_3$ and report that the apparent molal expansibilities of these salts are almost linear functions of $c^{1/2}$.

Using the relationship,

$$\bar{E}_2 = (\partial \bar{F}_2 / \partial P \partial T)_{n_1} = (\partial \bar{V}_2 / \partial T)_{P,n_1}, \tag{6.23}$$

Gucker (77) differentiated the limiting law for $\bar{V}_2$, Equation 6.14, with respect to temperature and obtained the limiting law for $\bar{E}_2$,

$$\bar{E}_2 = \bar{E}_2^\circ + S_E c^{1/2}. \tag{6.24}$$

In equation 6.24, $\bar{E}_2^\circ$ is the partial molal expansibility of the salt at infinite dilution, and

$$S_E = (A/2) \cdot S^{2/3} \cdot f(D,P,V,T)/D^{3/2} \cdot T^{1/2} \tag{6.25}$$

in which

$$A = (\pi N^3 \varepsilon^6 / 1000 \ k)^{1/2}, \tag{6.26}$$

$$S = \sum_{i=1}^{s} \nu_i z_i^2, \text{ and} \qquad (6.27)$$

$$f(D,P,V,T) = -(1/2) \cdot \left[3(\partial \ln D/\partial T) + (1/T) + \alpha \right] \qquad (6.28)$$

$$+ \left[3(\partial \ln D/\partial P) - \beta \right]$$

$$+ \left[3(\partial^2 \ln D/\partial P \partial D) - (\partial \beta/\partial T) \right].$$

For a particular solute, solvent, temperature, and pressure, it is seen that S_E is a constant, and therefore, $\bar{E}_2$ should be a linear function of $c^{1/2}$. Furthermore, under conditions of constant solvent, temperature, and pressure, S_E has the same value for salts of the same valence type. From Equations 6.4, 6.17, and 6.24, it can be shown that for very dilute solutions, the apparent molal expansibility should also be a linear function of $c^{1/2}$.

Similar to the case of the limiting law for the partial molal volume, the observation by Gucker (77) that apparent molal expansibilities of electrolytic solutions are linear functions of $c^{1/2}$ is not an experimental verification of the limiting law. From Equation 6.20 and the experimental fact that the coefficients of thermal expansions for dilute solutions are almost equal to the coefficient of thermal expansion of water, it can be seen that the experimental error in determining apparent molal expansibilities of very dilute solutions is extremely large. For this reason, the theoretical limiting law for expansibility has not yet been experimentally verified.

Apparent molal expansibilities at 25, 35, 50, and 75° C are plotted versus $c^{1/2}$ for aqueous solutions of lanthanum chloride and neodymium chloride in Figures 19 and 20, respectively. In addition, the data of Jones, et al. (34) for lanthanum chloride at 25 and 35° C are also given in Figure 19. In Figures 21 and 22, apparent molal expansibilities for some aqueous solutions of lanthanum chloride and neodymium chloride are plotted versus temperature.

Values of $\bar{E}_2$ at 25, 50, and 75° C are shown in Figure 23 as a function of $c^{1/2}$ for aqueous lanthanum and neodymium chloride solutions. In Figures 24 and 25, values of $\bar{E}_2$ are plotted versus temperature for some aqueous solutions of lanthanum chloride and neodymium chloride, respectively.

In Figure 26, values of $\bar{E}_1$ for aqueous lanthanum and neodymium chloride solutions are plotted versus molality, and in Figures 27 and 28, values of $\bar{E}_1$ are shown as functions of temperature for some aqueous solutions of lanthanum chloride and neodymium chloride, respectively.

From Figures 19 through 28, the following observations were made:

1. From Figures 19 and 20, it is seen that the apparent molal expansibilities of lanthanum and neodymium chloride are almost linear with respect to $c^{1/2}$. It is also seen from Figures 19 and 20 that the slopes of the ϕ_E versus $c^{1/2}$ curves for lanthanum and neodymium chloride are in general negative at 25° C, approximately zero at 35° C, and positive at temperatures greater than 35° C. From Figure 21, it is seen that the ϕ_E versus t curves of lanthanum chloride cross at about 37.7°C, whereas in Figure 22, it is seen that the curves for neodymium chloride cross at about
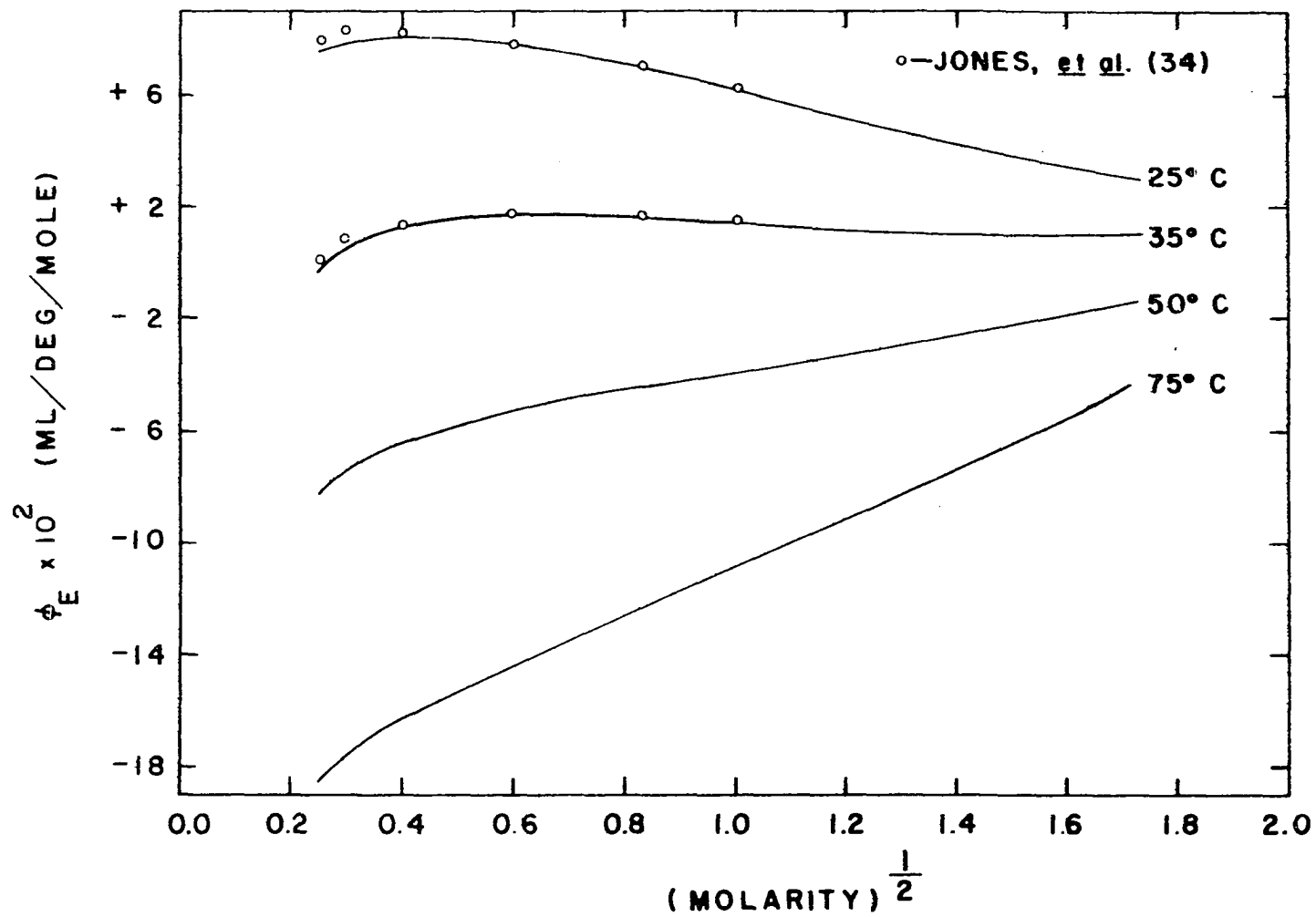
Figure 19. Apparent molal expansibilities of aqueous lanthanum chloride solutions at 25, 35, 50, and 75° C
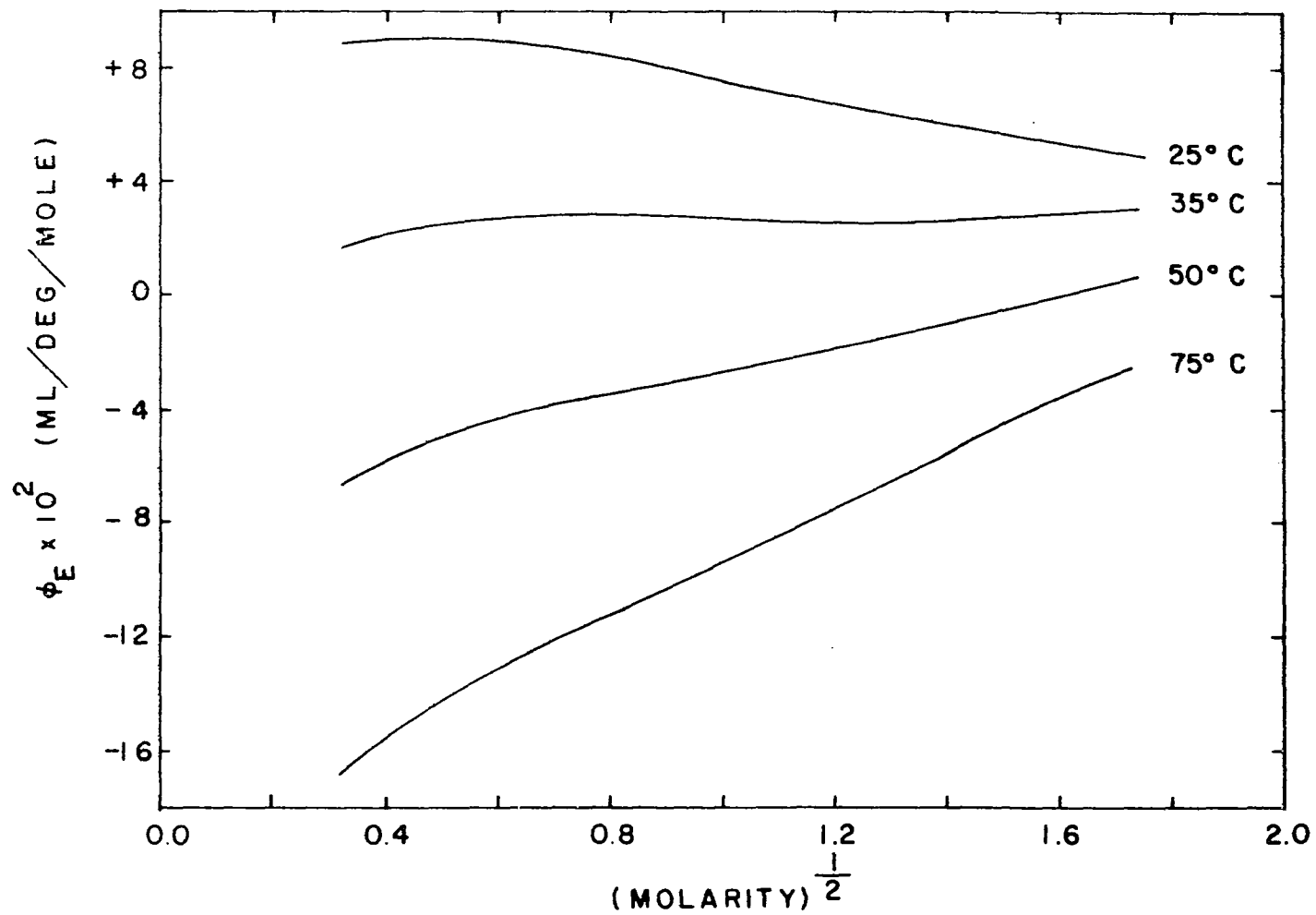
Figure 20. Apparent molal expansibilities of aqueous neodymium chloride solutions at 25, 35, 50, and 75° C
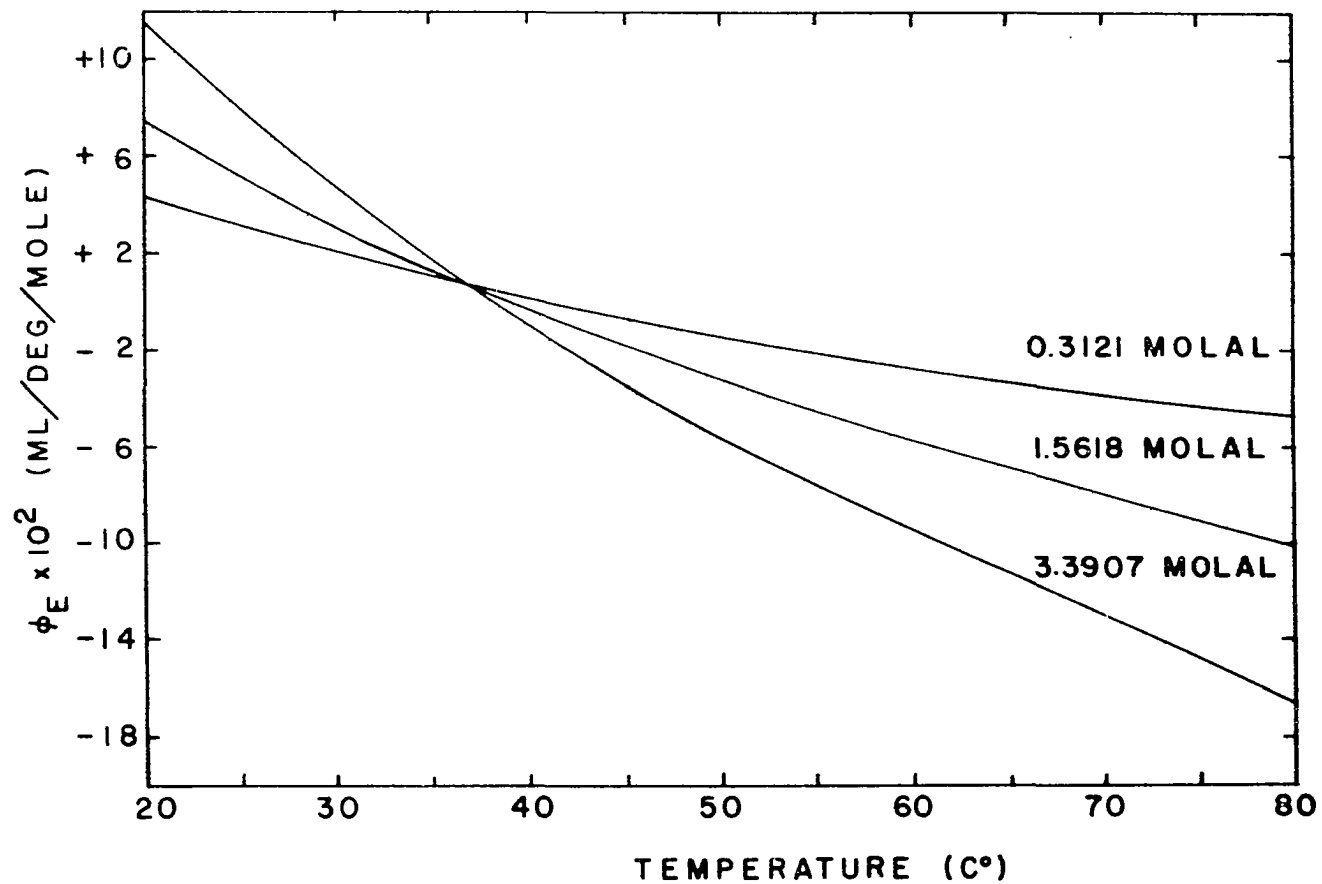
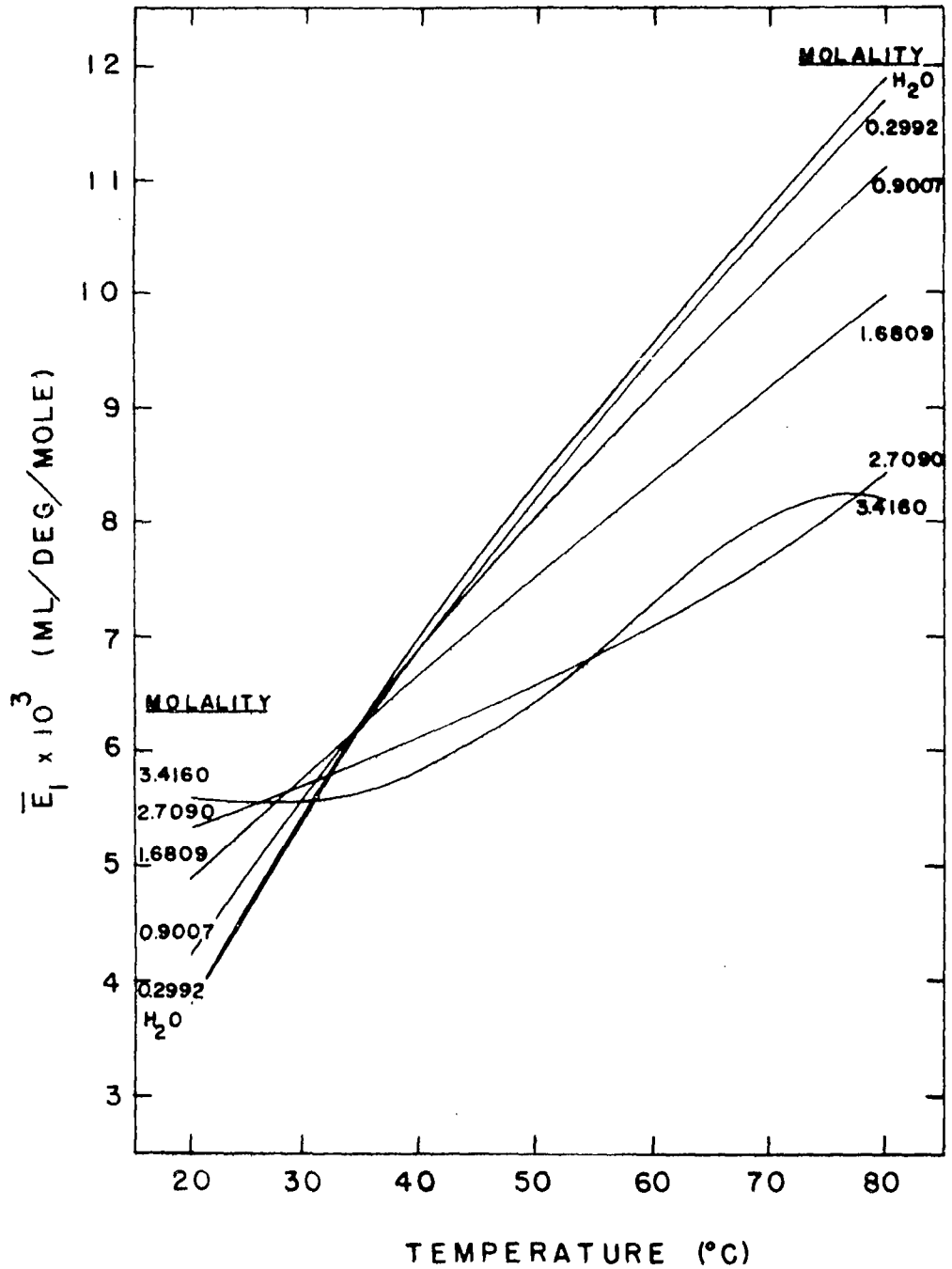Figure 21. Apparent molal expansibilities of some aqueous lanthanum chloride solutions
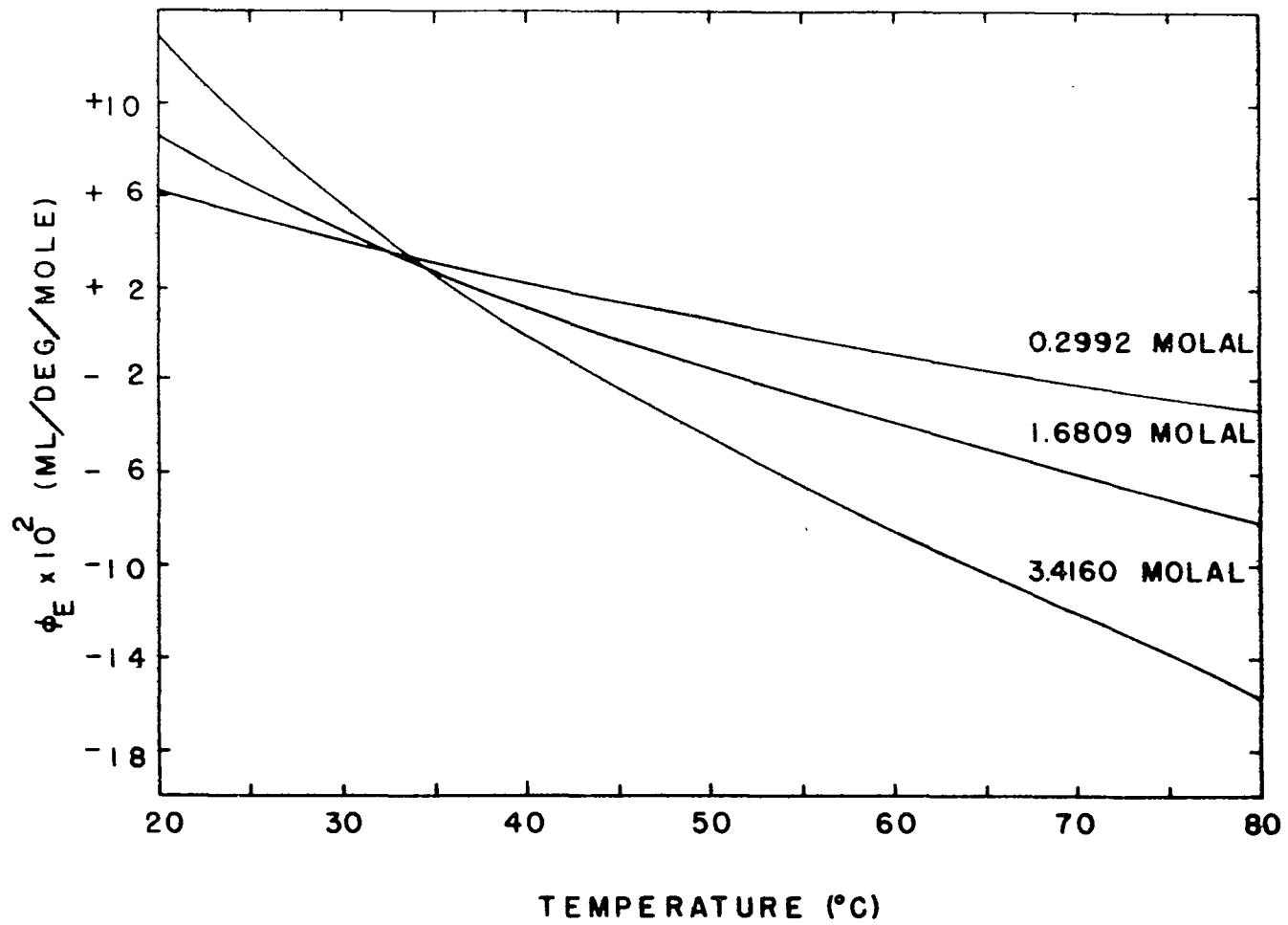
Figure 22. Apparent molal expansibilities of some aqueous neodymium chloride solutions
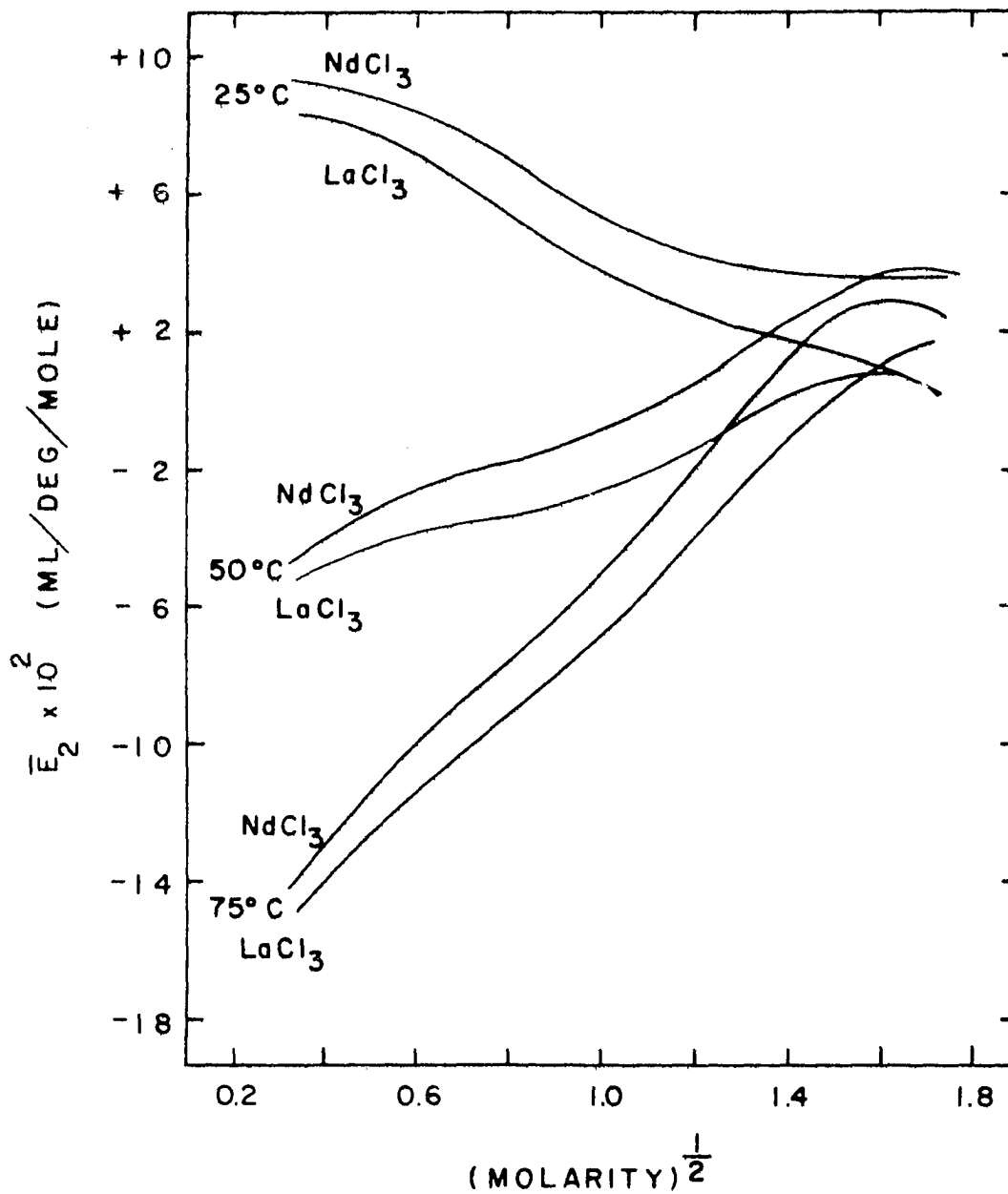
Figure 23. Partial molal expansibilities of lanthanum chloride and neodymium chloride in aqueous solutions of these salts at 25, 50, and 75° C
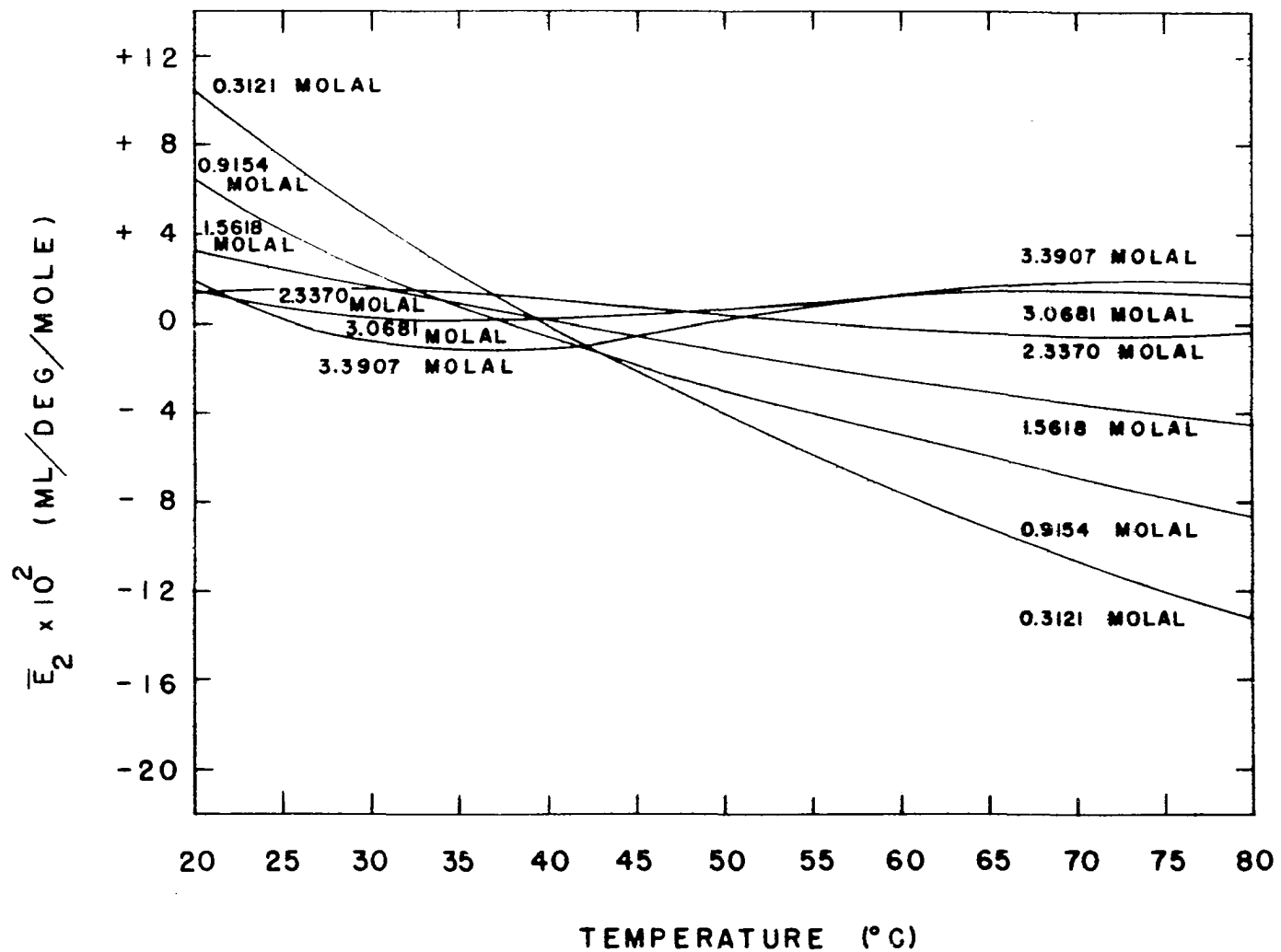
Figure 24. Partial molal expansibilities of lanthanum chloride in some aqueous solutions of this salt
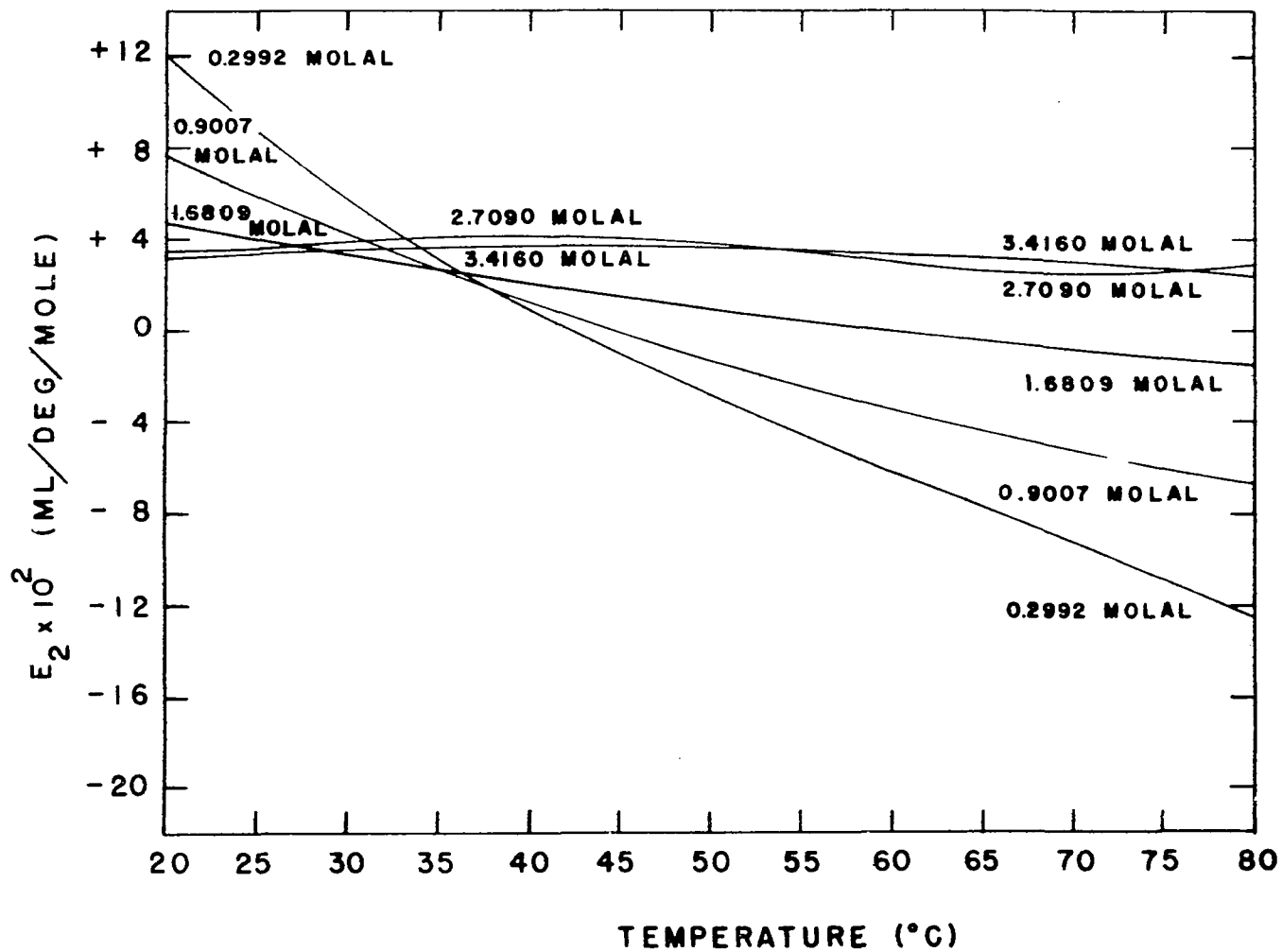
Figure 25. Partial molal expansibilities of neodymium chloride in some aqueous solutions of this salt
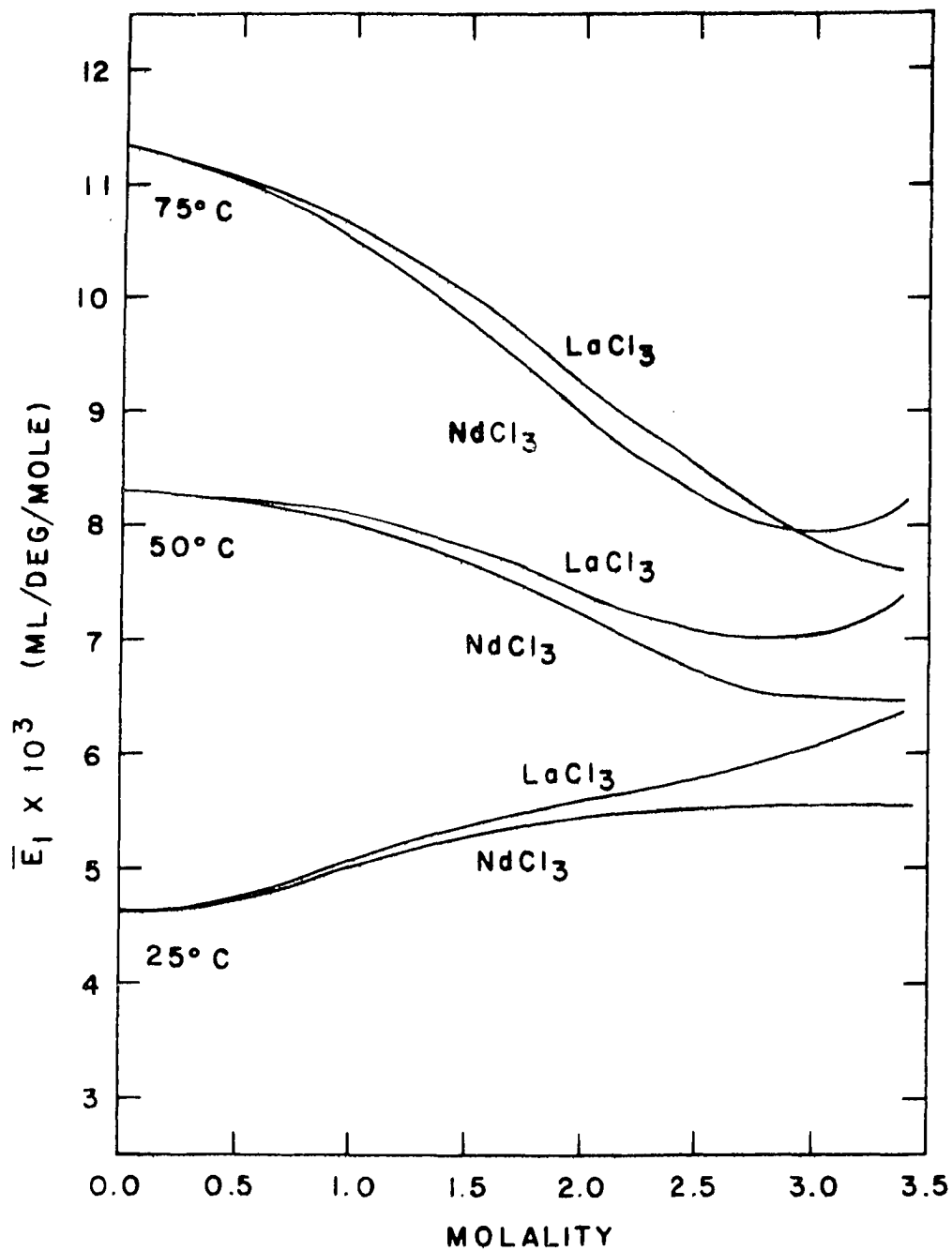
Figure 26. Partial molal expansibilities of water in aqueous lanthanum chloride and neodymium chloride solutions at 25, 50, and 75° C
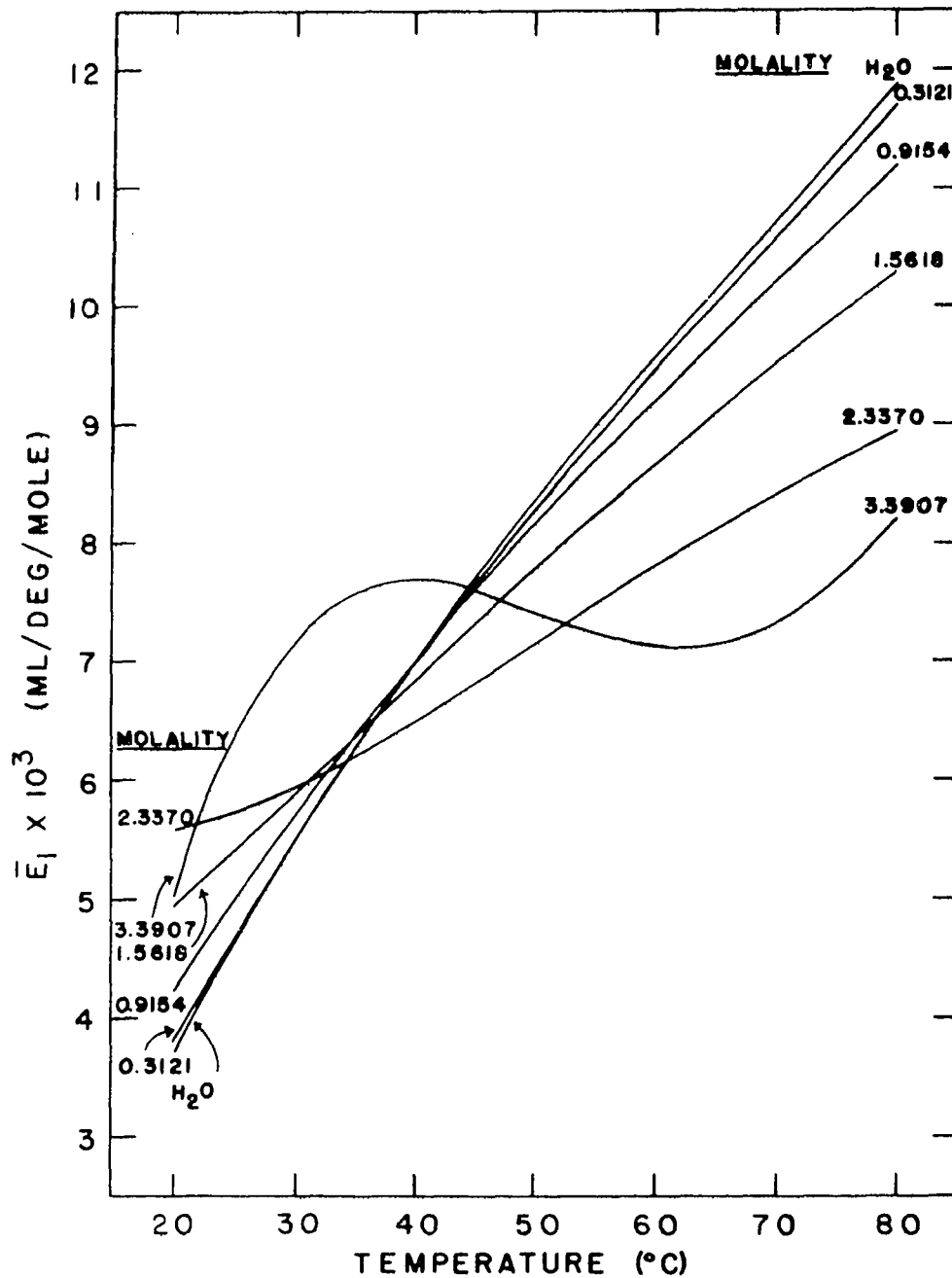
Figure 27. Partial molal expansibilities of water in some aqueous lanthanum chloride solutions

Figure 28. Partial molal expansibilities of water in some aqueous neodymium chloride solutions

32.7° C. However, the most concentrated solutions of each of these salts cross the other curves at temperatures slightly above the previously quoted temperatures. With all concentrations of the rare-earth chlorides, the values of ϕ_E decrease with temperature. In general, it is noted that the apparent molal expansibilities of neodymium chloride are larger than those of lanthanum chloride at the same temperature.

2. From Figure 23, it is seen that $\bar{E}_2$ is greater for neodymium chloride than for lanthanum chloride at the same temperature. Also, it is seen that the $\bar{E}_2$ versus $c^{1/2}$ plots deviate considerably from linearity, and furthermore, at the highest concentrations the values of $\bar{E}_2$ seem to converg to approximately 1×10^{-2} ml/deg/mole for lanthanum chloride and to approximately 3.3×10^{-2} ml/deg/mole for neodymium chloride for all temperatures. The plots of $\bar{E}_2$ versus temperature given in Figures 24 and 25 exhibit about the same behavior as was seen with ϕ_E in Figures 21 and 22. The principal difference is that the $\bar{E}_2$ curves for the most concentrated solutions oscillate in a sine-like manner.

3. From Figure 26, it is seen that the values of $\bar{E}_1$ for the aqueous neodymium chloride solutions are less than those of the lanthanum chloride solutions with the exception of the highest concentrations and temperatures. In general, at the lowest temperatures, the values of $\bar{E}_1$ for the solutions are larger than the value of $\bar{E}_1^{\circ}$, but at the higher temperatures, the reverse is true. The plots of $\bar{E}_1$ versus temperature given in Figures 27 and 28 are reminiscent of the plots of α versus temperature given in Figures 7 and 8. The prominent difference between these two sets of curves

is that the 3.3907 molal lanthanum chloride curve and the 3.4160 molal

neodymium chloride curve are definitely sine-like in the plots of $\bar{E}_1$

versus temperature.

VII. ERROR ANALYSIS

A. Reaction of Rare-Earth Chloride Solutions with Mercury

Vogel (47) observed that when a dilute air-free solution of lanthanum chloride was added to his dilatometer, a small amount of white precipitate was formed at the mercury-solution interface. He attributed this to a reaction between the mercury and lanthanum chloride yielding insoluble mercury (I) chloride.

The above observation was confirmed in this research for the 0.06362, 0.1167, and 0.3121 molal solutions of lanthanum chloride and for the 0.1050 and 0.2992 molal solutions of neodymium chloride. Only with the 0.06362 molal lanthanum chloride solution was the precipitate visible before the dilatometers were placed in the constant temperature bath. With the other solutions, the precipitate was visible only after the dilatometers were removed from the bath, one to two weeks after adding the solutions to the dilatometers, and even then, the precipitates in the approximately 0.3 molal solutions were just barely perceptible. It should be added that during the cooling down period of the dilatometers before removing them from the bath, some air was drawn into the solutions. As will be pointed out later, it is possible that the presence of oxygen in this air could have been either partly or totally responsible for the formation of precipitates in the approximately 0.1 and 0.3 molal solutions. Following the first solution run, the solutions were allowed to remain in the di- latometers for six weeks. After this extensive period of time, a precipitate

was also visible in the 0.6532 molal lanthanum chloride solution, but again the presence of oxygen may have been the cause. Measurements of the pH's of the solutions before and after the third run on solutions showed that during the run the pH's of the solutions increased somewhat. The amount of increase decreased rapidly with concentration, being about 2 pH units for a 0.1 molal solution, 0.4 pH unit for a 1.3 molal solution, and 0.2 pH unit for a 3.4 molal solution.

These observations made it necessary to ascertain whether or not the solutions had been contaminated by a reaction with mercury to such an extent that density measurements were unreliable. Furthermore, it was desirable to find out what the products of the reaction were.

Approximately 200 milliliters each of 0.1, 0.5, 1, 2, and 3 molal solutions of lanthanum chloride and neodymium chloride were added to bottles containing about 100 milliters of mercury apiece. The pH's of these solutions were measured before they were added to the mercury and then again at one day intervals for a period of about one week. It was found that the pH's of these solutions, which were not air-free, increased considerably. The pH's of the more dilute solutions increased very rapidly and then leveled off after a couple of days, but the pH's of the more concentrated solutions increased more slowly and did not level off until almost a week had elapsed. With all the solutions, the pH rise was considerably greater than with the air-free solutions used in the dilatometers. Furthermore, with these air-saturated solutions, precipitates appeared at all concentrations. These results indicated that the reaction of the air-saturated

solutions with mercury was greater than it was with the air-free solutions.

A qualitative test was carried out on the precipitates which had been formed, and indicated that it was mercury (I) chloride. Also, it was shown the solubility of mercury (I) chloride in the rare-earth chloride solutions was negligible, and that there was some Hg^{++}, although not necessarily present as free divalent ions, present in the rare-earth chloride solutions which had been above mercury.

In order to establish the maximum concentration of Hg present in the rare-earth chloride solutions, approximately 0.1, 0.5, 1, 2, and 3 molal solutions of lanthanum chloride and neodymium chloride were prepared. To each of these solutions enough mercury (II) chloride was added to make the concentration of mercury (II) chloride 0.05 mole percent of the total salt concentration. Using these control solutions plus the rare-earth chloride solutions which had previously been placed above mercury, the following two tests were made:

1. A few drops of a concentrated solution of HCl containing $SnCl_2$ were added to 20 milliliters of each of the lanthanum and neodymium chloride solutions which had been buffered with NH_4Cl. The $SnCl_2$ reduced the Hg^{++} to Hg^+ which then precipitated as mercury (I) chloride. By comparing the cloudiness of the control solutions with the other rare-earth chloride solutions, it was possible to estimate the amount of Hg^{++} present in those solutions which had reacted with mercury. These observations confirmed that with the possible exception of the 0.1, 0.5, and 1 molal rare-earth chloride solutions the amount of Hg^{++} present in the solutions which had

been placed above mercury was less than 0.05 mole percent, and even in the 0.1, 0.5, and 1 molal solutions the contamination was probably less than 0.1 mole percent of the total salt content in the solutions.

2. Twenty milliliter aliquots each of the control solutions and the solutions which had been above mercury were acidified with concentrated HCl, and then about one milliliter of approximately 0.8 molar sodium sulfide solution was added to each of these aliquots. By comparing the cloudiness present in these two sets of rare-earth chloride solutions caused by the formation of insoluble rare-earth sulfide, an estimate of the amount of mercury (II) present in those solutions which had reacted with mercury could be made. From this test it was concluded that the amount of Hg^{++} present in the 1 and 2 molal solutions of lanthanum chloride and the 1 molal solution of neodymium chloride which had been in contact with mercury was less than 0.1 mole percent. The amount of Hg^{++} present in the other lanthanum and neodymium chloride solutions was concluded to be less than 0.05 mole percent.

Tests with $SnCl_2$ carried out on the rare-earth chloride solutions which had been in the dilatometers during the third run on solutions indicated that the contamination of these solutions with Hg^{++} was considerably less than with the air-saturated solutions which had been in contact with mercury.

The results given above concerning the reaction of rare-earth chloride solutions with mercury are similar to the observations of Stock, Gerstner, and Köhle (80) on the reaction of mercury with air-saturated potassium

chloride solutions to yield mercury (I) chloride. It has also been reported (81, 82) that air-free hydrochloric acid does not react with mercury, although tests made in this laboratory showed that when hydrochloric acid is not air-free, a reaction with mercury occurs yielding mercury (I) chloride as one of the products.

In summary, it is safe to conclude that the rare-earth chloride solutions more concentrated than approximately 0.3 molal were contamined with less than 0.05 mole percent of mercury. The approximately 0.1 and 0.3 molal solutions were probably not contaminated with more than 0.1 mole percent of mercury and the 0.06 molal lanthanum chloride solution by not more than 0.2 mole percent of mercury. These percentage values are intended to include also the contamination caused by the formation of insoluble mercury (I) chloride. However, the contamination of the 0.06362 molal lanthanum chloride solution is particularly difficult to estimate since the amount of mercury (I) chloride formed was certainly not negligible. For this reason, among others, it is recommended that the values of the various thermodynamic properties of this solution be treated with a certain amount of skepticism. Furthermore, the mole percent contamination values given above are not ideally suited to the estimation of the effect of this contamination upon the values of the thermodynamic properties since the effect caused by the formation of mercury (II) in the solution may be compensated by some other change occurring in the solution. Nevertheless, the above percentage values will be assumed to be maximum

errors upon the molalities of the solutions caused by the reaction with mercury.

B. Other Errors

The estimation of the errors of the various solution thermodynamic properties which were calculated in this research is complicated by the use of the numerous empirical equations. It was felt that the best way to cope with this problem was to calculate the maximum differential errors in α, ϕ_V, ϕ_E, $\bar{V}_2$, $\bar{V}_1$, $\bar{E}_2$, and $\bar{E}_1$ using the expected errors in density, concentration, and temperature. The errors in the partial molal properties of the salt will be of the approximately the same order as the errors in the apparent molal properties. The expected errors in density, concentration and temperature were as follows:

1. There were two different kinds of density errors. First there was an error in the determination of the absolute density of the solution at 25° C. Since the absolute densities at 25° C were used to calculate the molalities of the solutions the absolute densities will be assumed to be correct, and the error will be attributed to the molality. The second kind of density error is the error in measuring the change in density with temperature. This error is partly due to an error in the calibration of the dilatometers. This error becomes negligible when calculating apparent molal volumes since the difference between the solution density and the density of water are affected equally, and hence the errors cancel. When calculating coefficients of thermal expansion, this error changes so

slowly with temperature that it becomes negligible. In addition to the above calibration error, there is an error in the withdrawal of mercury from the dilatometer. This error is too small to seriously affect the apparent molal volume, but is important in calculating the coefficient of thermal expansion, and therefore in calculating the apparent molal expansibility. By experimenting with a dummy dilatometer sidearm in which the capillary tubing was sealed off at one end, it was found that in most cases the withdrawal of mercury was accurate to 1×10^{-4} milliliter.

2. The error in concentration was essentially caused by the error in the analyses of the solutions of Saeger (50, 51) and Ayres (52), the error in the measurement of the absolute densities at 25° C, and the error in concentration caused by the reaction of the solutions with mercury. Saeger estimates that the probable error in his concentration is 0.05%. Reasonable values for the total concentration errors are 0.2% for a 0.1 molal solution, 0.15% for a 0.3 molal solution, and 0.1% for the solutions more concentrated than 0.3 molal.

3. The measurement of temperature should have been accurate in almost all cases to 0.001° C.

Assuming the absolute densities of the solutions at 25° C to be correct, the differential error in α as derived from Equation 5.1 is given by

$$\delta\alpha = [\alpha\delta(\Delta V)/\Delta V] + [\alpha\delta(\Delta T)/\Delta T]. \tag{7.1}$$

The value of ΔV was calculated from the equation

$$\Delta V = \alpha V \Delta T \tag{7.2}$$

in which α is obtained from Table 19, T = 1° C, and V = 100 milliliters.

Assuming the values of $(d - d_o)$ to be correct, the error in $\emptyset_V$ as derived from Equation 6.8 is given by

$$\delta\emptyset_V = (\emptyset_V - M_2/d) \cdot \delta m/m. \tag{7.3}$$

If the densities of the solutions, α_o, and d_o are assumed to be correct, the error in $\emptyset_E$ as derived from Equation 6.20 is given by

$$\delta\emptyset_E = \left[1000\delta\alpha/md\right] + \left[M_2\delta\alpha/d\right] + \left[(\emptyset_E - \alpha M_2/d) \cdot \delta m/m\right]. \tag{7.4}$$

The errors in $\bar{V}_2$ and $\bar{E}_2$ are expected to be of the same order as those in $\emptyset_V$ and $\emptyset_E$, respectively.

The error in $\bar{V}_1$ was calculated from

$$\bar{V}_1 = (M_1 V/1000) - (mM_1\bar{V}_2/1000). \tag{7.5}$$

Assuming the absolute densities of the solutions, and therefore V, to be accurate the resulting equation is

$$\delta\bar{V}_1 = (m\delta\bar{V}_2 + \bar{V}_2\delta m) \cdot M_1/1000. \tag{7.6}$$

The error in $\bar{E}_1$ is similarly calculated from

$$\bar{E}_1 = (M_1\alpha V/1000) + (M_1 m\bar{E}_2/1000) \tag{7.7}$$

and is seen to be

$$\delta\bar{E}_1 = (M_1 V\delta\alpha/1000) + (M_1 m\delta\bar{E}_2/1000) + (M_1\bar{E}_2\delta m/1000). \tag{7.8}$$

The errors in α, $\emptyset_V$, $\emptyset_E$, $\bar{V}_1$, and $\bar{E}_1$ were calculated for the 0.1050, 0.2992, 0.9007, 2.0853, and 3.4160 molal neodymium chloride solutions at 25° C. The same errors would also apply to lanthanum chloride solutions of

the same concentrations. In calculating these errors, values of α and d were obtained from Table 19, ϕ_V and $\bar{V}_2$ from Table 30, and ϕ_E and $\bar{E}_2$ from Table 34. These errors are tabulated in Table 35.

Table 35. Maximum differential errors in α, ϕ_V, ϕ_E, $\bar{V}_1$, and $\bar{E}_1$ for various aqueous neodymium chloride solutions at $25°$C

Molality	$\delta\alpha \times 10^4$	$\delta\phi_V$	$\delta\phi_E \times 10^2$	$\delta\bar{V}_1$	$\delta\bar{E}_1 \times 10^3$
0.1050	0.02	0.46	2.05	0.001	0.08
0.2992	0.02	0.33	0.65	0.002	0.07
0.9007	0.02	0.19	0.24	0.004	0.09
2.0853	0.02	0.15	0.11	0.007	0.10
3.4160	0.02	0.12	0.07	0.010	0.11

It is expected that the probable errors in α, ϕ_V, and ϕ_E are somewhat less than those listed in Table 35. The probable errors in $\bar{V}_2$ and $\bar{E}_2$ are expected to be somewhat larger than those for ϕ_V and ϕ_E, and the probable errors in $\bar{V}_1$ and $\bar{E}_1$ are probably very close to the maximum differential errors given in Table 35 for these properties.

Due to the reaction with mercury, the results obtained with the 0.06362 molal lanthanum chloride solution are considerably in doubt. Also, there is some doubt concerning the results obtained with the two most concentrated solutions of lanthanum chloride, particularly at the higher temperatures. Although no specific error was found for these solutions, it

is felt that it would be unwise to attempt an explanation for the behavior exhibited by these two solutions in the $\bar{V}_2$ versus $c^{1/2}$ and $\bar{E}_1$ versus $c^{1/2}$ plots at 75° C. On the other hand, the properties of the most concentrated neodymium chloride solutions also exhibit certain deviations, so it may be that the properties of the most concentrated lanthanum chloride solutions are as dependable as those of the other lanthanum chloride solutions.

VIII. SUMMARY AND CONCLUSIONS

An apparatus was constructed which was capable of measuring changes in densities of liquids and solutions with temperature with an accuracy of a few parts in the sixth decimal place over the temperature range of 20 to 80° C. The dilatometers used in this apparatus were calibrated with mercury from 20 to 80° C, and densities of water were determined at five degree temperature intervals from 40 to 80° C. In addition, densities of various aqueous lanthanum chloride and neodymium chloride solutions were determined at five degree temperature intervals from 20 to 80° C.

From the above density data, coefficients of thermal expansion of water and the rare-earth chloride solutions were computed. Also, values of ϕ_V, ϕ_E, $\bar{V}_2$, $\bar{E}_2$, $\bar{V}_1$, and $\bar{E}_1$ were computed for the various rare-earth chloride solutions over the temperature range of 20 to 80° C.

It was desirable to try and correlate this data with the nature of the rare-earth chloride solutions as much as possible. Such an undertaking, however, was extremely complicated due to the effects of hydration, formation of rare-earth chloride complexes, and hydrolysis upon the properties. Furthermore, the time-average structure of pure water is not known with any certainty over any temperature range, and in the most concentrated aqueous electrolytic solutions it is possible that a pseudo salt-like lattice of the ions is formed.

From an examination of the apparent and partial molal volumes of aqueous rare-earth chloride solutions, Ayers (52) and Saeger (50, 51) have suggested that a possible shift to a lower coordination number for the first

hydration layer about the rare-earth ions may take place toward the middle of the rare-earth series. Evidence for such a shift is also found with the crystalline rare-earth chloride hydrates in which there is a change from the heptahydrate to the hexahydrate in going from praseodymium to neodymium. Furthermore, Saeger suggests the possibility of two coordination numbers occurring in a rare-earth chloride solution simultaneously, with a change in the ratio of these two values occurring with changes in concentration as well as with a change from one rare-earth to another. Ayers and Saeger based these suggestions on their determinations of apparent molal volumes of some rare-earth chloride solutions. From their data, they found that the ϕ_V values decreased from lanthanum to neodymium, and then increased from neodymium to gadolinium at which the ϕ_V values began to decrease once again. They reasoned that if the coordination number decreased, there would be less contraction of the water, and hence the apparent molal volume would become larger.

It is perhaps possible to be a bit more specific about the effects which the ions in rare-earth chloride solutions have on the water structure. A recent x-ray diffraction study of water at room temperature has been carried out by Danford and Levy (7). From their data, they concluded that the time-average structure of water was almost identical with the ice I structure, except that the lattice structure is slightly expanded in water. Also, they concluded that in the water lattice some of the interstitial holes were occupied by other water molecules.

From an investigation of aqueous solutions of ammonium chloride, Fajans and Johnson (83) concluded that the chloride ion has little effect on the water structure. This might possibly be because the chloride ion can fit into one of the interstitial holes of the water lattice without causing much change in the surrounding lattice. If this is so, any change occurring in the water structure will probably be mostly due to the rare-earth ion.

Due to the high surface charge density of a rare-earth ion, it is expected that the dipoles of the water molecules in the first hydration layer will be strongly orientated toward the ion. Because of this strong ion-dipole orientation plus hydrogen bond formation among the water molecules, the water molecules out through the third hydration layer or so should be fairly tightly bound and well ordered. That such ordering about an ion increases with increasing surface charge density can be seen from the comparison of the lithium and cesium ions by Wang (84). Furthermore, it is expected that because of its larger surface charge density, the water structure about a neodymium ion will be more dense than about a lanthanum ion, assuming equal coordination numbers. Likewise, it is expected that the water structures about these ions will be more dense than the open structure of pure water, regardless of the coordination number.

From this research, it is seen that the values of $\bar{V}_1$ are in general lower for neodymium chloride solutions than for lanthanum chloride solutions of the same concentration. This is particularly true with the solutions more concentrated than 1.3 molal. An examination of Saeger's data (50, 51)

shows that the $\bar{V}_1$ values for aqueous gadolinium chloride solutions are, on the other hand, greater than those of neodymium chloride solutions. As stated previously, it has been suggested that this increase from neodymium chloride to gadolinium chloride is caused by a shift to a lower coordination number or a shift toward a higher concentration of the lower coordination number if an equilibrium between two coordination numbers is involved. Because of the decrease in ionic radius, a lower coordination number would indeed seem to become more probable for the rare-earths of higher atomic weight. If the coordination number decreased for a given rare-earth ion, it is expected that the number of water molecules in the second and third hydration layers would also decrease because of the ordering due to the ion-dipole orientation and the hydrogen bonding. Therefore, the number of water molecules in the more open pure water structure would be increased, which would indeed cause an increase in the values of $\emptyset_V$ and $\bar{V}_1$.

Since the values of $\emptyset_V$ and $\bar{V}_1$ for lanthanum chloride are greater than for neodymium chloride the coordination number or ratio of coordination numbers are expected to be about the same in both cases. The decrease in $\emptyset_V$ and $\bar{V}_1$ can then be explained by the increase in surface charge density in going from lanthanum to neodymium with the consequent tightening up of the hydration water structure.

If this model is correct, one would predict that the compressibility of the neodymium chloride solutions would be less than those of lanthanum chloride. Indeed, such is seen to be the case (85). However, one would also expect that the conductances and transference numbers of lanthanum

chloride solutions would be larger than those of neodymium chloride so-
lutions. Unfortunately, such is not the case (50, 51) although the
difference is not great. This discrepancy might possibly be due to
differences between the complexation of the lanthanum and neodymium ions
with chloride.

Except for the most concentrated solutions at the higher temperatures,
the value of $\bar{E}_1$ is greater for a lanthanum chloride solution than for a
corresponding neodymium chloride solution. This also is in accordance
with the assumption that the water molecules surrounding the neodymium ions
are more tightly bound than those about the lanthanum ions. The $\bar{E}_1$ values
for the more concentrated solutions of lanthanum and neodymium chloride at
the higher temperatures exhibit more complex behavior than this. However,
due to the complex nature of such solutions, this does not mean that the
model used above is not essentially correct.

The expansion of pure water is most likely due largely to a lengthening
of the hydrogen bonds with an increase in temperature. From an examination
of the $\bar{E}_1$ versus temperature curves for lanthanum chloride and neodymium
chloride, it is seen below about 35° C the $\bar{E}_1$ values for the rare-earth
chloride solutions are larger than the values of $\bar{E}_1^o$. Above about 35° C it
is seen that the reverse is true. These results seem to indicate that at
the lower temperatures, the hydrated water structure is more resistant to
expansion than the more open structure of pure water, whereas the reverse
becomes true at the higher temperatures. It has been seen that a decrease
in the expansion of the hydrated water structure about an ion probably

occurs with an increase in the surface charge density of the ion. There-fore, it is expected that with a decrease in surface charge density the temperature at which the $\bar{E}_1$ values of the salt solution become equal to $\bar{E}_1^\circ$ would increase. Indeed, it is found that this temperature is slightly higher for lanthanum chloride than for neodymium chloride. Past research (34) has also shown that this temperature increases with the salts $LaCl_3$, $BaCl_2$, KCl in the order given, which is further verification for this model.

Another observation about aqueous electrolytic solutions has been made by Wright (86) from a study of expansibility measurements. He observed from various data that the coefficients of thermal expansion of a number of aqueous electrolytic solutions leveled off at the higher concentrations, and he attributed this to the formation of a psuedo salt-like lattice in the most concentrated solutions. The same observation can be made from the data of this research.

In addition, from the $\bar{E}_2$ data obtained in this research it is seen that the values of $\bar{E}_2$ for the most concentrated solutions remain fairly constant over the temperature range. Furthermore, it is seen that the $\bar{E}_2$ values for the rare-earth chloride solutions begin to level out at the highest concentration. These results are also in agreement with the formation of a psuedo salt-like lattice in the more concentrated aqueous electrolytic solutions.

In order to verify the previous conclusions and to further clarify the nature of the rare-earth chloride solutions, more data will be necessary.

In particular, more temperature dependence data of the various properties of electrolytic solutions of all of the rare-earths are required. Also, determinations of the complexation of the rare-earth ions with chloride and other anions and determinations of the hydrolytic species formed during hydrolysis would be extremely valuable.

IX. BIBLIOGRAPHY

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X. ACKNOWLEDGMENTS