Relative Apparent Molal Heat Contents
and Related Thermodynamic Properties of Some
Rare Earth Nitrates and Perchlorates at 25°C

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and related thermodynamic properties of some
rare earth nitrates and perchlorates at 25°C

by

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Graduate Faculty in Partial Fulfillment of
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TABLE OF CONTENTS

	Page
ABSTRACT	v
I. INTRODUCTION	1
II. THEORETICAL INTRODUCTION	6
A. Thermodynamics	6
B. Solution Theory	17
C. Applications of Theories to Experimental Observations	27
III. EXPERIMENTAL DETAILS	36
A. Sample Preparation	36
B. Experimental Apparatus	45
C. Experimental Procedure	60
IV. RESULTS	73
A. Mathematical Treatment	73
B. Heats of Dilution	85
C. Calculated Thermodynamic Properties	194
D. Analysis of Data Treatment	196
V. DISCUSSION	209
A. Polynomial Fitted Equation	209
B. Interpretation of Heat Data	212
VI. BIBLIOGRAPHY	241
VII. ACKNOWLEDGEMENTS	249

Relative apparent molal heat contents
and related thermodynamic properties of some
rare earth nitrates and perchlorates at 25°C¹

John Lucas Derer

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The heats of dilution of aqueous $\text{Pr}(\text{NO}_3)_3$, $\text{Sm}(\text{NO}_3)_3$, $\text{Tb}(\text{NO}_3)_3$, $\text{Dy}(\text{NO}_3)_3$, $\text{Tm}(\text{NO}_3)_3$, $\text{Yb}(\text{NO}_3)_3$, $\text{Pr}(\text{ClO}_4)_3$, $\text{Sm}(\text{ClO}_4)_3$, and $\text{Dy}(\text{ClO}_4)_3$ solutions were measured over the concentration range of 1×10^{-3} molal to saturation (4 - 6 molal) at 25°C. Empirical polynomial equations, directly fitted to the heat of dilution data by least squares techniques, were used to smooth the heat of dilution data, and to express the relative apparent molal heat content, ϕ_L , as a function of multiple powers of $m^{1/4}$. The forms of equation used were able to fit heat of dilution data across the entire concentration range from infinite dilution to saturation with seven coefficients. The resulting equations were used to calculate relative partial molal heat contents of the solute, $\bar{L}_2$, and of the solvent, $\bar{L}_1$, for molality values at which heat of dilution data was collected. Error values for the $\bar{L}_1$ and $\bar{L}_2$ values were

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obtained from the heat of dilution errors by means of random variable (stochastic) techniques.

In dilute regions, the rare earth nitrate and perchlorate solution ϕ_L values approach the values predicted by the Debye-Huckel limiting law as concentration is decreased. The ϕ_L data for the rare earth perchlorates at higher concentrations can be explained in terms of two different coordination numbers for the cations, one occurring for the low atomic numbered rare earths below Nd, and another for the rare earths above Tb. In between these two regions, the heat data can be explained in terms of an equilibrium between the two forms. For the ϕ_L data of the nitrates, the two series effect is not dominant, but instead, the data can be correlated with trends in the stability constants of rare earth mononitrate complexes across the series, and has a pattern across the series similar to the one for the heats of formation for some other rare earth complexes.

I. INTRODUCTION

Aqueous electrolyte solutions cover over seventy percent of the earth's surface, and aqueous solution processes are involved in almost all phases of activity in the biosphere. Water has been studied and considered as a part of every formalized explanation of our environment since antiquity. In the last decades of the nineteenth century, the studies of physical properties of liquid solutions became a large area of specialization now included in the field of physical chemistry.

The successful prediction of the dilute solution properties of strong electrolytes by Debye and Huckel (1) has been the basis of modern electrolytic solution theory. Although the theory considers only electrostatic contributions and therefore is applicable only to extremely dilute solutions, it serves as the starting point for all extrapolations to somewhat higher concentrations for all strong electrolyte solutions. The extensive discussions of the theory and its applications by Harned and Owen (2), and Robinson and Stokes (3) are becoming classics in electrolytic solution theory.

At the same time, the properties of electrolytic solutions at greater than dilute concentrations have complex behavior patterns that are only vaguely understood. Properties of these solutions are influenced by ion-solvent interactions, modifications of solvent structure by ions as hydra-

tion occurs, and short range interactions between ions. Included in this non-ideal behavior of solutions, is the fact that the solvent, water, has a unique structure. The recent publication of Eisenberg and Kauzmann discusses the properties of water as a pure liquid (4). The studies of various aqueous solutions in non-dilute situations and the possible structures of the solutions that can explain experimental data have recently been compiled by Horne (5). The extent of interest in aqueous solutions is also indicated by the start of a several volume treatise by F. Frank (6), that intends to cover most of the work being done in water and aqueous solution studies.

In trying to develop a quantitative understanding of solutions, a useful procedure would consist of varying one parameter of the solution independently of all others, and measuring the result. Varying temperature, pressure, and solute concentration independently allows determination of the functional dependence of bulk properties on these parameters. The dependence of bulk properties on microscopic considerations such as degree of complexation, ionic size, or degree of interaction with solvent can most easily be studied with a series of solutes that display an orderly change in each of these properties without the masking effect of other concurrent property changes.

The rare earth salts provide a close approximation to this requirement. Including lanthanum, there are thirteen rare earths which are convenient to use as trivalent ions in solution to form a series with an orderly change in microscopic properties. The electronic structure of each rare earth ion differs only in the 4f subshells, which are shielded by the filled 5s and 5p subshells, making the chemical properties of the rare earths very similar. There is a regular contraction of ionic radius with increasing atomic number. The rare earths do not hydrolyze as much as most other tri-valent ions in aqueous solutions, and the hydrolysis can be controlled with acid titration methods. The rare earth salts form solutions of up to 0.1 mole fraction concentration with several different anions. The use of the chloride, nitrate, and perchlorate anions provides useful comparisons for elimination of anion effects such as anion size or degree of complexation.

With the availability of large amounts of very pure rare salts at the Ames Laboratory, the laboratory undertook an extensive study of many properties of aqueous rare earth salt solutions from infinite dilution to saturation (7,8,9,10,11, 12,13,14,15,16,17,18,19). This thesis extends the work by presenting the heat content properties of nine rare earth nitrates and perchlorates as a function of concentration change.

Thermodynamic properties of dilute electrolytic solutions can be compared to the theoretical properties predicted by the Debye-Huckel theory, to determine the amount of deviation from the theory. For salts that dissociate 100% into ions, the activity coefficients and heats of dilution are quantities that can be theoretically related to the electrical work involved in creating charges on ions in dilute solutions. The experimental heat of dilution data can be conveniently and accurately extrapolated to dilute concentration ranges where theoretical dilute solution properties begin to manifest themselves. The extrapolation is easiest for some uni-univalent salts with only a small amount of hydrolysis and complexation at low concentrations (20,21), but many higher charge type electrolytes (21,22,23,24) have the complication of strong hydrolysis and complexation at low concentrations. Rare earth salts provide data where these effects can be minimized in dilute solutions, and heat data useful for extrapolation can be obtained for 1-3 electrolytes. This work extends the mathematical treatments used to provide more consistent and perhaps more accurate extrapolations in the dilute regions where there is an absence of experimental data. At the same time, the mathematical methods developed here provide great convenience in data processing when used with modern computers.

This thesis reports the heats of dilution for $\text{Pr}(\text{NO}_3)_3$, $\text{Sm}(\text{NO}_3)_3$, $\text{Tb}(\text{NO}_3)_3$, $\text{Dy}(\text{NO}_3)_3$, $\text{Tm}(\text{NO}_3)_3$, $\text{Yb}(\text{NO}_3)_3$, $\text{Pr}(\text{ClO}_4)_3$, $\text{Sm}(\text{ClO}_4)_3$, and $\text{Dy}(\text{ClO}_4)_3$ at 25°C from 0.001 molal to saturation. The apparent molal heat content and its partial molal derivatives for the above salts are calculated from zero concentration to saturation. Together with the work of Mohs (14), the trends for energy properties as a function of concentration and cation are discussed.

At greater than dilute concentrations, the energy properties are discussed in terms of the hydration change and complexing that seems to occur in the nitrates and perchlorates. The heat of dilution data of thirteen rare earth chlorides (13,25) have been interpreted in terms of a hydration change occurring as a shift between two different inner-sphere complexes. The partial molal volumes (12,17) of some aqueous rare earth chlorides, nitrates, and perchlorates also seem to indicate a hydration shift as a function of atomic radius at any given concentration of salt solution. This shift in hydration for partial molal volumes of the chlorides has also been studied as a function of temperature (19).

II. THEORETICAL INTRODUCTION

A. Thermodynamics

As mentioned earlier, aqueous electrolytic solutions comprise one of the more important states of matter and the physical properties of many solutions have been determined with increasing accuracy as better techniques and equipment became available. The dependence of the thermodynamic properties of a given mass of solution on the change in the state of the system can be determined in such a way that the difference depends only on the initial and final states of the system, and not on the procedure used to change the system. When determined in this manner, these properties can be mathematically treated as exact differentials and the properties are extensive functions that can be related in thermodynamic theory. As a result, only a few thermodynamic variables are needed to describe the solution system over a large range of changes in the state of the system. Since only a few variables are needed, thermodynamic functions are in extensive use in many engineering and scientific applications. A recent symposium considered some of the uses (26).

Thermodynamic properties of solutions have their most simple functional dependence when the fugacity of the components follows Raoult's law. The values of the thermodynamic properties of the solution are then equal to the sum of the mole-fractional contributions of the pure component property

value, and these solutions are called ideal or perfect over the concentration range that the relationship holds. However, aqueous electrolytic solutions have electric and magnetic fields created by ions in the solution that interact with each other and with the directional hydrogen-bond structure of water. At the same time, most of the molecules and ions retain a high degree of mobility in the solution. For more concentrated solutions, complexation, hydration, and ion pairing introduces more complications. These factors all combine to produce a very complicated functional dependence that is not yet fully understood. In spite of these complications, the thermodynamic properties remain precise and only a few variables are still needed to characterize the solution.

To obtain information about interactions that occur in aqueous solutions, it is useful to examine excess thermodynamic properties of the solution, which consist of the thermodynamic properties of the solution without the ideal solution contribution. The definition of an ideal solution implies that forces between like molecules in a solution are the same as forces between unlike molecules in a solution. Aqueous electrolytic solutions differ drastically from this since water exists as a hydrogen bonded system, and the solute component interacts with other molecules primarily through electrostatic forces. Most electrolytic solutes do

not exist as pure liquids in the temperature range at which most experimental measurements are made on aqueous solutions. Therefore, excess thermodynamic properties are reported as if the ideal solution is the final state. The excess properties of electrolytic solutions will then reflect changes due to the disruption of the hydrogen-bonding structure of the water, any changes in the interactions between solute and solvent, and any changes in the solute complexes. In the case of heat of dilution data, the ideal heat of mixing or dilution is equal to zero at all concentrations. Because of this, the excess heat of mixing is also equal to the heat of dilution to a final state that is very closely approaching a pure solvent.

Thermodynamics provides concise descriptions of solution systems without recourse to molecular descriptions of the solutions. However, it is important to be able to relate thermodynamic property values to microscopic conditions in the solution so that the chemical reasons for the observed properties can be understood, and then used to predict property values for other situations. The interpretation of thermodynamic property behavior requires some knowledge of molecular properties. The presence of electrical charges in electrolytic solutions will cause an electrical work term to be involved in most changes of state. This electrical work plays a dominant role in dilute solutions, and this aspect will be

covered in the next section of this chapter.

Another way to obtain molecular model descriptions of solutions is through the application of statistical mechanics to the microscopic properties of the solution components. These applications use one of several models for calculating thermodynamic properties for liquids and liquid mixtures from microscopic properties (27,28,29,30,31). Each of these models requires some simplification of the situation in the liquid. For dilute solutions, statistical mechanics has been used to analyze the electrostatic models and provide further insight into their validity and applicability (32,33,34,35). For non-dilute electrolytic solutions, the hydration, complexations, ion pairings, and other solute ion interactions preclude the possibility of any simple statistical mechanical model ever being able to describe the solution structure. The relationships that have been developed between microscopic and macroscopic properties in general, indicate that thermodynamic properties are related to statistical averages of molecular properties. The thermodynamic properties are thus also useful in judging the validity of any statistical theory of solutions developed in the future.

In calorimetry, the absorption or evolution of heat energy, q , is monitored while some change in the state of a system occurs. In general, the heat absorbed or evolved by a system is not a thermodynamic function of state. In dilution

calorimetry of aqueous electrolytic solutions the change of state occurs as a mixing process, where a salt initially in a solution of water is allowed to further dilute into more water. The experiment is performed in such a manner that the heat evolved or absorbed can be related to the internal energy of the system, E , through the use of the first law of thermodynamics. Several good reviews of thermodynamics, as applied to solutions and their components, can be found in the literature (2,36,37).

The first law of thermodynamics defines the change in the internal energy of a system, ΔE , as related to the heat absorbed or evolved, and to the work done on or by the system. Mathematically, the first law is expressed as in Equation 2.1,

$$\Delta E = q - w \quad (2.1)$$

where q is the absorbed energy and $-w$ is the work done on the system. If heat is evolved or work is done by the system, the sign associated with the quantity is changed. In general, q and w are not exact differentials but depend on the path along which the change of state occurs. The work term in the equation represents all of the possible sources of work, but in dilution calorimetry, w is restricted to volume change work, $P\Delta V$, and the system is held at constant pressure during the dilution process. The ΔE in the dilution

process represents the change in the internal energy of the system as the system goes from an initial state to some final state. In order to compare the internal energy of solutions at different concentrations, some common reference point is used as the standard state. For internal energy properties, the solution at infinite dilution is picked as the standard state, since the internal energy of an ideal solution is also equal to this. In theoretical discussions of heat properties, the final state is picked to be the standard state. Experimental heat changes are not measured directly to infinite dilution because of constraints on experimental setups, and must instead be adjusted by some means to the standard state. The values of thermodynamic properties at the standard state are indicated by a superscript o . Restricting work to volume change work, and restating Equation 2.1 in terms of the initial and the standard state yields Equation 2.2.

$$q = E^i - E^o + P(V^i - V^o) \quad (2.2)$$

A new function, the enthalpy, is defined by Equation 2.3,

$$H = E + PV \quad (2.3)$$

where H is the enthalpy of a system, and E , P , and V are used as before. If the enthalpy is determined at constant

pressure, Equation 2.3 can be explicitly stated in terms of the initial and the standard state as in Equation 2.4.

$$H^i - H^o = E^i - E^o + p(v^i - v^o) \quad (2.4)$$

Substitution of Equation 2.4 into Equation 2.2 yields Equation 2.5.

$$q = H^i - H^o = \Delta H \quad (2.5)$$

Equation 2.5 states that under the conditions of the dilution experiments, the heat evolved or absorbed is an exact thermodynamic function.

It is of interest to determine the enthalpy as a function of the numbers of moles of each substance in the system under study. If temperature and pressure are held constant in the system, Euler's theorem allows us to write Equation 2.6,

$$H(n_1, n_2) = n_1 \bar{H}_1 + n_2 \bar{H}_2 \quad (2.6)$$

where $\bar{H}_j$ is defined as the partial molal heat content of the "j"th component of the solution at constant temperature and pressure with the concentration of the other component held constant. Substituting Equation 2.6 into 2.5 yields Equation 2.7.

$$\Delta H = n_1 (\bar{H}_1^i - \bar{H}_1^o) + n_2 (\bar{H}_2^i - \bar{H}_2^o) \quad (2.7)$$

A relative heat content, L , that represents the excess heat content of a solution, is defined in Equation 2.8.

$$L = \Delta H = H^i - H^o \quad (2.8)$$

Equation 2.7 then becomes Equation 2.9.

$$L(n_1, n_2) = n_1 \bar{L}_1 + n_2 \bar{L}_2 \quad (2.9)$$

In making measurements of the heat contents it is impossible to measure the partial molal heat contents of the solvent and solute separately. It is therefore convenient to attribute all of the enthalpy change with concentration to the solute alone. This total enthalpy change is called the relative apparent molal heat content and is defined in Equation 2.10 using the symbol ϕ_L .

$$\phi_L = \frac{L(n_1, n_2) - n_1 \bar{L}_1^o}{n_2} \quad (2.10)$$

Substituting Equation 2.9 into 2.10 and realizing that the relative heat content of the solvent at infinite dilution is zero, Equation 2.10 can then be expanded to Equation 2.11.

$$n_2 \phi_L = L(n_1, n_2) = n_1 \bar{L}_1 + n_2 \bar{L}_2 \quad (2.11)$$

Using Equation 2.11, the relative partial molal heat contents can be obtained by differentiation to yield Equations 2.12 and 2.13,

$$\bar{L}_2 = m_2 \left(\frac{\partial \phi_L}{\partial m_2} \right)_{T,P,m_1} + \phi_L \quad (2.12)$$

$$\bar{L}_1 = \frac{-m_2^2 M_1}{1000} \left(\frac{\partial \phi_L}{\partial m_2} \right)_{T,P,m_1} \quad (2.13)$$

where n_2 is replaced by m_2 , the number of moles of solute in 1000 grams of water, and n_1 is expressed as a function of M_1 , the molecular weight of water, in Equation 2.14.

$$n_1 = 1000/M_1 \quad (2.14)$$

It is impossible to determine ΔH values directly from the initial concentration to infinite dilution, and experimental samples are diluted to some final concentration greater than infinite dilution. This is done by diluting a sample of solution containing n_1 moles of solvent and n_2 moles of solute into n_1^* moles of pure solvent. The observed heat of dilution, $\Delta H(\text{dil})$, is the difference in relative heat contents between the initial and final states, as given in Equation 2.15.

$$\begin{aligned} \Delta H(\text{dil}) = & (n_1 + n_1^*) \bar{L}_1^f + n_2 \bar{L}_2^f - n_1 \bar{L}_1^i \\ & - n_2 \bar{L}_2^i - n_1^* \bar{L}_1^o \end{aligned} \quad (2.15)$$

Data collected for heats of dilution was reported as heats of dilution per mole of solute, and so, simplifying with Equation 2.10, Equation 2.15 becomes Equation 2.16.

$$\Delta H_{i-f} = \phi_L(m_i) - \phi_L(m_f) \quad (2.16)$$

Various methods for estimating $\phi_L(m_f)$ values are discussed in the section on applications of theories to experimental observations, and the method used in this research is discussed in the section on mathematical treatment of data.

Values of relative partial molal heat contents obtained from the relative apparent molal heat contents can then be combined with excess partial molal free energy values to yield relative partial molal excess entropy values for the solute using Equation 2.17. Since the enthalpy of mixing for an ideal solution is equal to zero, the partial molal enthalpy of the standard state is also the partial molal enthalpy of the ideal solution at any concentration.

$$\bar{F}_2 - \bar{F}_2^{\text{id}} = \bar{F}_2^{\text{ex}} = \bar{H}_2 - \bar{H}_2^0 - T(\bar{S}_2 - \bar{S}_2^{\text{id}}) \quad (2.17)$$

The excess partial molal free energy of the solute is given in Equation 2.18, in which v represents the number of ions per molecule of solute, R is the universal gas constant, T is the absolute temperature, $\gamma_{\pm}$ is the mean molal activity coefficient, $f_{\pm}$ is the mean mole fractional activity coefficient, and the mole fraction of the solvent, N_1 , is defined in Equation 2.19.

$$\bar{F}_2^{\text{ex}} = vRT \ln(f_{\pm}) = vRT \ln(\gamma_{\pm}) - vRT \ln(N_1) \quad (2.18)$$

$$N_1 = 55.51 / (55.51 + vm) \quad (2.19)$$

Since experimental data is collected in the form that $\gamma_{\pm}$ can be directly calculated, the right hand side of Equation 2.18 is used to calculate the excess partial molal free energy of the solute. The right hand side of this equation occurs because of the relationships between different standard state definitions, as discussed by Harned and Owen (2). The use of the excess partial molal free energy for the solute avoids computational problems by eliminating the partial molal free energy of the solute in the ideal solution at infinite dilution from the total partial molal free energy of the solute. At infinite dilution, the total partial molal free energy of the solute is equal to negative infinity.

Combining Equations 2.17, 2.18 and the definition of $\bar{L}_2$ yields the relative partial molal excess entropy values as calculated from available mean molal activity coefficient data according to Equation 2.20.

$$T(\bar{S}_2 - \bar{S}_2^{\text{id}}) = \bar{L}_2 - RT \ln(\gamma_{\pm}) + RT \ln(N_1) \quad (2.20)$$

The partial molal excess entropy of the solvent is obtained from the thermodynamic relationship for the solvent that is analogous to Equation 2.17. The excess partial molal free energy of the solvent is defined in terms of the activity data for the solvent by Equation 2.21,

$$\bar{F}_1^{\text{ex}} = RT \ln(a_1/N_1) \quad (2.21)$$

where a_1 is the activity of the water. The equation for the partial molal excess entropy of the solvent is then given by Equation 2.22.

$$T(\bar{S}_1 - \bar{S}_1^{id}) = \bar{L}_1 - RT \ln(a_1/N_1) \quad (2.22)$$

B. Solution Theory

Aqueous solutions of many compounds show very different behavior when compared to ideal solution properties. The hypothesis by Arrhenius (38,39) that certain solutes can dissociate into ions in solutions led to an adequate solution theory for weak electrolytes that only partially dissociate when put into solution. For strong electrolytes such as sodium chloride, colligative properties seemed to indicate that dissociation was not complete, while other properties seemed to indicate total dissociation. The theory used for weak electrolytes did not account for this properly. A different theory of solutions was needed but early attempts to provide a theoretical description of strong electrolytes were less than adequate.

In 1910 Gouy (40) developed a mathematical model of the excess charge density to be found in the solution near a charged electrode. In his model, he was first to suggest that ionic charges could be represented by a continuous cloud distribution, whose electrostatic potential and charge densi-

ty could be treated by Poisson's equation. With the substitution of a charged ion for the charged electrode, this would later be useful in developing an electrostatic model of an electrolytic solution. In 1912 and 1913 Milner (41,42) attempted to develop an equation for the electrical work involved in separating the charged ions found in an electrolytic solution. He summed up the contribution of each ion-ion interaction to arrive at an equation for the total energy involved. In presenting some experimental data related to osmotic coefficients, he extrapolated a closed expression for the property at infinite dilution, that implied a square root dependence on concentration. The equations that resulted for the general case were too involved to be convenient at the time, and the implication of square root of concentration dependence for dilute concentrations of solution was missed until it was pointed out later empirically by Lewis and Randall (43). Later, the square root dependence was obtained directly as a result of the successful electrostatic treatment of dilute aqueous solutions.

An important quantitative theory of dilute solutions was published by Debye and Huckel in 1923 (1,44). They managed to compute the electrical work done in charging completely dissociated ions in solution to yield an expression for the free energy involved in this process. The initial state for the calculation was hypothetical uncharged ions that were

dispersed in the solution in the same way that charged ions were. The final state of the calculation was the same ions in the same distribution with all ions now charged. As the Debye-Huckel theory was developed into its most successful form, the following assumptions were used to describe the solution:

1. Strong electrolytes are treated as completely dissociated, rigid, spherical ions with a mean distance of closest approach, a .
2. The calculations are carried out for each ion as a central ion and all other ions and solvent molecules form a continuous medium with a uniform dielectric constant. The results for each ion are then summed over all ions. The results are then summed over all ions. As infinite dilution is approached, the dielectric constant is equal to the dielectric constant of water, D .
3. The solution as a whole is electrically neutral. The continuous medium defined above, therefore, surrounds the central ion with an ion cloud whose charge balances the central ion charge, and whose distribution about the central ion is described by the Boltzmann distribution function,

$$\rho(r) = \sum_j z_j n_j \exp(-z_j e \psi(r) / kT) \quad (2.23)$$

where $\rho(r)$ is the charge density of the cloud as a function of the radial distance from the central ion, $z_j e$ is the charge on each of n_j ions in the ion cloud, $\psi(r)$ is the electronic potential as a function of the radial distance, k is Boltzmann's constant and T is the absolute temperature.

4. The electrostatic potential of the ion can be related to the charge density by Poisson's equation.

$$\nabla^2 \psi(r) = -4\pi\rho(r)/D \quad (2.24)$$

5. The Poisson equation implies that the potentials of various ions must be linearly superimposable. Since the Boltzmann distribution function is not linear, an approximation must be made for the function by expanding it as an infinite series and truncating the series at the first non-zero term to yield the following functional form.

$$\rho(r) = \sum_j n_j z_j^2 e^2 \psi(r) / kT \quad (2.25)$$

6. The departure of the solution from ideal behavior is due solely to the electrical work involved in charging the ions in solution.

Using these assumptions, Debye and Huckel derived an expression for the electrical potential at any given point

about the central ion. Rigorous derivations and detailed discussions of the results are presented in many texts (2,3, 37,45,46). The important steps in the derivation involve the linearization of the Boltzmann function, and the combination of the linearized Boltzmann function with the Poisson equation to yield a useful description of the solution structure. At the same time, the approximations made in the derivation causes the model to only agree with experimental properties of very dilute solutions.

The electrical potential from the results of Debye and Huckel's work, and the excess free energy of the solute can be related. The expression for the excess free energy is then given in Equation 2.26.

$$\Delta \bar{F}_2^{\text{ex}} = \nu N k T \ln(f_{\pm}) = - \sum_i \nu_i z_i^2 e^2 N K \tau / 3D \quad (2.26)$$

where N is Avogadro's number, ν is the total number of ions into which one molecule of solute dissociates, ν_i is the number of ions having charge $z_i e$, and $f_{\pm}$ is the mean rational ionic activity coefficient. Equation 2.27 defines K , the reciprocal of the distance between the central ion and the position of maximum charge in the ion cloud. Equation 2.28 defines τ , a series expansion in Ka , which occurs in the equation for the electrical work involved.

$$K = (\sum_i \nu_i z_i^2)^{1/2} (4\pi N e^2 / 1000 D k T)^{1/2} c_i \quad (2.27)$$

$$\tau = \frac{3}{(Ka)^3} [(Ka)^2/2 - Ka + \ln(1 + Ka)] \quad (2.28)$$

In Equation 2.27, c is the molar concentration of the solution. The excess molar enthalpy of dilution with respect to infinite dilution is obtained by applying the Gibbs-Helmholtz relationship to Equation 2.26. The excess molar enthalpy of dilution is equivalent to the relative apparent molal heat content ϕ_L , expressed in molar units. The expression for ϕ_L is given in Equation 2.29 and Equation 2.30.

$$\phi_L = \Delta \bar{H} = -T^2 \frac{\partial}{\partial T} \left[\frac{\Delta \bar{F}^{ex}}{T} \right] \quad (2.29)$$

$$\phi_L = -T^2 \frac{\partial}{\partial T} \left[-\frac{Ne^2}{3} \sum_i v_i z_i^2 \frac{TK}{DT} \right] \quad (2.30)$$

The expression in Equation 2.30 was first obtained by Owen and Brinkley (47) with corrections later added by Vanderzee and Swanson (48). The fully expanded form for ϕ_L is given in Equation 2.31.

$$\begin{aligned} \phi_L = & -A \left[\frac{1}{1+Ka} \left(\frac{1}{T} + \frac{\partial \ln D}{\partial T} \right) + \frac{\alpha \sigma}{3} \right] c^{1/2} \\ & + A \left[\sigma - \frac{1}{1+Ka} \right] \left[\frac{\partial \ln(a)}{\partial T} \right] c^{1/2} \end{aligned} \quad (2.31)$$

where α is the thermal expansibility of the solvent and the functions A and σ are defined below.

$$A = \frac{NTe^2}{2D} \left[\frac{4\pi Ne^2}{1000DkT} \right]^{1/2} \left[\sum_i v_i z_i^2 \right]^{3/2} \quad (2.32)$$

$$\sigma = \frac{3}{(Ka)^3} \left[1+Ka - \frac{1}{1+Ka} - 2\ln(1+Ka) \right] \quad (2.33)$$

At infinite dilution, τ , σ , and Ka approach values of 1, 1, and 0, respectively. Substitution of these values into Equation 2.31, yields the limiting form of ϕ_L at infinite dilution as stated in Equation 2.34.

$$\phi_L = -A \left(\frac{\partial \ln D}{\partial T} + \frac{1}{T} + \frac{\alpha}{3} \right) c^{1/2} \quad (2.34)$$

At extremely dilute concentrations, the molarity of the solution is equal to the molality multiplied by the density of the solvent. In the limit of infinite dilution, ϕ_L can then be expressed in terms of molality as in Equation 2.35,

$$\begin{aligned} \phi_L &= -Ad^{1/2} \left[\frac{\partial \ln D}{\partial T} + \frac{1}{T} + \frac{\alpha}{3} \right] m^{1/2} \\ &= A_H m^{1/2} \end{aligned} \quad (2.35)$$

where d is the density of water.

In the original derivation of the limiting law, the electrostatic work properties were calculated for the process of charging all of the ions in solution simultaneously.

Guntelberg proposed and Bjerrum (49) first used a charging process where only the central ion in the model was uncharged

in the initial state, and the ion cloud was already charged in both the initial and final states of the process change. The electrostatic properties were then calculated for the charging process of the central ion. For the Debye-Huckel model of an electrostatic solution, the two methods of calculating the excess properties yield the same results.

The statistical mechanical analysis of the Debye-Huckel model has been carried out in detail. Fowler (32) pointed out that the use of the Boltzmann distribution function does not allow the properties to be an integrable function of ionic charge, while linearizing the distribution function corrects this to allow calculated properties to be consistent with statistical mechanical principles. Onsager (33) and Kirkwood (34) pointed out that non-linearized versions of the Debye-Huckel model have errors in their electrical potential caused directly by the departure from the linearized version. Kirkwood and Poirrer (35) developed the statistical mechanical basis of the Debye-Huckel theory and demonstrated the validity of the limiting law at infinite dilution unambiguously.

Onsager's consideration of the electrostatic model of electrolytic solutions shows that for the linearized version of the model, the Debye charging process, used in the original determination, and the Guntelburg charging process will yield the same results for solution property equations, while

non-linearized versions will give different equations. Applying the two charging processes to any version of the electrostatic solution model gives a practical test of validity for the model. The attempts of Muller (50), Gronwall et al. (51), and LaMer et al. (52) to extend the model to higher concentrations by using higher terms in the Boltzmann distribution function fail to meet this criteria, and even though some empirical improvement may occur in the agreement of theory with experiment, this approach cannot yield any expanded theory that relates properties to fundamental physical constants.

Another method of extending the Debye-Huckel limiting law to higher concentrations involves the use of additional parameters to account for effects due to hydration, incomplete dissociation, and the presence of other fields. The first such parameter used was the mean distance of closest approach parameter, a , in the fully developed limiting law. It accounts for the effect of a central ion that has a volume greater than that of a point charge. This parameter doesn't explain away all of the deviation that occurs at higher concentrations, and Bjerrum (53) replaced the a term with a parameter that included contributions from ion-pair formation. Other work in this area includes that of Huckel (54), Scatchard (55), Stokes and Robinson (56) Wicke and Eigen (57,58), and Glueckauf (59). However, all methods that use

an added parameter cannot assign a value to the parameter from theoretical considerations alone, and rely on experimental data to determine numerical values for the parameter. This provides a useful empirical relationship in many cases, but does not provide an expanded understanding of microscopic solution properties on a theoretical basis. A qualitative analysis of activity and heat properties of higher concentration liquids is given by Bockris and Reddy (45). By defining a free energy term that compensates for the energy used in the hydration of a water molecule into a certain hydration sphere about the central ion, he can explain the existence of changes in the properties as a function of concentration. This can empirically explain the existence of endothermic heats of dilution over certain concentration ranges. However, the occurrence of endothermic heats has many causes and the use of this term does tend to be too simplistic to be real. More recently, Mayer has developed a theory of ionic solutions based on a virial development for the osmotic pressure of a solution (60) similar to his cluster theory of imperfect gases (61). Poirrer (62) has obtained expressions for thermodynamic properties of solutions using Mayer's results. Friedman and several co-workers have extended Mayer's work to mixtures of ionic solutes (63) and have made comparisons with experimental data (64,65). In the case of dilute solutions, Mayer's model becomes identical to that of Debye

and Huckel. Mayer's method avoids the linearization problem inherent in the Debye model, but since the theory still considers only electrostatic contributions, it cannot be expected to be accurate in greater than dilute solutions.

The limiting law theory based on electrostatic considerations represents the most concise and precise theory of electrolytic solutions that is available to date. Any theory of non-dilute solutions will need to agree with the limiting law as lower concentrations are approached, but to obtain a theory of solutions in more concentrated solutions, solvent structure, short-range ion-solvent interactions, and complex formation will need to be more completely understood.

C. Applications of Theories to Experimental Observations

The solution theory of strong electrolytes predicts excess free energy values for solutions in concentration ranges where electrostatic forces are the only source of non-ideal behavior of solution properties. Through the use of thermodynamic theory, the theoretical values for heat properties of electrolyte solutions at these concentrations can be calculated. The concentration range for which these calculations are applicable includes the standard state for the heat properties of solutions. At the same time, experimental heat of dilution data is generally obtained in concentration ranges where excess properties are also influenced by non-

electrostatic interactions among the components in the solution, and experimental data obtained at concentrations close to the standard state is subject to greater inaccuracies because of experimental difficulties. As a result, theoretical equations of heat properties are important as extrapolation equations for extending experimental data results to their standard states. Since non-electrostatic influences exist in the experimental data, empirical terms are usually introduced to compensate for these influences. The use of empirical parameters is also useful for smoothing data above the range where electrostatic theory applies. To date, much of the work in fitting heat data for solutions has concentrated on using theoretical equations as extrapolation functions. As extrapolation functions, the theoretical equations suggest certain characteristic dependences on concentration for the experimental data.

One characteristic of limiting law behavior arises from the fact that heat properties are defined in relative terms according to Equation 2.8. Using this equation to assign a value of zero to ΔH° sets a value of zero at infinite dilution for ϕ_L , $\bar{L}_1$, and $\bar{L}_2$. This behavior is generally introduced into an extrapolation function by not including any non-zero constant term in the equations for these properties.

A second characteristic arises from Equation 2.35, where A_H has a particular value representing the slope of the ϕ_L

equation at infinite dilution. The limiting slopes of $\bar{L}_1$ and $\bar{L}_2$ are also related to A_H through Equations 2.12 and 2.13. The value of A_H depends on the physical properties of the solvent, the charge distribution on the ions formed by the solute, and on several physical constants. In calculating a particular value for A_H , the largest source of uncertainty comes from the dielectric constant value and its temperature derivative as experimentally determined for water. The expansibility data for water and the physical constants represent a negligible source of error for this calculation. Using the expansibility data of Kell (66), the value of A_H can be calculated using several recent sources of dielectric constant data. Using the data of Wyman and Ingalls (67), Equation 2.35 yields a value of 6931 for A_H . Using Lees' values (68), A_H is calculated to be 7012. Using the data of Malmberg and Maryott (69) A_H equals 6736. The relatively recent data of Owen et al. (70) yields 7004, and a check by Vidulich and coworkers (71) yields dielectric constant values close to Owen's and Lees' values. The source of error in the dielectric data is generally attributed to problems of standardization for the experimental setup. These problems are yet to be resolved, and the calculated value of A_H will have significant uncertainty in it until the problems are solved. In this work, A_H will be set at 6990, which is a weighted average of the above data, excluding that of Malmberg and

Maryott.

Instead of using the limiting slope value, A_H , it is possible to use the expanded equation for ϕ_L as given in Equation 2.31. Two new parameters that are used in this form of equation are the Debye-Huckel parameter, a , and its temperature derivative. The Debye-Huckel parameter is different for each electrolyte but accuracy is limited by the fact that non-electrostatic contributions of heat can exist in the data used to determine the value. The value of the derivative cannot be determined accurately because experimental data is not generally accurate enough to distinguish the temperature dependence of the Debye-Huckel parameter from the temperature dependence of the experimental data due to other factors. If a form of equation, based on Equation 2.31, is used for extrapolation, then uncertainties that occur for A_H also occur in this form of equation, and in addition, the uncertainties due to the Debye-Huckel parameter and its temperature derivative are significant.

The characteristics listed above have been incorporated into extrapolation procedures in many different ways. One of the earliest attempts at extrapolation was the short chord method developed by T. Young and co-workers (21,72,73) and modified by Robinson and Wallace (23). This procedure took advantage of an experimental arrangement that allowed calculation of the slope of ϕ_L at low concentrations.

In the short chord method, two solutions of the same initial concentration, m_1 , are diluted to different final concentrations, m_2 and m_3 , close to each other, such that the average of the square roots of the final concentration occurs in the concentration region close to infinite dilution. To minimize errors, both dilutions are usually carried out in the same calorimeter container, under the same conditions. The difference between the two heat of dilution values obtained experimentally, is equal to the heat of dilution, ΔH_{3-2} , that occurs in diluting a solution at concentration m_3 to concentration m_2 . This is related to the average slope, $\bar{P}_i$, of ϕ_L as a function of $m^{1/2}$ between the two final concentrations as given in Equation 2.36.

$$\bar{P}_i = - \Delta H_{3-2} / (m_2^{1/2} - m_3^{1/2}) \quad (2.36)$$

The average slope is related to the true slope, S , by Equation 2.37,

$$\bar{P}_i = \frac{\int_{m_2}^{m_3} S \, dm^{1/2}}{(m_3^{1/2} - m_2^{1/2})} \quad (2.37)$$

in which Young and coworkers used Equation 2.38 to represent the true slope.

$$S = A_H + Bm + cm^{1/2} \quad (2.38)$$

Values of $\bar{P}_i$ are obtained from experimental data using Equa-

tion 2.36 and the values of the coefficients in Equation 2.38 can be obtained from the data by mathematical or graphical techniques. The integral of Equation 2.38 with respect to the square root of the molality yields an equation for ϕ_L in the dilute concentration region, if the integration constant is set equal to zero. If accurate, properly spaced $\bar{P}_i$ points can be obtained, it is possible to determine an accurate value for each coefficient. But in actual practice, experimental errors contained in the original measured heat of dilution data is transferred to the $\bar{P}_i$ data in such a way that scattering increases quickly in the $\bar{P}_i$ points as the average final molality value decreases. As a result, A_H values are obtained from Equation 2.35 and are substituted into Equation 2.38 to allow a more accurate determination of the other coefficients.

At about the same time, Scatchard and coworkers (74,75) were studying the application of forms of Equations 2.26 and 2.31 to several experimentally determined properties of electrolytic solutions at dilute concentrations. Their work became the basis for other applications of these equations. Owen and Brinkley (47) have discussed the application of Equation 2.31 to sodium chloride data at 25°C in the form given in Equation 2.39,

$$\phi_L = \left[-A \frac{1}{1+Ka} \left(\frac{1}{T} + \frac{2 \ln D}{\partial T} \right) + \frac{g\alpha}{3} \right] c^{1/2} + Bc \quad (2.39)$$

while Guggenheim and Prue (76) studied the same form of equation as a function of molality instead of molarity. In each case, sodium chloride data was fitted to Equation 2.39 which is derived from Equation 2.31 in two steps. The first adjustment is to set the temperature derivative of the Debye-Huckel parameter equal to zero. The second consisted of adding an empirical parameter with a linear dependence on concentration. This form of the equation provided good fits in the 0.1 to 0.0007 m concentration region for the sodium chloride data. More recently, Vanderzee and Swanson (48,77) have fitted sodium perchlorate, perchloric acid, and barium perchlorate to an equation similar to the Owen-Brinkley equation. The principal difference in their fitting equation was that the temperature derivative of the Debye-Huckel parameter was set at a non-zero value adjusted to give the best fit for the data. The fit was accurate in the range from infinite dilution to about 0.7 molal for the 1-1 electrolytes and 0.07 molal for the 1-2 electrolyte. Jones and Wood (78) used Owen and Brinkley's form of the fitting equation with an added second empirical term, with a $3/2$ power dependence in concentration, to fit lithium perchlorate data up to about 0.1 molal.

The extrapolation of heat data to infinite dilution has, until recently, depended on graphical methods to obtain a

best fit of data to one of the theoretical equations. This is one reason why simplifications, such as setting the temperature derivative of the Debye-Huckel parameter equal to zero, have been common. With the availability of modern electronic computers, more sophisticated analytical methods of fitting data are becoming practical. In 1969, H. F. Gibbard, Jr. (79) introduced an analytical way of fitting data to an equation similar to Equation 2.39. The difference in his equation was the use of a three or four term polynomial in powers of molality to fit sodium chloride data over a concentration range from 0.2 molal to 6.0 molal.

In other recent work, Bahe (80,81) has developed an equation for ϕ_L data in very dilute concentration regions (<0.05 molal) with a cube root dependence on concentration.

The use of the above fitting functions for data extrapolations has improved the ability to obtain more accurate extrapolations of heat data to its standard state, but improvements to present methods are still needed. First, the inaccuracy in the experimentally determined parameters for the theoretical equations limit the ability to determine the exact relationship of the experimental data to theoretical parameters. This is especially the problem involved in trying to use the temperature derivative of the Debye-Huckel parameter for which no experimental value is known. The use of theoretical parameters also involves the danger of forcing

experimental data to fit a theoretical curve which cannot properly represent the effects of non-electrostatic interactions when present. In this situation, if the theoretical parameters are kept at theoretical values, the extrapolation may be forced to smooth out these effects, and if theoretical parameters are adjusted to values that give the best fits, their theoretical meaning may be lost. At the present state of the art, there still exists a need for better, more general procedures, that may better represent solution data. This is especially true for higher concentration data, where improved methods are needed to provide greater insight into the functional dependence of heat properties on concentration and other parameters.

III. EXPERIMENTAL DETAILS

A. Sample Preparation

Stock solutions of the six rare earth nitrate and three rare earth perchlorate solutions were prepared from the corresponding rare earth oxide purified by ion exchange methods (82) in the rare earth separation group of the Ames Laboratory. The purity of the oxides was determined from their emission spectra and the results are listed in Table 1.

The oxide was dissolved in the appropriate C.P. grade concentrated acid to yield a stock solution whose concentration was near that of a saturated solution. As the acid finished reacting with the oxide, heat was applied and oxide or acid was added, if needed, to yield a solution near a pH of 3 to 5. This was indicated by a murkiness in the solution. When no solid oxide was left in the beaker, the murkiness was filtered out through a sintered glass funnel. Cooled samples of the stock solution were titrated with a .5 normal solution of the same acid using a Sargeant model D recording titrator. The overall reaction involved in the titration can be given by equation 3.1.

After obtaining the equivalence point of the sample, usually near a pH of 1 or 2, the stock solution was titrated to the same point. Stock solutions are highly viscous and

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

OXIDES	ANALYSES IN WEIGHT PERCENT*		
Pr_6O_{11}	Ca: (0.020) Fe: <0.010 Si: <0.025	La: (0.005) Ce: (0.075) Na: (0.060)	Sm: <0.010
Sm_2O_3	Ca: <0.002 Fe: (0.004) Si: 0.004	Y : <0.005 Pr: 0.020 Nd: 0.020	Eu: 0.010 Gd: (0.030)
Tb_4O_7	Ca: (0.002) Fe: (0.005)	Si: <0.005 Gd: (0.020)	Dy: <0.010
Dy_2O_3	Er: <0.020 Ho: <0.050	Y : (0.007)	
Tm_2O_3	Ca: 0.003 Si: <0.006 Y : (0.001)	Ho: (0.020) Er: (0.003) Yb: 0.008	Lu: (0.030)
Yb_2O_3	Ca: 0.040 Fe: 0.005	Tm: <0.002 Lu: <0.002	Er: <0.002

*The less-than symbol, <, indicates that the element was detected but was present in an amount less than the number reported, which is the lower limit of the quantitative analytical method. Parentheses, (), indicate that the element was not detected and the number reported is again the lower limit of the quantitative analytical method.

the reaction between the acid and the colloidal oxide particles and their complexes is slow. The stock solution was therefore heated overnight. The solution would usually become basic with respect to the equivalence point, and the titration process was repeated the next day. This was continued over several days until, finally, the solution remained at its equivalence point after a long period of heating. If at any time the solution became acidic with respect to its equivalence point, a little oxide was added to make it basic, and the entire heating, filtering, and titrating procedure was repeated.

When the pH of the solution remained constant at the equivalence point, the solution was ready for bottling. The perchlorate solutions were first filtered through a 0.25 to 0.45 micron membrane filter to remove undissolved solid particles, analyzed as mostly silica, which could be detected as bright specks of light in the beam of a laser passing through the solution. All the solutions were then bottled in flasks fitted with a male ground glass joint, with a coating of silicone grease at the top, and sealed with a ground glass cap. Properly prepared solutions capped in this manner have not changed concentration to within 0.1% over a period of more than five years. These bottled solutions were then used as primary stock solutions. Two methods were used to analyze the perchlorate and nitrate solution concentrations.

EDTA method: Samples of rare earth electrolyte solutions were delivered into flasks by weight burettes. The sample weights were obtained by differences in the burette weight before and after delivery. Enough sample was used to need 50 to 80 grams of a 1.5 to 2.0×10^{-4} moles per gram EDTA solution. To each sample, 250 ml. of pH 5 buffer was added. The buffer was prepared by adding 109 grams sodium acetate and 25 ml. of acetic acid to two liters of conductance water. Four or five drops of xylenol orange indicator were added to yield a purple-red color in the sample solution. The samples were titrated with the EDTA solution from another weight burette to the yellow endpoint of xylenol orange indicator. When the yellow color would first appear in the titration, pyridine was added a few milliliters at a time, and the color changed back to the original purple. At the endpoint, the main species in solution is the rare earth-EDTA complex, which would shift to the pyridine phase of the solution, letting the complexing reaction go to completion. With the addition of more titrant, the color shifted once more to the yellow and more pyridine was added to shift the color back to purple again. The titration was considered complete when one drop of titrant produced a sharp change from purple to yellow, and an excess of pyridine did not shift the color back again.

The EDTA solution was standardized against a rare earth electrolyte solution prepared from a pure metal sample of a rare earth within 3 atomic number units of the unknown. Going further away along the lanthanide series caused discrepancies between the endpoint of the standard and the endpoint of the unknown. The weighed metal sample was dissolved in a weighed mixture of acid and conductance water to yield a slightly acidic mixture. Care was taken to minimize water loss during the reacting. Mass spectra analyses of the metal were used to correct for the molar concentration of rare earth actually in the sample. This was done by subtracting out the mass of the impurities not expected to react with the EDTA, and calculating the effective change in molar concentration due to impurities that replace some moles of rare earth in the reaction by themselves reacting with the EDTA.

Four samples of rare earth unknown were run for each determination. This method had a precision of $\pm 0.05\%$. If one sample deviated by more than $\pm 0.1\%$, it was not averaged into the reported concentration value. If more than one sample deviated by $\pm 0.1\%$, the analysis procedure was repeated.

Sulfate Gravimetric Method: Empty crucibles were first fired in a muffle furnace repeatedly for periods of 24 hours at 550°C , and cooled in a desiccator over anhydrous magnesium perchlorate, until daily weighings of the crucibles yielded a constant weight.

To analyze a solution, a sample of the solution was then weighed out into each crucible such that 3 to 5 grams of anhydrous sulfate would be produced at the end of the pyrolysis procedure. Rare earth nitrate samples were then first decomposed with excess HCl on a hot plate to eliminate the nitrate ion, which would readily co-precipitate with the sulfate ion. This was repeated a second time before sulfuric acid was added. Rare earth perchlorate solutions have a slight tendency to co-precipitate but carrying out the procedure with care usually avoided co-precipitation. If co-precipitation with sulfate ions did occur, as indicated by high weight values, ammonium chloride was added to react with the perchlorate ion, and a new sulfuric acid treatment was carried out.

The basic sulfuric acid treatment consisted of adding 1 molar sulfuric acid to the crucibles until the stoichiometric requirements for forming rare earth sulfate were exceeded. The solution was next heated to dryness at 150°C. Then the heat was gradually increased to 325°C and held at this temperature until the evolution of sulfur trioxide was complete. During this treatment the crucibles were covered with fluted pyrex watch glasses. The curvature of the glass facilitated the washing of any splattered sample on the cover back into the crucible. However, great care was taken to avoid any splattering of sample. After the vaporization of sulfur tri-

oxide was complete, the crucibles were fired in the muffle furnace at 550°C. After cooling, the preceding steps were repeated. Finally, the crucibles were fired at 550°C until a constant weight was obtained.

Using 4 unknowns, this method yielded a precision of $\pm 0.1\%$. If only one sample deviated by more than $\pm 0.2\%$, it was not averaged in with the other three values. If more than one sample deviated by that amount, the procedure was repeated. The two methods agreed with each other to within $\pm 0.1\%$.

These two analytical methods were used on primary stock solutions, saturated solutions, and secondary stock solutions used in this research. Saturated solutions were prepared by putting some primary stock solution into a desiccator over anhydrous magnesium perchlorate at reduced pressures until crystals formed in the solution. The slurry was then transferred to a capped flask and equilibrated at 25.0°C in a water bath for three to six weeks with daily shaking. After this period, the liquid portion of the mixture was decanted, such that no solid crystals could be visually detected in the decanted liquid. This saturated solution was stored in the same kind of flask as that used for primary stock solutions. Secondary stock solutions of about 0.3 molal were prepared from the primary stock solutions by weighing out the proper amount of primary stock and water. Most of the solution

preparation and analysis in this research was done in cooperation with the work of Joseph Rard (15). Secondary stock solutions were mainly prepared for salt solutions that were to be shared with co-workers, and were not needed as a stock solution when concentrations of less than 0.01 molal were not used.

Dilutions were made from the stock solutions and, in a few cases, from the saturated solutions by weighing out an appropriate amount of rare earth solution into a flask from a weight burette, and adding an appropriate amount of conductance water from another weight burette. Dilutions were generally prepared to have increments of 0.1 in the square root of the molality from 0.01 or 0.04 molal to saturation. The saturated solutions prepared as above were the highest concentration used in the dilution series. The primary and secondary stock solutions were used or not used in the series, depending on the amount left after dilutions were prepared and on the way they fitted into the increment pattern of the series.

All of the glassware, filters, and porcelain equipment used in the preparation and analysis of stock solutions, saturated solutions, and dilutions were precleaned in alcoholic KOH solution. After rinsing, the equipment was soaked overnight in a 1 N acid solution corresponding to the anion to be found in the prepared solution that this equipment was being

used for. The equipment was then soaked and rinsed several times with conductivity water and dried.

The conductivity water used in all of the work was prepared by fractional distillation from a potassium hydroxide-potassium permanganate solution in a modified Barnsted E-1 tin-lined conductivity still. The specific conductance of the water was less than 1×10^{-6} mho/cm.

All measured weight values were obtained with calibrated weights, and were corrected to eliminate the effects of the buoyancy of the air and the buoyancy of the brass weights used. The density of the air was calculated from the temperature, pressure, and relative humidity readings in the room where weighings were done. All atomic weights used in this research were the values assigned by the IUPAC in July, 1969 and are based on carbon-12.

The dilution process itself contributed a systematic error of $\pm 10^{-4}\%$. This is about equal to the uncertainty in the atomic weight of rare earths that have been most accurately measured. The least accurately measured atomic weights for rare earths have an uncertainty of $\pm 0.07\%$. Therefore, the overall uncertainty in the concentration of the solutions was about equal to the uncertainty in the analysis procedure for the stock solution, i.e., $\pm 0.1\%$. This uncertainty constituted a significant source of error for studies of physical properties across the lanthanide series, but existed

as a systematic error for heat properties as a function of concentration.

B. Experimental Apparatus

The experimental heat data was collected using a differential adiabatic solution calorimeter, that consisted of two calorimetric containers suspended in a water-tight submarine jacket that contained air at atmospheric pressure. The submarine jacket was completely surrounded by a water bath that kept the jacket walls at the same temperature as the average temperature of the two calorimetric containers. Between dilutions the temperature difference between the two containers was $<10^{-5}$ °C. The containers held the samples, and the liquid that the samples were diluted into. The electrical circuitry was designed to allow either container to be used as the dilution chamber, while the other container acted as a temperature reference.

The calorimeter and the accessory equipment, that was used in the heat of dilution measurements, was located in a room with its own air conditioning system. The mean temperature of the room was 23.5°C with a range from 22.5° to 24.0°C. The atmospheric pressure varied from 720 to 750 mm Hg, with a mean at 740 mm Hg. The temperature was controlled with a bellows-type thermostat that was also sensitive to atmospheric pressure to some extent. This resulted in a slow drift in temperature directly correlated with drifts in at-

mospheric pressure. However, the calorimeter support equipment did manage to eliminate errors due to atmospheric fluctuations for data measurements during normal weather conditions.

The differential adiabatic solution calorimeter used in this research was originally built by Naumann (83) following the plans of Gucker et al. (84). Major modifications have since been incorporated by Eberts (85), Csejka (86), and DeKock (25), and parts of the calorimeter have been rebuilt by Pepple (13) and Mohs (14). In the course of this research, the calorimeter was partially dismantled and rebuilt to reduce noise generation at mechanical and electrical connections. The associated electronic measuring equipment was cleaned, adjusted, and recalibrated wherever necessary. Modification of the thermopile well in the calorimeter containers improved the stability of the thermopile signal.

An off-line teletypewriter remote terminal to the IBM 360 computing system was introduced into the project for the first time. With the appropriate CPS/PL1 language programs, it became possible to make fast accurate estimates of the amounts of heat input needed in the reference can to balance the heat given off by a sample dilution. With this computing ability, the temperature difference between the containers after a break was smaller, and errors due to temperature imbalance were minimized. The time spent bringing the tempera-

tures in the containers back into balance after a break was also shorter. It became possible to quickly detect discrepancies between predictions and measurements, which permitted quicker resolutions of the problem involved.

The calorimeter and its associated electrical circuits will now be discussed in detail. Figure 1 shows a schematic diagram of the calorimeter assembly. Figures 2 and 3 are schematic diagrams of the electrical circuits involved. Reference to the figures will be designated (i-X) where i is the figure number and X is the label in that figure for the part discussed.

A double walled 22-gallon water bath served as an adiabatic jacket for the calorimeter. Exploded mica served as an insulating medium between the inner copper tank wall and the outer galvanized iron casing on a plywood base. The bath contained 1/4-inch copper cooling coils (1-A) through which tap water flowed at a constant rate. A 500-watt Calrod heater, placed near the cooling coils, was used to heat the bath water to within .05°C of the working temperature. A water bath lid, consisting of a 1/4-inch aluminum plate and a 1/2-inch plywood top with 1 3/4-inches of hair felt insulation in between, was suspended 54 inches above the floor on a sturdy angle-iron frame. The water bath was mounted on a platform on a movable angle-iron frame. The platform could be raised with an attached hydraulic jack to the level of the

Figure 1. Adiabatic differential calorimeter

lid when in use.

A 100-gallon-per-minute centrifugal stirrer was suspended through the water bath lid near the outside edge, and pointed so that water was stirred over and around the submarine jacket.

An adiabatic heat shield (1-B), which also served as a submarine jacket around the calorimeter containers, was suspended in the center of the bath, from a water-jacket lid that was attached to the water bath lid with eight brass tubes. The tubes were hollow to provide access to the interior submarine and container spaces for stirrer shafts, sample holder rods, and electrical leads. The submarine jacket lid was made from 1/4-inch monel plate.

The walls of the submarine jacket were constructed of 1/8-inch monel sheets and the bottom was constructed of 1/4-inch monel plate. Horizontally, it consisted of straight parallel sides terminating in semicircular ends. The jacket was attached to its lid by means of 20 machine screws countersunk in a 1/4-inch by 1/4-inch inconel strip which was welded to the upper inside edge of the submarine wall. An 1/8-inch rubber O-ring covered with Apiezon L grease served as a seal between jacket and lid.

A second 500-watt Calrod heater passed through the lid, and encircled the adiabatic heat shield horizontally. This heater was connected to the adiabatic temperature control

system which maintained adiabatic conditions to within $\pm 0.0005^{\circ}\text{C}$.

Two calorimeter containers (1-C) were suspended from calorimeter container lids inside the submarine jacket. The two container lids were constructed of 30-mil tantalum sheet and were each attached to the submarine jacket lid by two thin-walled stainless steel tubes (1-H). These tubes were placed directly under two of the brass tubes holding the submarine jacket lid up, and a stirrer shaft (1-E) and a sample holder rod (1-F) passed through the tubes into the interior of the containers. A heater well (1-D) and a control thermel tube (1-G) also passed through the lid.

The calorimeter containers were constructed from 15-mil tantalum in the form of a cylinder, 4 inches in diameter and six inches deep. A rectangular well, welded into the side of each container, was used to hold the main thermopile (1-J). A 1/4-inch rim extended horizontally outward from the top of each container. A brass ring provided support below the lid. Eight brass machine screws were threaded, from beneath, through the brass ring, and passed through the rim, through the container lid, and through a matching brass ring on top of the lid. Eight brass nuts held the screws in place. For ease in assembly, the containers were lifted into place on a small platform raised by a jack. A thin coat of Apiezon L grease on the rim provided a vapor tight seal for the assem-

bly.

The heater well in each container lid held a 99-ohm heater to supply heat for calorimetric measurements and a 1.5-ohm trickle heater. The calorimeter heaters were made from non-inductively wound 38 B and S gauge manganin wire. In each case, the wire was wound around a thin mica strip, annealed, and inserted into the heater walls. Melted wax filled the wells to hold the heaters secure.

The trickle heater used current from mercury cell batteries to compensate for differences in residual heat flow around each container. Most of this heat flow came from two sources: frictional heating of water by the stirring action; and small differences in heat flow along the supports and components of the two containers. Each stirrer generated about 3×10^{-3} calories per minute, and the total difference in heat generation and flow that was compensated by the trickle heaters amounted to a maximum of 2×10^{-3} calories per minute. The trickle heater circuit is presented in detail in Figure 3.

Stirrers (1-F) passed into the containers to provide rapid mixing for the liquid inside. Two semicircular vanes, set at an angle of 60° to each other, were riveted at the end of the stirrer shafts. The shafts consisted of three parts: a lower section of tantalum rod, an upper section of stainless steel rod, and a one-inch spacer of formica rod coated

with Apiezon L grease. The formica spacer replaced a nylon spacer that formerly connected the lower section to the upper section. The replacement was made to provide a less flexible joint, and thus helping to avoid off-center stirring, and the resultant shift in heat input due to stirring action. No loss of thermal insulation was noticed after the substitution. The stirrer shaft was held in place by two New Departure number 77R4A sealed bearings, one mounted immediately above the submarine lid, and the other mounted just above the water bath lid. A 325 RPM synchronous motor (1-M), mounted above the water bath lid, drove the stirrers by means of pulley assembly using an O-ring as a drive belt.

The sample holder rods passed into the containers from the outside to allow the positioning and the breaking of sample bulbs over the sample breakers (1-N). Each holder rod consisted of three parts: a tantalum rod to which a sample holder was attached, a stainless steel rod extending above the bath lid, and a one inch length of stainless steel tube connecting the two rods. The sample breaker was constructed from a 2 1/4-inch length of 1/4-inch tantalum tube which was flattened at the upper end and cut to form a point. The breaker was then cemented to the bottom of the container with melted Apiezon W wax.

Thin-walled annealed pyrex bulbs, holding the samples to be diluted, were clamped into the sample holder by their

stems. The approximately spherical bulbs had diameters from 2 cm to 3.5 cm. Only one bulb with a diameter greater than 2.5 centimeters fitted into the container at a time, and these were only used for the more dilute solutions. Otherwise, two bulbs were held vertically staggered in each holder. The sample in the first bulb was mixed with the liquid in the container by manually lowering the holder rod until the bulb broke against the breaker. The second bulb was similarly broken after rotating the holder rod 180°.

The control thermels were made from 36 B and S gauge copper wire and 30 B and S gauge constantan wire. Five thermels in series formed each control thermopile. 36 B and S gauge copper leads extended from the control thermopiles and were connected to a teflon junction block (1-K) mounted to the underside of the submarine lid. One end of each control thermopile was held by 1/4-inch tantalum tube welded into the container lid (1-G). The other end was in the copper tube (1-L) which extended into the water bath from the submarine lid. Melted paraffin wax provided support for the wires in the tubes.

The calorimeter adiabatic temperature control circuit and all of the heater circuits are diagrammed in Figure 2.

The control thermels for each can (2-J, 2-J') were connected into the control circuit that provided adiabatic control of the bath. From the teflon junction block (1-K), a

8

Figure 2. Schematic diagram of calorimeter heater circuits

shielded four-conductor cable carried the thermel signals to a Leeds and Northrup silver contact rotary switch (2-K). For test purposes, the switch was wired so that either thermel signal, both thermel signal in series, or the difference in thermel signals could be sent to the bath controller (2-L). In normal operation the thermel signals were in series. An Ayrton shunt (2-M) in the circuit divided the thermel voltage level during the calorimeter warmup to allow monitoring the relative temperature between the cans and the bath as adiabatic conditions were approached. The bath controller amplified the signal to operate a Thyatron relay switch that sent current from a Variac transformer (2-P) to the 500-watt Calrod bath heater when needed. Adiabatic conditions were maintained to within $\pm 0.0005^{\circ}\text{C}$.

The temperature of the water bath could be read to a hundredth of a degree from a thermometer suspended through the bath lid. The thermometer was calibrated over the operating temperature range with an NBS platinum resistance thermometer in conjunction with a Leeds and Northrup G-2 Mueller temperature bridge.

The leads from the 99-ohm heaters (2-A, 2-A') in each of the heater wells (1-D) were connected to the teflon junction block on the underside of the submarine jacket lid. All heater leads were made from 30 B and S gauge copper wire. Potential leads of 36 B and S gauge copper wire were soldered

to the midpoints of the calorimetric heater leads. From the junction block, a six conductor shielded cable carried the circuit pathway to two Leeds and Northrup silver contact rotary switches (2-C,2-D) which regulated the heater circuit. Switch 2-C was wired so that the potential drop across either heater, across both heaters in series, across the standard resistor (2-E), or across a dummy heater (2-F) could be measured. Switch 2-D was wired so that current could be passed through either heater, through both heaters in series, or through a dummy heater. When switch 2-D was set to allow current through either one or both heaters, an electronic timer was also engaged.

A Hamner triscaler Series-number-36 timer (2-G) monitored the duration of current passage through heaters. The time standard was obtained in the following manner. A Hewlett-Packard model 100ER quartz frequency standard was monitored and standardized by a Textran VLF tracking receiver used for phase comparison of frequency standard output with the radio station NLK/NPG carrier frequency, accurate to one part in 10^{10} . A one megahertz phase locked signal was outputted from the HP frequency standard to a General Radio 1163-A coherent decade frequency synthesizer, which, in turn, outputted a coherent 100 kilohertz signal. This signal was divided by 100 in a decade frequency divider and the output was sent to the electronic timer. The electronic timer mea-

sured the time to the nearest thousandth of a second. The measured time obtained from the timer was accurate to at least one part in 10^7 .

Low discharge rate lead storage batteries provided the current sources for the calorimetric heaters. The following arrangements were used: two two-volt batteries in parallel (2-V1,2-V2), two six-volt batteries in parallel (2-V3,2-V4), and five six-volt batteries (2-V3,2-V4,2-V5,2-V6,2-V7) connected to give a twelve-volt working potential. An A.C. source was used to bring the calorimeter containers to operating temperature, and was disconnected at all other times.

The resistance of each calorimetric heater was determined by measuring the potential drop across the heater and across the standard resistor while the same current was flowing through each. The resistance of the heaters remained constant to within .006% throughout the course of this work.

The potentiometer (2-I) was a Leeds and Northrup type K-2. The standard resistor and the standard cell had been calibrated by the National Bureau of Standards and were constant to within a few parts in 10^5 . The main thermopile (1-J) detected the temperature differences between the two calorimetric containers to produce the heat data obtained in this research. The circuit diagram for the main thermopile detection circuit is diagrammed in Figure 3.

CIRCUIT FOR MAIN THERMEL

CURRENT SOURCE FOR TRICKLE HEATERS

Figure 3. Schematic diagrams of the thermopile and trickle heater circuits

The main thermopile consisted of two 30-junction thermopiles (3-U, 3-U') connected in series with 36 B and S gauge copper leads. Each half of the thermopile was constructed over a thin 7 centimeter by 12 centimeter mica sheet. The two 30-junction thermopiles were separated from each other with a thin mica sheet and placed in a copper casing which fitted snugly into the thermopile wells in the containers. The empty spaces in the thermopile were filled with melted paraffin wax. The empty space in the thermopile wells was filled by pouring molten Wood's metal mixture into the well and then pushing the copper-clad thermopile, covered with a thin coat of Apiezon L grease, into the mixture until the mixture solidified. The grease prevented seizure and the solidified Wood's metal provided a form-fitted chamber for the thermopile. The Wood's metal chamber greatly improved the stability of the signal from the main thermopile, and some increase in the response of the thermopile due to the higher heat conductivity of the metal was noticed. To further minimize noise in the thermopile signal, foam rubber pads were placed around the edge of the well in the container to seal and cushion the thermopile in the well. A large O-ring was stretched around both calorimeter containers to squeeze the containers and the thermopile into a snug fit.

The thermopile leads were connected to the teflon junction block described earlier. The thermopile signal was

carried through four-conductor shielded cable to a Leeds and Northrup silver contact rotary switch (3-V) wired to pass the signal through with either polarity. From the switch the signal was fed into a Liston Becker model 14 breaker type D.C. amplifier (3-W). The amplifier output was passed through a Liston Becker filter circuit (3-X) to reduce the noise level and displayed on a 60-millivolt Brown recording potentiometer (3-Y). A Stabiline type IE-5101 voltage regulator (3-Z) provided the constant voltage power supply for the amplifier and recorder.

C. Experimental Procedure

The following procedure was used to obtain the heats of dilution of rare earth salt solutions at $25.00 \pm 0.02^\circ\text{C}$.

Samples of each of the rare earth salt solutions, prepared from its stock solution, were introduced into the thin-walled glass bulbs with a stainless steel tipped syringe. No droplets of solution were allowed to collect in the neck of the sample bulb, since any drops that were not in direct contact with the main body of solution would not mix when the bottom of the bulb was broken. The bulbs were weighed with calibrated weights before and after filling to determine the amount of sample in each bulb. The stem of the bulb was capped with a teflon plug during all of the weighings. After the weighings, the bulbs were sealed with melted Apiezon W wax. The weights obtained were corrected to eliminate buoy-

ancy effects. Sample sizes ranged from about 14 grams for the most dilute solutions to about 0.1 grams for some of the most concentrated, with a weighing accuracy of ± 0.2 milligrams.

The sample sizes used for each experimental run were chosen so that the following guidelines were met: first, limits of size as given in the last paragraph were used because of bulb size limitations for the largest samples, and because of the limit of balance accuracy for the smallest sample sizes; second, the total numbers of moles of rare earth salt in one container was usually limited to no more than 8×10^{-3} moles to allow short-chord calculations for a useful concentration range; and third, whenever possible, the sample size was chosen so that the amount of actual chemical heat given off by the dilution process ranged from 2 to 3 calories.

The last guideline listed above was developed from a study of the past performance of the calorimeter apparatus when used with a procedure similar to the one used in this work. The results of the study are given in Figure 4 and are discussed in detail in connection with the mathematical treatment of the experimental results.

On the day of a run, conductivity water was weighed into the calorimeter containers so that the total weight of the samples and water was approximately 900 grams. Immediately

after weighing, the containers were attached to their covers in the calorimeter apparatus. The weights of water were corrected for buoyancy effects, and were accurate to ± 10 milligrams.

Once the calorimeter containers were in place, the rest of the apparatus was assembled. Once assembled, the containers and the water bath were separately heated with A.C. current until they all reached approximately 24.90°C , and the containers and bath were within $.001^{\circ}\text{C}$ of each other. The adiabatic control system was then allowed to take over and retain adiabatic conditions to within $\pm .0005^{\circ}\text{C}$. By the time that adiabatic conditions had been reached, the main thermopile circuitry was warmed up enough to indicate a rough value of the temperature difference between the two calorimeter containers. Using experience as a guide, the temperature at which adiabatic control was established was adjusted by heating so that when the calorimeter container temperature difference was later minimized, the final temperature would be about 24.95°C . After adiabatic control was achieved, one of the calorimeter containers was heated with direct current from the batteries to achieve a difference of less than 0.0001°C between the two containers. As the difference between the containers was being minimized, a coarse gain control on the D.C. breaker amplifier was used to increase the sensitivity of the recording potentiometer until the limiting

temperature difference was reached. The apparatus was then allowed to stabilize itself for about one hour, during which time the trickle heater was turned on to help establish a straight line trace with a near-zero slope on the recording potentiometer.

When the apparatus was stable, a set of calibrating heats was carried out to determine the characteristics of the calorimeter and its assembly for that particular run. The set consisted of one heat to determine the heat capacity ratio of the calorimeter cans, and three heats to calibrate the recording chart. To ensure a constant current for all the heatings done in the experimental run, a dummy resistance box replaced the heater in the circuit between heats. At least 45 minutes before a heating, the dummy resistance box was set to simulate the resistance of the heater or heaters to be used next, and the appropriate batteries passed current through the dummy, until the current was stable. At the beginning of an experimental heat, the current was switched from the dummy to the container heater or heaters, and then was returned to the dummy after the heating was finished.

The heat-capacity-ratio heat consisted of approximately 345 seconds of 12-volt current passed through the heaters of both containers in series, to yield about 30 calories of heat in each can. The difference in the heat capacity of each container, with its contents, caused a difference in the tem-

perature rise in each can. The temperature difference after the heating caused a certain trace on the chart of the recording potentiometer that was displaced from the trace observed before the heating. This displacement allowed one to calculate a heat capacity ratio for the two cans. This ratio was used to correct for heat capacity effects when electrical heat in the reference can was used to balance the chemical heat given off in the other can. The ratio determined during each run differed from unity by less than ± 0.02 percent. If it was anticipated that the ratio would end up outside those limits because of container contents, the amount of water in each of the containers was adjusted during the water weighings to bring the ratio within the limits stated above.

The heats to calibrate the recording chart consisted of from .05 to .10 calories of heat input into one of the cans by a .06 to .07-volt current from the 2-volt battery source with an added resistance in series with the heater. Since the heat capacity ratio was close to unity, the three values obtained were averaged without regard to the container used. The heat input caused a displacement on the chart that was measured to obtain the relationship between calories input and displacement observed. The Liston-Becker amplifier was set at a course gain of 19 during all runs and this yielded a sensitivity of about 4.0×10^{-4} calories per millimeter of displacement on the recording chart.

After the set of calibrating heats was finished, the samples were run next. A dilution experiment was carried out by switching a current, set at an estimated voltage proper for the job, from the dummy resistance to the calorimetric heater of one container for about 65 seconds, reading the potential drop across the standard resistor, and halfway through the heating period, breaking the sample bulb in the opposite container. The electrical heat was almost always estimated to within one percent, and under ideal conditions was often estimated to within 0.5 percent. At the beginning of a set of runs of dilutions for a new salt, the estimates were sometimes less accurate until a trend could be established. If a discrepancy was spotted during the dilution procedure for this reason, or for any other reason, a small measured amount of heat was added from the 2-volt source into the appropriate container to bring the chart trace back on scale. Within 20 minutes, the tracing would stabilize to a constant slope usually displaced across the chart within a distance corresponding to 0.04 calories. The chart tracing was then allowed to continue until 45 minutes to one hour had elapsed since the dilution break. The chart moved at a speed of 0.5 inches per minute. After one hour, the role of the containers was reversed, and the procedure was repeated using the heater in the container that had the bulb that had been used in the previous determination. This reversing procedure

was followed until all of the bulbs in both of the containers had been used.

The electrical heat generated in a calorimeter container was calculated according to Equation 3.2,

$$q(\text{el.}) = \frac{R_H (E_S)^2 t}{4.184 (R_S)^2} \quad (3.2)$$

where R_H is the resistance of the heater, R_S is the resistance of the standard resistor, E_S is the voltage across the standard resistor, read during the heating procedure, t is the time in seconds, and 4.184 is the joule-calorie conversion constant.

The value of the chemical heat given off during dilution was calculated from the electrical heat, after compensating for four important extraneous heat influences.

First, the equilibrium vapor pressure of water above a salt solution decreases as the concentration of the solution increases. This caused water to evaporate into the free volume of the sample bulb when a break is made in the bulb. Water has an endothermic latent heat of vaporization of 10,514 calories per mole at 25°C, according to Rossini et al. (87). Under the conditions occurring in this research, this corresponds to a value of up to 0.05 calories for the most concentrated solutions. The correction for this was estimated according to Equation 3.3 which yielded Equation 3.4 that was

used in this work.

$$q(\text{evap.}) = \frac{273 \Delta P_v}{298 \cdot 760 \cdot 22400} V \quad 10514 \text{ calories} \quad (3.3)$$

$$q(\text{evap.}) = 0.000566V \cdot \Delta P_v \text{ calories} \quad (3.4)$$

In the above equations, V is the free volume of the bulb in milliliters and ΔP_v is the difference in the vapor pressure over the sample solution initially and after dilution. The difference in vapor pressure was obtained by calculation from osmotic coefficient data obtained for the rare earth salts by co-workers in the group (88). The relationship used in the calculations was the one stated by Pitzer and Brewer (37), and given in Equation 3.5,

$$\Delta P_v = 23.756(1. - \exp(-.07206 \times m \times \phi)) \quad (3.5)$$

where m is the molality of the solution initially and at that concentration. The vapor pressure of the solution after dilution was considered to be equal to pure water within the accuracy limits needed for ϕ is the osmotic coefficient of the solution this correction factor. Similarly, the heat of vaporization due to the condensation of water vapor from the air in the calorimeter container with concentration change was considered to be negligible.

Second, the breaking of a sample bulb wall released a small amount of heat. A correction was applied to all sample breaks. Although the amount was usually small enough to be

within the limits of accuracy of the measurements, it was included to minimize systematic errors in the data. The extremely thin-walled sample bulbs deformed elastically when pressed against a small spring balance. The correction factor was based on S , the scale factor, numerically equal to the number of ounces of pressure needed to slightly deform the bulb wall. The values of S ranged mostly from 0.75 to 1.5 in 0.25 increments. The heats of breaking of several bulbs was measured and the relationship obtained is given in Equation 3.6.

$$q(\text{open}) = 0.0005 \times S \text{ calories} \quad (3.6)$$

Third, the chemical heat associated with a sample break was usually matched by the electrical heat to within 0.05 calories. To compensate for whatever difference remained, the trace of the recording potentiometer after the break was extrapolated back with a straight line to the time of the break. At the point on the chart corresponding to the moment of the break, the displacement of the extrapolated line from the line recorded before the break was used to calculate the correction. Using a value of 4×10^{-4} calories per millimeter for the displacement calibration factor of a particular run, the correction factor can be calculated according to Equation 3.7,

$$q(\text{chart}) = 4.0 \times 10^{-4} \times D \text{ calories} \quad (3.7)$$

where D is a signed value of the displacement between tracings in millimeters. For each run, the calibration factor obtained during the heat calibration part of the run was used in place of the value used above.

Fourth, the heat capacity ratio was applied to the electrical heats that were introduced into the reference can, to convert the value to a corresponding amount of heat in the other can. No heat capacity ratio correction was needed for electrical heat inputs into the sample container. Since the ratio was close to unity, no difference was discernible in applying or not applying the ratio correction to the $q(\text{chart})$ value. If the heat capacity of the "i"th container is denoted by $C(i)$, the ratio can be indicated by $C(\text{dil.})/C(\text{ref.})$ when converting reference container electrical heat values to dilution container chemical heat values. When the roles of the containers was reversed during an experimental run, the numerical value of the heat capacity ratio became the reciprocal of the previously used value.

Combining all of the correction factors, the chemical heat evolved due to the dilution is given by Equation 3.8,

$$q(\text{dil.}) = q'(\text{el.}) \times C(\text{dil.})/C(\text{ref.}) + q(\text{chart}) + q(\text{evap.}) - q(\text{open}) - q(\text{el.}) \quad (3.8)$$

where ' indicates heating that occurs in the reference con-

tainer and unprimed q 's occur in the dilution container. The last term in Equation 3.8, which represents electrical heating in the dilution container, usually was equal to zero, but was used when small amounts of heat were added while bringing the potentiometer trace back on scale.

The accuracy of this calorimetric method was tested by measuring the enthalpy of neutralization of hydrochloric acid with sodium hydroxide. Experimental runs, with four samples of acid each, were run several times at the beginning, at the midpoint, and at the end of the period during which the experimental work in this project was carried out. The neutralization of HCl was chosen as a test reaction because it was well-characterized and could be carried out in almost the same manner as a dilution experiment.

The hydrochloric acid standard was made from constant boiling hydrochloric acid by a co-worker according to the procedure of Foulk and Hollingsworth (89). Triplicate analyses indicated that the concentration was .15849 molal with 0.03 percent deviation. Samples of the hydrochloric acid solution were introduced into the sample bulbs, weighed, and sealed in the same manner that the rare earth samples were handled.

Carbonate free concentrated sodium hydroxide was prepared by standard methods (90).

Conductivity water was weighed out in the same manner as before and, just before attaching the calorimeter containers to their lids, three drops of the concentrated sodium hydroxide solution were added to each container to give a carbonate free solution of about 0.003 molal sodium hydroxide. This gave approximately a four-fold excess of base over acid in each container to minimize the effects of any absorbed carbon dioxide in the solution. As the non-limiting reactant, the concentration of sodium hydroxide was known to within 10 percent to calculate the ionic strength contribution to the experimental heat measurements.

The neutralization reaction is given by Equations 3.9 and 3.10 where ΔH_n is the enthalpy of neutralization of the acid at an ionic strength of 0.003 and ΔH° is the enthalpy of neutralization at zero ionic strength (infinite dilution).

Equation 3.9 was derived from experimental data by combining Equations 3.11, 3.12, 3.13, and 3.14.

$$\text{NaCl (0.003m)} = \text{NaCl (0.00075m)} ; \Delta H(\text{II}) \quad (3.13)$$

$$\text{HCl (0.1585m)} = \text{HCl (0.003m)} ; \Delta H(\text{III}) \quad (3.14)$$

The heat of neutralization at infinite dilution was calculated using Equation 3.15,

$$\Delta H_n = \Delta H(\text{exp.}) - \Delta H(\text{I}) - \Delta H(\text{II}) - \Delta H(\text{III}) \quad (3.15)$$

where the values of $\Delta H(\text{I})$, $\Delta H(\text{II})$, and $\Delta H(\text{III})$ were calculated using the apparent molal heat contents of NaOH, NaCl, and HCl taken from the literature (87,91).

The heat of neutralization was corrected to infinite dilution using Equation 3.16.

$$\begin{aligned} \Delta H^\circ = \Delta H_n - \phi_L (\text{NaCl, 0.003m}) + \phi_L (\text{NaOH, 0.003m}) \\ + \phi_L (\text{HCl, 0.003m}) \end{aligned} \quad (3.16)$$

A total of 13 samples were run. The average enthalpy of neutralization at 25°C was $\Delta H_n = -13.360$ calories per mole with a standard deviation of 16 calories per mole. The average enthalpy of neutralization at infinite dilution was $\Delta H^\circ = -13,337 \pm 16$ calories per mole. This result compares favorably with the value obtained by Vanderzee and Swanson (91), and by Hale, Izatt, and Christensen (92) who both reported -13336 ± 18 calories per mole.

The experimental precision of these measurements was 0.20%. With an uncertainty of 0.05% in the HCl concentration value, the total uncertainty in ΔH° is 0.25%.

IV. RESULTS

A. Mathematical Treatment

In this work, heats of dilution were measured under two experimental situations: (1) a sample of solution containing n_1 moles of solute at a molality m_1 was diluted into pure water with the evolution of q_1 calories of heat to yield a solution at molality m_2 , and (2) a sample of solution containing n_2 moles of solute at molality m_1 was diluted into the previous solution at molality m_2 with the evolution of q_2 calories of heat to yield a solution at molality m_3 . The integral heats of dilution of these two processes are given in Equations 4.1 and 4.2,

$$\Delta H_{1-2} = q_1/n_1 \quad (4.1)$$

$$\Delta H_{1-3} = (q_1 + q_2)/(n_1 + n_2) \quad (4.2)$$

where ΔH_{i-f} corresponds to the heat of dilution of a sample from molality m_i to molality m_f . Since heat content as a function of concentration is an additive quantity, the heat involved in diluting m_3 to m_2 can be obtained from the experimental data by subtracting Equation 4.2 from Equation 4.1.

The molal heats of dilution, as defined above, were smoothed and extrapolated to infinite dilution by the methods of multiple linear regression analysis. The statistical nomenclature used in this work is defined by Bevington (93) and corresponds closely to the standard nomenclature used in

statistics. Most of the least squares fitting was performed by a matrix inversion program identical to the one given by Bevington, although in the preliminary analysis of apparent molal heat content data, an orthogonal polynomial least squares routine was also used.

In the course of this research, it became apparent that a new form of equation for fitting heat of dilution data over the entire concentration range was needed. If possible, the form of equation that was developed should be convenient to use with multiple linear regression analysis techniques in a large electronic computer. The resulting equation would then also be convenient to use in programable electronic desk calculators, to quickly calculate any of the heat properties from the equations using standard polynomial-value calculating programs. To fit the data over the entire concentration range, the equation form would need to be flexible enough to include non-electrostatic contributions to the heat values. At the same time, no theoretical values can be predicted for the Debye-Huckel equation parameters, a , the distance of closest approach, and $d(a)/dT$. If either of these terms is to be used in the fitting equation, it must be included as an experimentally determined value, that is subject to large uncertainties, or as another parameter to be adjusted to its best value in a least squares fitting procedure. Because of these reasons and because these parameters are only theoretic-

cally meaningful in extremely dilute solutions, these parameters were not used in this work, and a more convenient form of empirical equation was developed. The form of equation used here successfully fitted heat of dilution data from about $1.6 \times 10^{-3} \text{ m}$ up to saturation (ionic strengths about equal to 36).

In fitting the data, weighting factors were used during all phases of the mathematical analysis to represent the expected error in the data due to uncertainties and random fluctuations in the data taking process. If experimental considerations had allowed time enough for many separate determinations of ΔH values for each solution at an initial molality value, then the standard deviation of the $\phi_L(m_1)$ obtained from these determinations can be used as a basis for the weighting factors for $\phi_L(m_1)$ and ΔH values. The particular relationship between weighting factors for ΔH values and $\phi_L(m_1)$ values will be discussed in detail later.

The data in this work usually consisted of about 4 ΔH values with a common initial molality value, from which the same number of $\phi_L(m_1)$ values could be calculated. The standard deviation values for these four values would be subject to large fluctuations, since the four points could easily deviate substantially from a Gaussian distribution about the mean value. To minimize this problem, the standard deviation values need to be smoothed over a large number of experimen-

tal determinations carried out under the same conditions. To do this, a correlation must be found between the standard deviation values and some experimental parameter that varies in a simple manner as experimental conditions vary. $\phi_L(m_1)$ values could not be used as an experimental parameter for this purpose because values of about 1000 cal/mole occur for very different molality values and experimental arrangements in the calorimeter with the different solutions studied in this work. A much simpler parameter to use for this purpose is q , the quantity of heat change that occurs in the calorimeter during the break.

Early in this work, a set of standard deviation values for $\phi_L(m_1)$ values measured by Mohs (14) was plotted as a function of q_{Av} , the arithmetic mean of all of the measured heat values for a solution at a particular initial molality value. These are shown in Figure 4. There are 92 sample standard deviation points in the figure, which represent about 325 experimental measurements of the heats of dilution, taken from 220 sample standard deviation points available from the work of Mohs (14). The points were picked in such a way that a relatively even distribution occurred along the q axis and points were included from all of the salts studied, but without any regard for the standard deviation values.

The pattern of standard deviation values in Figure 4 is due to different factors that contribute in the low and high

Figure 4. Statistical error in data as a function of measured heat

ends of q values. The sharp increase in the values at low heat of dilution values was due to the decreasing signal-to-noise ratio of the experimental apparatus. The slower increase of standard deviation values at higher q values was caused by three factors. The most important of these was the fact that large q values were usually obtained for highly concentrated salt solutions where the value of n_i , the number of moles of solute in the sample, was small. As a factor in the denominator of Equations 4.1 and 4.2, the n_i values magnified the error values for ΔH , which was calculated from the q values. Two smaller effects that contributed to the error included that fact that n_i values were known with less precision as their value decreased, and the fact that larger departures from adiabatic conditions occurred during the bulb-breaking and heating procedure when q values increased.

To obtain a standard deviation value that was smoothed over a large number of sample values, the standard deviation values plotted in Figure 4 were fitted to linear equations as a function of q_{AV} . Equation 4.3 indicates the equation used for solutions with average measured heat values of less than 1.49 calories, and Equation 4.4 is the equation used above 1.49 calories,

$$S(q_{AV}) = 4.656 - 2.298 \times q_{AV}; \quad q_{AV} < 1.49 \text{ cal.} \quad (4.3)$$

$$S(q_{AV}) = 0.1339 + 0.7471 \times q_{AV}; \quad q_{AV} > 1.49 \text{ cal.} \quad (4.4)$$

where $S(q_{AV})$ is the sample standard deviation assigned to

the data having q_{AV} . These equations are also plotted in Figure 4. In the few cases where q_{AV} was less than 0.3 calories, a standard deviation of 10.0 cal./mole was used as the basis of the weighting factor.

After fitting procedures were completed for the data in this work, no significant difference in the values of sample standard deviations in this work was discernible when compared to the data in Figure 4. Furthermore, analysis of the earlier work of DeKock (25) and Pepple (13) did not show any significant difference in the standard deviation of their data points when compared to later work.

In the preliminary analysis of fitting equations for the data, sample standard deviations, as calculated by Equations 4.3 or 4.4, were equated to the square root of the variance, σ_i , that can be assigned to every average $\phi_L(m_1)$ value. The weighting factor, w' , was then calculated for each average $\phi_L(m_1)$ value using Equation 4.5.

$$w' = 1/(S(q_{AV}))^2 \quad (4.5)$$

In the final fittings, heat of dilution data was fitted directly as a function of initial molality m_i and final molality m_f , where f equals 2 or 3. To do this it was necessary to redefine weighting factors for heat of dilution data from weighting factors available for $\phi_L(m_1)$ data, because no sample standard deviation can be directly calculated for

heats of dilution in this work. The relationship between heats of dilution and $\phi_L(m_1)$ is defined in Equation 2.16 and can be applied as in Equation 4.6.

$$\phi_L(m_1) = \Delta H_{1-f} + \phi_L(m_f) \quad (4.6)$$

In obtaining $\phi_L(m_1)$ values, a $\phi_L(m_f)$ equation is used to provide a factor that is added to heat of dilution data. If the function is reasonably correct in the region of m_f , it will provide a value for $\phi_L(m_f)$ that is wrong only by a small error factor. The error will be passed along to the $\phi_L(m_1)$ value. When repeat measurements are made at molality m_1 , similar errors will be passed along to the $\phi_L(m_1)$ values each time, but only the differences in the errors of the $\phi_L(m_f)$ values will introduce scatter in the $\phi_L(m_1)$ values. The error contributions of the $\phi_L(m_1)$ terms are negligible when compared to the scattering that already exists in the sample standard deviation values. A subsequent comparison of $\phi_L(m_f)$ values calculated with the aid of Mohs' $\phi_L(m_f)$ equations and the equations used for $\phi_L(m_f)$ values in this work, did not show any shift in the overall scatter of the points given in Figure 4. Therefore, if a reasonably good function is used to represent $\phi_L(m_f)$, the scattering error passed to the $\phi_L(m_1)$ value will be small. Then, the error in the $\phi_L(m_1)$ points will essentially be equal to the error in the corresponding ΔH_{1-f} point.

The weights calculated for the experimental ΔH values are therefore based on the weights assigned to $\phi_L(m_1)$ data from Figure 4. In calculating ΔH weighting values from $\phi_L(m_1)$ weighting values, two factors must be included in the calculation. One factor consists of a normalization weight that accounts for the fact that ΔH_{1-3} values are calculated from the total of two sample dilutions, one of which is the sample dilution used to calculate ΔH_{1-2} , as is evident when comparing Equation 4.1 with 4.2. To account for this, the relative weights of ΔH_{1-2} and ΔH_{1-3} are renormalized so that the weighting factors correctly reflect the error contributions of each ΔH value to the average $\phi_L(m_1)$ value. The normalization weight for ΔH_{1-2} is given in Equation 4.7.

$$w_{1-2} = \frac{\frac{1/(S(q_1))^2}{(S(q_1))^2} + \frac{1}{(S(q_1))^2 + (S(q_2))^2}}{\quad} \quad (4.7)$$

The corresponding normalization weight for ΔH_{1-3} is given in Equation 4.8.

$$w_{1-3} = \frac{\frac{1/\{(S(q_1))^2 + (S(q_2))^2\}}{\frac{1}{(S(q_1))^2} + \frac{1}{(S(q_1))^2 + (S(q_2))^2}} \quad (4.8)$$

The second factor is based on the average weight for the $\phi_L(m_1)$ value obtained from the two ΔH_{1-f} values that are being weighted. The average weight that is used for $\phi_L(m_1)$ values is doubled when used with the heat of dilution values

since the normalization is carried out over two heat values. The total weighting factor for ΔH_{1-f} is given in Equation 4.9,

$$w_{1-f}^i = w_{1-f} \times 2 / \{S(\frac{1}{2}(q_1 + q_2))\}^2 \quad (4.9)$$

where f is again equal to 2 or 3. Using these weighting factors for the data in this work, the average of all the weighting factors, that are used with the set of heat of dilution values for a solution at molality m_1 , will equal the weighting factor of the corresponding average $\phi_L(m_1)$ value. Small errors may occur in assigning weighting factors for heat of dilution values. The effect of these small errors is negligible in the fitting process, because the fitting procedure concerns itself only with the relative values of the weighting factors during the fitting. Where reduced chi squared values are used in testing fits, a small error in its absolute value may occur, but its relative value is still valid in testing goodness of fit.

A preliminary analysis of data obtained by previous workers (13,14) was carried out on a remote computer terminal programmed to be able to quickly change forms of the fitting equation to be tested. The apparent molal heat content data was fitted to polynomials using various powers of the molality as shown in Equation 4.10.

$$\phi_L(m_1) = \sum_j A_j m^{p_j} \quad (4.10)$$

In each fit, the powers would be a series of integers or fractions such that $p_j = j/2, j/3, j/4, j/6, j/8, \text{ or } j/16$. In some cases, logarithmic functions of molality were also added to attempt better fitting of high concentration values to an equation. As a result of this testing, the best fits of various rare earth salts, as judged by reduced chi squared values, were obtained for a polynomial with a power series in $m^{1/4}$.

Another result of the testing was that lower reduced chi squared values were obtained if the lowest power term of the polynomial had a functional dependence in the square root of molality, as is predicted by the Debye-Huckel limiting law.

It was also determined that in the $1/4$ power series, seven coefficient terms were sufficient to adequately represent rare earth nitrate and perchlorate data. The rare earth chlorides could usually be adequately fitted with six coefficients. A fit was considered adequate if its reduced chi square value indicated that the error in the fit was about equal to the weighted average of the expected error in the data. It was also noticed that better results could be obtained with non-consecutive sets of powers; that is, j values need not be consecutive integers.

When fitting data to a quarter power series in molality with a set of seven different j values in any one fit, it

also became apparent that while values of j up to 16 (corresponding to m^*) were useful in yielding better fits, substituting higher values of j did not improve the fits.

Applying the results of the above analysis, the heat of dilution data presented in this work was fitted directly as a function of $1/4$ powers of molality, using the weighting procedure described earlier. Equation 4.6 can be written as Equation 4.11.

$$\Delta H_{1-f} = \phi_L(m_1) - \phi_L(m_f) \quad (4.11)$$

Each of the terms on the right hand side of the equation can be represented by a power series in molality as in Equation 4.12.

$$\Delta H_{1-f} = \sum_j A_j m^{p_j} - \sum_k B_k m^{p_k} \quad (4.12)$$

The heat of dilution is a continuous function of concentration below the saturation point of the solution. Therefore, if the form of the polynomial is general enough, and the experimental data is accurate enough, a form of equation can hopefully be found such that $A_j = B_k$. In such a case, Equation 4.12 becomes Equation 4.13,

$$\Delta H_{1-f} = \sum_j A_j (m_1^{p_j} - m_f^{p_j}) \quad (4.13)$$

and this represents the form of equation used in this research. In this form of the equation the number of coeffi-

ponents is limited to seven while p_j represents some quarter power of molality up to m^4 . At the same time, p_j values are labeled with consecutive j values from 1 to 7, and the value of p_j no longer is necessarily equal to $j/4$. In the fitting procedure, the values representing the left hand side of Equation 4.13 were used as the dependent variables and the quantity inside the parentheses on the right side of the equation was used as the independent variable in the matrix building steps of the fitting procedure.

B. Heats of Dilution

In the final analysis of the data, the earlier work of Mohs (14) on nitrate and perchlorate salts was treated in the same manner as the data obtained in this work. The resulting polynomial fits were eventually compared with the fits of data obtained in this work to select the most common form equation possible for each anion.

The data for each rare earth salt was processed in a fitting program that (1) generated sets of seven powers in quarters with $1/2$ as the lowest power and the other six being a possible combination of the quarter powers between $3/4$ and $16/4$, (2) fitted the data to each of all of the possible combinations of powers, (3) checked to insure that the elimination of one term to give a fit of less terms, would not yield a better fit, and (4) gave a sorted output of the best possible fit to the worst possible fit, using the criteria of the

reduced chi squared. The results from this analysis for each salt usually yielded a set of 10 to 50 equations with standard deviations within 0.5 standard deviation units of the best value. In general, any of these equation forms could be used to represent the data on the basis of the chi squared criteria. The final choice of equations depended on further considerations to provide the best representation of the data for all of the salts.

One problem that occurs in fitting heat data is the need to extrapolate to infinite dilution from data that ends in more concentrated regions. This problem is most serious in cases where significant non-Debye-Huckel type of behavior exists in the data from which extrapolation is to be made. In fitted equations using the form of Equation 4.13, the coefficients found in the $m^{1/2}$ term were up to 50% larger than the value predicted by the Debye-Huckel limiting law at infinite dilution. However, slope values calculated for ϕ_L as a function of $m^{1/2}$ were approaching the limiting law values smoothly in the region of the low concentration experimental data, and only began to seriously deviate at concentration values of less than 2×10^{-4} m. To provide ideal behavior at infinite dilution, the data was refitted to an equation where the coefficient in the $m^{1/2}$ term had a value of 6990, the calculated theoretical value for a 1-3 electrolyte. This new fitting equation was the same in form as Equation 4.13 except

that A_1 was assigned the theoretical value, and a total of six coefficients were allowed to vary to yield the best fit. This new equation yielded a standard deviation value with no more than 0.5 cal/mole increase when compared to the old form of equation with the same set of powers. With this modification, all of the nitrates could be represented by a common set of powers in the first five terms except for $\text{La}(\text{NO}_3)_3$. Some perchlorates could be fitted with the same set of low powers that was used for the nitrates, but a set of powers with the same first three powers for all the perchlorates was used instead. Again the lanthanum salt was an exception. In all cases, the equations had standard deviation values that were no more than 0.2 standard deviation units greater than the lowest value of standard deviation obtained from all of the possible forms of equation tested.

Another possible source of problems in this fitting process is the assumption used to obtain Equation 4.13 from Equation 4.12. For this type of data, this could occur if a radical change in property values occurred between the lowest concentration data available and infinite dilution. The fitting equation properly reflected the ΔH_{3-2} values used in the fits and when the ΔH_{3-2} were eliminated from the fitting process and a new fit was obtained, the slope values for the two fits agreed to within 1% at all low concentrations. Since the scatter in the $\bar{P}_1$ points is larger than this, no

better form of equation at low concentrations can be expected for the data used in this work. The equations used in this work were based on both ΔH_{1-f} and ΔH_{3-2} values to obtain the best fits in the dilute region.

In deciding on the final form of equation to be used for the data, the above considerations were included in a three step procedure to obtain the best fits. First, the theoretical limiting slope value was included in the fitting equation; second, the equations used had common low term powers, where possible, for salts of a common anion; and third, higher powers were picked by selecting powers that were common to adjacent cations when possible.

The experimental data obtained in this work are listed in Table 2 along with the values predicted by the fitted equation used to represent the data. The first column tabulates the initial molality of the solution, m_i , for which a heat value was to be found. All of the m_1 values for a salt are listed first in decreasing order, and following them, all of the m_3 values used for ΔH_{3-2} values are tabulated. The m_3 values are listed in the same order that they occur in the second column of the table as final molalities for determining ΔH_{1-f} values. In the second column, all of the final molalities for the corresponding initial molalities are listed. If the value is starred (*), it is an m_3 value, with the corresponding m_2 value in the dilu-

tion scheme being given immediately above. The third column lists ΔH_{1-f} values obtained experimentally, and ΔH_{3-2} values calculated from experimental ΔH_{1-f} values. The fourth column lists ΔH_{i-f} values calculated from the fitting equation used to represent the data. The fifth column lists σ_i , the reciprocal of the square root of the weighting factor, used in weighting the data in the fit. In the form given, this value corresponds to the average error to be expected in that particular data point.

To be able to compare the data presented in this work with the data of Mohs (14), his data were reorganized into the same format, and are presented in Table 3. The calculated value from the new fits is presented in the fourth column as before. The weighting factors for his data were calculated in the same manner as for the data in this work.

The P_j and A_j values used in the fitted equations to represent the experimental data are given in Table 4 for all of the nitrates, and in Table 5 for all of the perchlorates. The first term is the same for all of the salts and its coefficient and power is given at the top of the tables. The other six terms of the equation are given in vertical pairs to the right of the salt label in the table. The top number of the vertical pair is the power used in the term, while the lower number is the coefficient in the term. The coefficients and powers given can be directly substituted into

Table 2. Observed and calculated heats of dilution of aqueous rare earth solutions at 25°C.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
Praseodymium Nitrate				
4.990	11.672	-	2072.5	-
	23.792*	2008.2	1999.6	1.718
	11.447	2068.9	2074.3	1.554
	25.521*	1986.6	1991.4	2.345
4.833	15.897	1940.1	1942.0	1.881
	32.435*	1862.5	1860.9	2.610
4.465	29.026	1657.7	1653.0	2.766
	56.874*	1563.2	1561.8	3.640
	30.348	1651.8	1647.5	2.809
	57.095*	1563.6	1561.2	3.580
4.002	29.619	1391.5	1393.3	2.437
	60.850*	1293.2	1294.5	3.302
	29.148	1395.0	1395.2	2.441
	61.532*	1292.1	1292.8	3.382
3.618	29.500	1186.6	1194.4	2.480
	27.608	1191.4	1202.5	1.928
	54.937*	1107.1	1110.3	2.542
3.444	31.994	1100.2	1097.9	2.046
	64.678*	1002.1	999.5	2.688
	31.273	1108.1	1100.8	1.944
	59.614*	1015.8	1011.8	2.444
2.978	27.082	905.8	903.2	1.453
	55.006*	810.1	808.5	1.890
	27.657	-	900.6	-
	55.401*	809.0	807.4	1.472
2.564	36.139	701.1	701.7	1.444
	72.379*	599.1	601.6	1.792

*f=3 for this sample and its corresponding f=2 (unstarred) value is given immediately above it.

Table 2. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
	36.861	699.6	699.1	1.456
	72.703*	599.6	600.9	1.789
2.200	43.186	559.7	560.9	1.295
	85.265*	461.9	458.7	1.703
	42.909	560.8	561.8	1.277
	85.396*	457.2	458.5	1.707
1.922	56.614	456.7	456.0	1.870
	57.553	451.3	453.6	1.878
1.684	58.723	409.3	412.9	1.766
	56.925	418.9	417.5	1.736
	56.975	419.0	417.4	1.737
1.448	52.398	411.5	411.5	1.583
	51.195	415.3	414.9	1.562
1.226	50.327	418.6	418.4	1.551
	50.606	421.6	417.6	1.568
1.106	46.917	435.9	436.3	1.510
	45.570	440.2	440.4	1.482
0.9174	38.480	483.6	485.8	1.385
	38.571	485.5	485.5	1.393
0.6430	27.532	580.7	577.5	1.349
	27.511	578.4	577.6	1.366
0.5006	26.814	608.1	609.3	1.279
	28.060	600.3	603.9	1.268
0.3582	19.314	671.1	670.2	1.906
	38.098*	590.1	588.5	3.200
	19.496	-	669.2	-
	38.608*	589.4	586.7	2.620
0.2534	16.837	687.3	690.1	2.121
	33.097*	611.5	612.2	3.402

Table 2. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
0.1693	21.581	654.4	647.5	1.710
	20.129	654.5	655.2	1.908
0.09997	14.846	632.0	636.6	2.695
	14.910	633.1	636.2	2.683
0.05127	8.2285	590.2	591.8	3.640
	8.3510	586.5	590.6	3.631
0.01927	3.1114	501.3	483.4	4.330
	3.2329	482.5	481.3	4.330
0.002552 $\square$	11.447	82.3	82.9	2.510
0.003243	15.897	77.6	81.1	2.827
0.005687	29.026	94.5	91.2	3.975
0.005710	30.348	88.3	86.3	3.930
0.006085	29.619	98.3	98.8	3.590
0.006153	29.148	102.8	102.4	3.664
0.005494	27.608	84.3	92.2	2.775
0.006468	31.994	98.1	98.4	2.936
0.005961	31.273	92.2	88.9	2.690
0.005501	27.082	95.7	94.7	2.067
0.007238	36.139	102.0	100.1	1.976
0.007270	36.861	100.1	98.2	1.977
0.008527	43.186	97.7	102.1	1.860

$\square$ Remaining data for this salt are for ΔH_{3-2} values.

Table 2. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
0.008540	42.909	103.6	103.3	1.859
0.003810	19.314	81.0	81.8	3.384
0.003310	16.837	75.8	77.8	3.616
Samarium Nitrate				
4.284	15.802	1792.0	1793.6	1.659
	29.737*	1731.9	1732.1	2.157
	14.409	1802.8	1801.6	1.677
	31.842*	1720.3	1724.8	2.495
3.827	18.780	1459.8	1452.9	1.652
	37.463*	1388.4	1382.2	2.229
	20.313	1442.8	1445.5	1.713
	38.787*	1375.2	1378.3	2.229
3.461	24.635	1180.9	1180.3	1.726
	48.859*	1108.0	1105.5	2.289
	25.643	1177.5	1176.2	1.807
	52.177*	1097.2	1097.8	2.436
3.228	30.097	1006.4	1011.6	1.771
	59.452*	928.9	934.1	2.307
	28.541	1016.6	1017.2	1.727
	58.023*	935.6	937.0	2.302
2.778	31.633	742.8	744.6	1.388
	63.544*	664.8	664.2	1.791
	31.542	743.2	744.9	1.388
	63.867*	662.9	663.6	1.798
2.457	70.313	486.0	490.1	2.429
	70.052	491.9	490.5	2.447
	35.222	572.3	571.2	1.093
	70.083*	491.6	490.5	1.659
	36.508	569.6	567.3	1.121
	72.004*	488.8	487.1	1.665

Table 2. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
2.125	70.909	348.7	350.4	1.795
	71.201	348.1	349.9	1.798
1.935	132.806	206.9	206.2	1.987
	133.916	206.9	205.1	2.001
1.647	180.097	94.3	94.4	1.283
	178.929	95.3	95.2	1.288
1.428	186.943	60.5	56.5	2.294
	143.633	91.0	90.5	1.926
	65.631	188.3	190.4	2.098
	65.946	186.5	189.8	2.113
1.124	126.406	97.1	95.2	2.099
	126.771	95.7	94.8	2.129
0.9781	99.803	133.6	134.4	1.880
	101.536	132.1	132.2	1.868
0.8045	85.703	174.8	175.6	1.538
	84.026	176.7	178.1	1.567
0.6532	48.414	277.6	273.4	1.869
	57.000	252.1	254.0	1.670
	58.020	252.0	251.9	1.619
0.4402	51.873	311.4	313.4	1.289
	51.816	312.5	313.5	1.283
0.3450	38.289	371.5	369.5	1.694
	37.021	375.0	373.2	1.767
0.2655	28.582	418.4	415.2	2.166
	28.817	417.2	414.4	2.154
0.1495	17.875	463.2	464.1	2.932
	16.252	471.9	472.8	3.060
0.09923	14.812	457.4	463.4	3.242
	13.344	472.3	472.3	3.341

Table 2. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
0.04669	4.7180	479.1	483.1	4.185
	5.3097	478.1	476.0	4.128
0.007381□	1.4480	305.6	310.1	4.563
0.002974	15.802	60.1	61.4	2.360
0.003184	14.409	82.4	76.8	2.677
0.003746	18.780	71.4	70.8	2.424
0.003879	20.313	67.6	67.2	2.438
0.004886	24.635	72.9	74.8	2.497
0.005218	25.643	80.3	78.5	2.650
0.005945	30.097	77.6	77.5	2.524
0.005802	28.541	81.1	80.2	2.509
0.006354	31.633	78.1	80.3	1.962
0.006387	31.542	80.2	81.2	1.969
0.007008	35.222	80.8	80.7	1.775
0.007200	36.508	80.8	80.1	1.786

Dysprosium Nitrate

4.539	7.5458	3184.3	3182.5	1.502
	15.273*	3123.1	3119.3	2.110
	7.5630	3180.3	3182.3	1.518
	15.522*	3118.9	3117.7	2.160
4.323	9.5384	2968.4	2968.8	1.799
	20.294*	2894.6	2894.1	2.635
	11.124	2949.2	2955.2	1.993
	22.267*	2882.5	2883.4	2.762

Table 2. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
3.925	12.948	2589.3	2599.2	2.128
	28.111*	2509.6	2513.2	3.162
	12.104	2604.5	2605.6	2.023
	26.479*	2530.4	2520.7	3.035
3.625	16.118	2338.4	2332.6	2.264
	32.610*	2251.5	2249.3	3.126
	15.557	2342.6	2336.3	2.196
	31.377*	2264.5	2254.4	3.033
3.193	15.369	2004.7	2005.6	1.967
	33.921*	1914.4	1912.0	2.928
	16.702	-	1996.9	-
	29.988*	1924.5	1928.3	1.776
2.384	18.804	-	1452.0	-
	37.608*	1365.4	1365.8	1.753
	20.098	1436.8	1444.6	1.681
	18.028	1461.4	1456.6	1.611
	37.116*	1371.7	1367.7	2.210
	17.879	-	1457.5	-
	36.147*	1371.7	1371.3	1.717
2.210	22.393	1345.4	1338.2	1.757
	43.681*	1251.6	1250.6	2.281
	22.978	1329.5	1335.2	1.810
	46.285*	1231.1	1242.1	2.405
	19.659	1358.2	1353.1	1.669
	42.523*	1259.0	1254.5	2.368
	20.111	1340.6	1350.6	1.660
	42.144*	1251.6	1255.8	2.303
2.020	31.740	1204.3	1203.0	2.223
	63.900*	1103.7	1100.5	2.925
	30.734	1211.3	1207.2	2.176
	62.557*	1105.1	1103.9	2.880
1.752	20.793	1146.6	1145.6	1.434
	41.975*	1054.2	1055.1	1.901
	20.793	-	1145.6	-
	41.631*	1056.6	1056.3	1.489

Table 2. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
1.535	31.024	1029.3	1025.2	1.856
	62.288*	928.3	923.8	2.406
	30.795	-	1026.2	-
	62.148*	923.8	924.1	1.875
1.209	39.180	912.5	915.7	1.985
	74.544*	814.3	816.4	2.444
	37.758	918.6	920.9	1.967
	74.633*	814.3	816.2	2.483
1.045	43.768	870.7	872.3	2.149
	87.056*	764.3	762.4	2.707
	43.371	-	873.7	-
	87.039*	761.6	762.4	2.065
0.8602	38.799	865.1	865.4	1.957
	80.763*	755.5	751.2	2.552
	38.426	871.7	866.8	1.973
0.6748	35.563	858.0	856.7	1.748
	70.459*	756.0	753.4	2.206
	36.333	855.1	853.8	1.773
	72.034*	750.9	749.8	2.233
0.4661	25.335	869.9	871.9	1.298
	49.461*	781.4	780.7	1.648
	25.137	866.8	872.9	1.304
	50.428*	777.1	777.8	1.690
0.3571	19.567	-	877.7	-
	39.166*	793.2	790.2	1.746
	19.584	874.6	877.6	1.200
	38.809*	788.6	791.5	2.088
0.2350	17.881	844.0	839.1	1.524
	17.804	845.2	839.6	1.535
0.1574	17.132	790.6	785.7	1.837
	17.076	789.5	786.0	1.850

Table 2. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
0.09473	14.348	708.9	716.3	2.529
	14.373	710.3	716.1	2.522
0.03454	4.9441	591.3	601.5	4.045
	4.8552	588.5	602.6	4.060
	4.8870	607.7	602.2	4.036
	4.5640	612.2	606.6	4.072
0.001527 $\square$	7.546	61.2	63.2	2.282
0.001552	7.563	61.5	64.6	2.331
0.002029	9.538	73.9	74.7	2.832
0.002227	11.124	66.7	71.8	2.992
0.002811	12.948	79.7	86.0	3.392
0.002648	12.104	74.1	84.9	3.252
0.003261	16.118	86.9	83.3	3.388
0.003138	15.557	78.0	81.9	3.287
0.003392	15.369	90.2	93.5	3.141
0.003712	18.028	89.7	89.0	2.398
0.004368	22.393	93.8	87.6	2.496
0.004628	22.978	98.5	93.1	2.622
0.004252	19.659	99.1	98.6	2.556
0.004214	20.111	89.1	94.8	2.494
0.006390	31.740	100.6	102.6	3.194
0.006256	30.734	106.2	103.4	3.142
0.004198	20.793	92.4	90.4	2.073

Table 2. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
0.006229	31.024	101.0	101.5	2.634
0.007454	39.180	98.2	99.3	2.700
0.007463	37.758	104.3	104.6	2.730
0.008706	43.768	106.4	110.0	2.978
0.008076	38.799	109.5	114.2	2.791
0.007046	35.563	102.0	103.3	2.425
0.007203	36.333	104.3	104.0	2.456
0.004946	25.335	88.5	91.2	1.810
0.005043	25.137	89.7	95.1	1.850
0.003881	19.584	86.0	86.1	2.200

Terbium Nitrate

4.738	8.5020	3750.5	3751.7	1.948
	17.043*	3690.4	3687.2	2.720
	8.7475	3755.5	3749.4	1.989
4.502	9.2895	3509.9	3517.5	1.977
	18.462*	3450.1	3451.7	2.736
	9.7226	3504.7	3513.6	2.075
	19.478*	3449.3	3445.8	2.897
4.038	9.8811	3097.8	3093.5	1.902
	20.401*	3029.0	3022.0	2.715
	10.646	3092.7	3087.0	2.028
3.592	15.753	2668.3	2670.2	2.524
	31.850*	2589.7	2588.4	3.507
	14.646	-	2677.6	-
	31.834*	2585.3	2588.4	3.024

Table 2. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
3.249	16.005	2388.6	2390.4	2.239
	30.784*	2321.3	2314.7	2.977
	13.585	2399.8	2406.8	2.064
	29.393*	2319.0	2320.6	3.048
	14.077	2405.1	2403.3	2.086
	29.165*	2329.3	2321.6	2.961
2.917	19.453	2109.0	2114.2	2.436
	39.066*	2020.2	2027.3	3.324
	19.704	2105.2	2112.8	2.456
	39.148*	2027.4	2027.0	3.335
2.587	20.100	1871.0	1872.1	2.653
	19.758	1873.8	1874.0	2.211
	39.663*	1794.3	1786.7	3.016
2.274	17.864	1677.3	1678.2	1.779
	35.181*	1593.0	1596.3	2.370
	17.170	1688.7	1682.4	1.748
	34.408*	1606.5	1599.3	2.368
1.960	23.010	1466.9	1466.1	2.012
	22.691	1470.2	1467.8	1.989
	46.328*	1366.6	1373.9	2.684
1.705	26.190	-	1321.9	-
	53.834*	1221.6	1222.6	2.232
	27.113	1321.9	1317.6	2.094
	54.654*	1211.5	1220.3	2.760
1.440	29.280	-	1196.2	-
	58.121*	1097.7	1099.0	2.077
	29.749	1199.8	1194.2	2.061
	59.057*	1093.9	1096.5	2.670
1.215	31.241	-	1110.7	-
	62.004*	1011.5	1011.6	2.030
	31.232	1100.4	1110.7	2.014
	63.073*	1005.1	1008.9	2.654

Table 2. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
0.9848	30.769	1053.5	1050.0	1.860
	60.441*	952.2	953.1	2.375
	31.197	1043.5	1048.3	1.878
	61.084*	953.2	951.4	2.412
0.8056	34.019	999.8	996.4	1.957
	67.564*	898.4	894.8	2.510
	34.826	997.7	993.3	2.025
	70.774*	894.3	887.2	2.643
0.6627	34.872	964.6	962.9	1.935
	69.330*	862.6	860.4	2.477
	34.553	958.5	964.2	1.941
	70.237*	860.9	858.2	2.541
0.4885	30.994	935.1	937.1	1.695
	62.116*	836.4	836.7	2.188
	31.433	935.8	935.2	1.721
	62.844*	839.8	834.8	2.224
0.3622	23.266	926.4	930.3	1.293
	46.116*	841.1	840.1	1.678
	27.626	906.8	909.5	1.476
0.2513	26.947	853.7	854.5	1.690
	27.217	856.8	853.2	1.714
0.1615	23.925	788.8	788.1	1.416
	23.414	791.0	790.7	1.393
0.09093	13.754	729.8	730.5	2.558
	14.388	729.8	726.1	2.457
0.03919	6.1935	619.9	614.8	3.853
	6.4255	617.9	612.1	3.824
0.001704□	8.502	60.1	64.5	2.943
0.001846	9.289	59.8	65.8	2.965
0.001948	9.723	55.4	67.8	3.135

Table 2. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
0.002040	9.881	68.8	71.6	2.928
0.003185	15.753	78.7	81.8	3.797
0.003078	16.005	67.3	75.8	3.245
0.002939	13.585	80.8	86.2	3.273
0.002917	14.077	75.8	81.8	3.197
0.003907	19.453	88.8	86.9	3.609
0.003915	19.704	77.8	85.8	3.624
0.003966	19.758	79.5	87.3	3.275
0.003518	17.864	84.3	81.9	2.583
0.003441	17.170	82.2	83.1	2.574
0.004633	22.691	103.6	93.8	2.919
0.005465	27.113	110.5	97.3	3.013
0.005906	29.749	105.9	97.6	2.923
0.006307	31.232	95.3	101.8	2.897
0.006044	30.769	101.3	97.0	2.606
0.006108	31.197	90.4	96.9	2.645
0.006756	34.019	101.4	101.7	2.753
0.007077	34.826	103.4	106.1	2.890
0.006933	34.872	102.0	102.6	2.717
0.007024	34.553	97.6	105.9	2.777
0.006212	30.994	98.7	100.4	2.397

Table 2. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
0.006284	31.433	96.0	100.4	2.436
0.004612	23.266	85.3	90.2	1.837
Thulium Nitrate				
6.028	9.9901	5994.5	6002.2	3.645
	20.668*	5931.7	5931.6	5.275
	11.337	5992.0	5991.3	3.967
	22.182*	5921.1	5923.7	5.433
5.499	10.539	5450.9	5429.5	3.441
	21.244*	5389.8	5360.4	4.851
	10.744	5415.6	5427.8	3.459
	21.453*	5350.7	5359.3	4.829
5.016	10.707	4913.5	4916.2	3.159
	21.582*	4841.0	4846.7	4.438
	10.514	-	4917.8	-
	19.107*	4857.0	4860.1	2.889
4.412	12.980	4252.5	4249.8	3.305
	26.325*	4167.2	4174.6	4.648
	13.491	4242.6	4246.1	3.378
	26.724*	4173.1	4172.8	4.661
3.997	15.334	3779.9	3778.8	3.448
	15.470	3783.7	3777.9	3.412
	30.303*	3694.1	3702.5	4.627
3.765	17.102	3513.0	3510.4	3.465
	32.987*	3427.5	3434.4	4.630
	17.555	3497.8	3507.7	3.571
	34.306*	3418.9	3429.3	4.837
3.246	19.065	2934.9	2927.1	3.175
	35.783*	2857.5	2851.9	4.135
	17.536	2937.9	2935.9	3.051
	35.105*	2856.0	2854.4	4.206

Table 2. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
2.906	19.530	2558.7	2559.5	2.891
	37.661*	2482.2	2480.1	3.845
	19.037	2560.7	2562.3	2.842
	37.115*	2485.0	2482.1	3.819
2.558	20.383	2200.8	2198.8	2.665
	41.115*	2112.2	2112.2	3.658
	20.521	2191.4	2198.1	2.614
	39.768*	2116.5	2116.7	3.479
	20.571	2201.9	2197.8	2.755
	20.554	2197.6	2197.9	2.604
	39.368*	2121.2	2118.1	3.429
2.249	22.281	1894.5	1896.6	2.451
	43.292*	1813.6	1812.8	3.246
	27.055	1876.6	1873.9	2.928
	52.876*	1786.5	1784.0	3.877
	26.173	1877.4	1877.9	3.434
	26.999	-	1874.2	-
	52.662*	1801.0	1784.6	3.107
	27.569	1873.4	1871.6	2.946
	52.991*	1784.0	1783.7	3.845
	26.639	1875.3	1875.8	2.871
	51.703*	1787.6	1787.3	3.783
1.961	27.636	1627.9	1626.5	3.151
	26.861	1627.1	1630.0	2.499
	51.627*	1539.2	1542.8	3.245
1.696	33.977	1397.1	1404.1	2.663
	64.222*	1308.6	1313.3	3.382
	35.358	1396.3	1398.9	2.741
	65.840*	1310.4	1309.4	3.443
1.445	30.025	1260.9	1262.4	2.053
	53.074*	1181.0	1184.8	2.478
	29.340	1259.8	1265.3	2.010
	51.824*	1184.2	1188.3	2.431

Table 2. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
1.210	37.173	1118.4	1115.5	2.167
	62.244*	1043.5	1041.3	2.511
	40.501	1104.5	1103.9	2.263
	65.073*	1034.0	1034.4	2.560
0.9978	26.814	1073.3	1071.4	1.586
	47.537*	995.3	995.9	1.909
	30.715	1055.1	1054.7	1.825
	57.176*	975.6	968.8	2.272
0.8194	26.151	1021.6	1017.2	1.380
	25.407	1018.9	1020.6	1.330
	42.479*	954.8	954.6	1.753
	26.430	1017.2	1015.9	1.940
	27.149	-	1012.7	-
	44.975*	941.6	946.6	1.572
	26.223	1021.0	1016.9	1.376
	43.681*	953.4	950.7	1.770
	25.787	1019.0	1018.9	1.393
	44.090*	947.7	949.4	1.746
0.6164	26.343	965.7	961.2	1.439
	48.515*	881.3	880.7	1.764
	27.184	957.6	957.4	1.471
	50.195*	873.6	875.7	1.807
0.4799	22.600	-	941.1	-
	40.151*	863.6	869.3	1.858
	22.758	936.3	940.3	1.110
	40.579*	861.0	867.8	1.695
	23.041	938.4	938.9	1.589
	23.958	934.7	934.4	1.184
	42.614*	860.5	861.1	1.692
0.3602	19.401	921.5	916.0	1.260
	34.939*	845.8	845.9	2.435
	19.858	913.5	913.5	1.278
	34.408*	850.7	847.9	2.540
	19.651	914.7	914.7	1.252
	34.856*	851.0	846.2	2.409
	19.700	912.3	914.4	1.236

Table 2. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
	35.612*	840.5	843.4	2.334
0.2144	14.041	871.9	864.8	2.064
	25.491*	805.5	800.9	3.510
	14.023	867.1	864.9	2.066
	25.720*	800.5	799.8	3.473
	11.831	879.9	880.7	2.345
	21.565*	821.7	820.2	3.754
	11.747	885.9	881.4	2.378
	20.962*	820.1	823.3	3.888
0.1617	17.666	787.8	790.5	1.758
	16.558	794.1	797.2	1.921
	14.732	803.1	808.9	2.197
0.09131	13.213	709.4	706.9	2.697
	11.191	723.9	722.1	2.967
	11.419	720.9	720.3	2.940
0.03459	3.4955	595.1	603.7	4.222
	4.1489	589.4	593.9	4.147
0.002067□	9.990	62.8	70.6	5.679
0.002218	11.337	70.9	67.5	5.896
0.002124	10.539	61.1	69.1	5.243
0.002145	10.744	64.8	68.5	5.226
0.002158	10.707	72.4	69.5	4.799
0.002633	12.980	85.4	75.1	5.024
0.002672	13.491	69.5	73.3	5.053
0.003030	15.470	89.6	75.4	5.028
0.003299	17.102	85.5	76.0	5.044

Table 2. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
0.003431	17.555	78.9	78.4	5.258
0.003578	19.065	77.4	75.2	4.523
0.003511	17.536	81.9	81.5	4.560
0.003766	19.530	76.6	79.4	4.192
0.003711	19.037	75.7	80.2	4.156
0.004112	20.383	88.7	86.6	3.969
0.003977	20.521	74.9	81.3	3.792
0.003937	20.554	76.4	79.8	3.744
0.004329	22.281	80.9	83.8	3.541
0.005288	27.055	90.1	89.9	4.230
0.005299	27.569	89.3	87.9	4.204
0.005170	26.639	87.7	88.4	4.130
0.005163	26.861	87.9	87.2	3.552
0.006422	33.977	88.5	90.8	3.715
0.006584	35.358	85.9	89.5	3.789
0.005307	30.025	79.9	77.6	2.747
0.005182	29.340	75.7	77.0	2.693
0.006224	37.173	74.9	74.1	2.805
0.006507	40.501	70.4	69.4	2.874
0.004754	26.814	78.0	75.5	2.117
0.005718	30.715	79.5	85.9	2.505

Table 2. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
0.004248	25.407	64.1	66.0	1.914
0.004368	26.223	67.6	66.1	1.940
0.004409	25.787	71.3	69.4	1.922
0.004852	26.343	84.4	80.5	1.950
0.005019	27.184	84.0	81.7	1.997
0.004058	22.758	75.3	72.5	1.812
0.004261	23.958	74.2	73.3	1.825
0.003494	19.401	75.7	70.2	2.542
0.003441	19.858	62.8	65.6	2.645
0.003486	19.651	63.7	68.5	2.516
0.003561	19.700	71.8	71.0	2.440
0.002549	14.041	66.3	63.9	3.707
0.002572	14.023	66.7	65.0	3.672
0.002156	11.831	58.2	60.6	3.991
0.002096	11.747	65.8	58.0	4.124

Ytterbium Nitrate

6.650	5.5780	6792.0	6793.7	2.387
	11.806*	6748.0	6736.4	3.545
	6.0643	6784.4	6788.1	2.529
5.761	7.1650	5915.7	5928.0	2.575
	14.448*	5874.8	5869.6	3.647
	7.0983	5943.9	5928.7	2.547

Table 2. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
5.306	6.8908	5456.1	5449.5	2.329
	7.1886	5441.8	5446.5	2.397
	14.595*	5397.3	5387.4	3.412
4.816	7.8896	4876.8	4887.6	2.325
	15.670*	4829.0	4828.5	3.236
4.445	8.5378	4435.0	4446.2	2.318
	17.359*	4382.2	4383.0	3.293
	9.1106	4438.6	4441.1	2.442
	18.202*	4383.2	4378.2	3.410
3.994	10.749	3884.6	3883.7	2.480
	21.081*	3821.4	3819.0	3.392
	10.821	3876.9	3883.1	2.488
	21.075*	3825.9	3819.0	3.391
3.576	12.571	3368.3	3364.6	2.553
	25.352*	3301.4	3293.1	3.571
	12.573	3365.7	3364.6	2.582
	25.781*	3300.5	3291.1	3.671
3.226	12.301	2949.5	2949.1	2.323
	27.112*	2872.2	2867.9	3.522
	14.690	2940.6	2932.7	2.569
	29.104*	2869.9	2859.5	3.521
2.552	19.523	2149.2	2153.8	2.509
	39.467*	2070.6	2070.8	3.463
	19.495	-	2153.9	-
	40.125*	2067.4	2068.6	2.887
2.249	22.166	1839.3	1841.3	2.415
	44.468*	1755.0	1756.0	3.282
	21.961	1841.1	1842.3	2.430
	45.084*	1752.2	1754.1	3.365
1.963	25.592	1573.0	1574.0	2.419
	53.269*	1476.8	1479.7	3.351
	26.670	1567.4	1569.2	2.476
	54.169*	1476.1	1477.3	3.364

Table 2. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
1.687	29.920	1345.3	1348.4	2.352
	60.104*	1250.9	1254.9	3.129
	29.858	1346.6	1348.6	2.369
	60.830*	1248.4	1253.2	3.183
1.461	30.091	1200.2	1206.8	2.082
	58.814*	1111.3	1117.2	2.696
	29.425	1212.5	1209.5	2.086
	58.915*	1118.0	1117.0	2.748
1.211	31.112	1082.8	1079.3	1.969
	62.800*	984.9	984.1	2.584
	31.036	1081.8	1079.6	1.986
	63.777*	983.3	981.8	2.646
1.015	33.021	1002.2	998.8	1.909
	65.486*	905.7	904.6	2.456
	33.457	1000.3	997.2	1.924
	65.814*	905.7	903.9	2.462
0.8362	35.211	943.1	940.4	1.846
	69.056*	855.8	846.2	2.598
	35.344	939.0	939.9	1.930
	70.999*	845.6	841.9	2.505
0.6894	36.809	-	901.7	-
	73.671*	798.8	803.3	1.884
	36.230	906.7	903.8	2.347
	36.755	900.0	901.9	1.889
	35.567	908.5	906.1	1.889
	72.538*	808.2	805.7	2.460
0.4975	31.381	880.8	881.2	1.580
	60.245*	789.1	793.2	1.974
	31.983	-	878.9	-
	66.482*	776.4	778.5	1.746
0.3732	21.696	886.1	888.8	1.437
	23.207	883.1	881.4	1.203
	45.225*	801.0	798.9	1.610
	22.220	883.6	886.2	1.149

Table 2. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
	43.736*	801.5	803.4	1.605
	22.299	884.8	885.8	1.190
	44.650*	800.8	800.6	1.586
0.2334	25.248	799.4	802.5	1.500
	26.043	801.3	798.9	1.548
0.1596	21.737	751.5	751.4	1.247
	23.925	743.8	740.8	1.343
0.08900	14.059	681.7	679.4	2.652
	13.658	687.0	682.1	2.692
0.03993	6.6410	578.5	575.2	3.852
	6.8633	576.4	572.8	3.827
0.001181□	5.578	44.0	57.3	3.804
0.001445	7.165	40.9	58.4	3.938
0.001460	7.189	44.5	59.1	3.682
0.001567	7.890	47.8	59.1	3.504
0.001736	8.538	52.8	63.1	3.554
0.001820	9.111	55.4	62.9	3.690
0.002108	10.749	63.2	64.7	3.682
0.002108	10.821	50.9	64.1	3.683
0.002535	12.571	66.9	71.5	3.863
0.002578	12.573	65.2	73.4	3.962
0.002711	12.301	77.3	81.2	3.768
0.002910	14.690	70.6	73.3	3.821
0.003947	19.523	78.6	83.0	3.753

Table 2. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
0.004447	22.166	84.4	85.3	3.566
0.004508	21.961	88.9	88.2	3.646
0.005327	25.592	96.2	94.4	3.631
0.005417	26.670	91.4	92.0	3.655
0.006010	29.920	94.3	93.5	3.411
0.006083	29.858	98.2	95.5	3.464
0.005881	30.091	88.8	89.6	2.952
0.005891	29.425	94.5	92.5	3.000
0.006280	31.112	97.9	95.2	2.823
0.006378	31.036	98.5	97.8	2.883
0.006549	33.021	96.5	94.2	2.692
0.006581	33.457	94.6	93.3	2.701
0.006906	35.211	87.3	94.2	2.808
0.007100	35.344	93.4	97.9	2.742
0.007254	35.567	100.3	100.4	2.691
0.006024	31.381	91.7	88.0	2.174
0.004523	23.207	82.1	82.6	1.753
0.004374	22.220	82.0	82.8	1.736
0.004465	22.299	84.0	85.2	1.728

Table 2. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
Praseodymium Perchlorate				
4.695	4.3586	6622.3	6625.7	1.737
	8.3484	6594.0	6588.0	2.353
	4.0220	6625.6	6629.7	1.634
	7.8535	6601.0	6591.9	2.254
4.255	5.3322	5488.4	5489.0	1.799
	10.604*	5450.8	5445.6	2.514
	5.5215	5483.5	5487.0	1.839
	10.793*	5448.1	5444.3	2.532
3.862	6.6604	-	4602.3	-
	13.047*	4550.8	4556.3	2.057
	6.1428	4606.5	4607.1	1.761
	12.419*	4567.1	4560.1	2.496
	7.1657	-	4597.8	-
	14.268*	4544.0	4549.3	2.269
	7.1976	4595.0	4597.5	2.019
	14.370*	4544.3	4548.8	2.822
3.398	6.7974	3666.3	3662.9	1.682
	15.531*	3612.2	3604.4	2.670
	8.5256	-	3648.6	-
	17.094*	3603.8	3596.5	2.179
2.930	12.332	2751.7	2752.5	1.987
	23.274*	2700.7	2699.1	2.622
	11.859	2756.5	2755.5	2.036
	24.636*	2698.7	2693.7	2.927
2.508	15.362	2022.1	2026.9	1.909
	31.492*	1956.7	1961.2	2.680
	15.665	2016.5	2025.4	1.912
	31.267*	1956.9	1961.9	2.627
2.150	18.208	1491.4	1489.6	1.706
	38.917*	1413.5	1415.8	2.444
	17.525	1496.4	1492.9	1.674
	38.164*	1420.6	1417.9	2.445

Table 2. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
1.966	25.514	1227.4	1227.0	1.925
	54.304*	1143.5	1146.1	2.704
	24.422	1230.6	1231.2	1.862
	52.341*	1146.4	1150.5	2.633
1.773	32.347	991.8	989.5	1.929
	67.934*	904.9	905.1	2.627
	31.656	996.6	991.8	1.934
	68.556*	906.6	903.9	2.702
1.521	44.733	726.8	727.3	1.836
	86.942*	647.2	646.3	2.296
	41.083	729.9	736.8	1.794
	87.263*	646.3	645.8	2.407
1.305	36.255	610.7	605.5	1.300
	74.613*	522.2	521.2	1.653
	36.232	606.4	605.6	1.298
	74.013*	526.1	522.2	1.659
1.119	49.791	483.3	482.5	1.326
	100.293*	396.0	394.8	1.689
	51.468	473.7	478.7	1.324
	102.515*	387.9	391.9	1.702
0.9529	38.593	461.3	461.3	1.295
	76.345*	381.0	380.7	2.587
	37.905	463.2	463.2	1.285
	76.020*	384.6	381.3	2.517
0.7096	58.126	380.3	386.1	1.626
	58.280	379.3	385.7	1.627
0.5042	47.716	422.8	418.0	1.499
	45.822	424.6	422.6	1.448
	44.984	429.2	424.7	1.440
0.3820	32.523	474.1	472.8	1.455
	33.342	468.1	470.2	1.411

Table 2. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
0.2564	31.696	484.3	485.1	1.457
	31.653	482.4	485.3	1.470
0.1608	20.866	516.3	515.2	2.409
	20.794	512.5	515.5	2.431
0.09976	14.491	517.5	512.5	3.090
	14.664	512.3	511.6	3.085
0.04174	6.7044	470.1	463.4	3.997
	6.7086	470.2	463.3	3.995
0.000835 $\square$	4.359	28.3	37.7	2.558
0.000785	4.022	24.6	37.8	2.443
0.001060	5.332	37.7	43.4	2.720
0.001079	5.521	35.3	42.7	2.746
0.001242	6.143	39.3	47.0	2.695
0.001437	7.198	50.7	48.8	3.054
0.001553	6.797	54.2	58.5	2.841
0.002327	12.332	51.0	53.5	2.861
0.002464	11.859	57.8	61.7	3.154
0.003149	15.362	65.4	65.8	2.898
0.003127	15.665	59.6	63.5	2.850
0.003892	18.208	77.9	73.8	2.635
0.003816	17.525	75.7	75.0	2.629
0.005430	25.514	83.8	80.9	2.924
0.005234	24.422	84.2	80.7	2.844

Table 2. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
0.006793	32.347	86.9	84.5	2.854
0.006856	31.656	90.1	87.8	2.924
0.008694	44.733	79.6	81.0	2.529
0.008726	41.083	83.6	91.0	2.620
0.007461	36.255	88.5	84.3	1.815
0.007401	36.232	80.3	83.4	1.821
0.01003	49.791	87.3	87.7	1.855
0.01025	51.468	85.7	86.8	1.866
0.007634	38.593	80.3	80.5	2.693
0.007602	37.905	78.6	81.9	2.624

Samarium Perchlorate

4.640	5.8309	6275.6	6292.2	2.231
	11.675*	6240.2	6246.7	3.142
	5.6833	6306.4	6293.6	2.211
	11.562*	6266.0	6247.4	3.159
4.324	7.6591	5478.4	5477.9	2.624
	16.190*	5423.2	5423.1	3.879
	7.6784	5475.7	5477.7	2.594
	15.851*	5428.2	5424.9	3.752
4.006	8.9919	4748.3	4756.2	2.698
	19.360*	4695.9	4696.7	4.059
	9.8104	4741.4	4750.2	2.847
	20.158*	4693.6	4693.1	4.094

Table 2. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
3.433	11.142	-	3602.8	-
	22.168*	3555.4	3546.1	2.723
	10.706	3606.2	3605.7	2.372
	21.936*	3554.8	3547.1	3.388
3.051	12.445	2913.6	2906.4	2.209
	25.233*	2852.2	2845.7	3.102
	12.282	2909.5	2907.4	2.208
	25.487*	2838.6	2844.7	3.160
2.560	18.103	2072.6	2075.6	2.250
	36.291*	2006.2	2008.4	3.096
	17.368	2078.6	2079.2	2.199
	35.564*	2009.2	2010.6	3.081
2.244	24.360	1596.7	1600.9	2.304
	48.619*	1525.1	1528.0	3.119
	24.435	1594.2	1600.6	2.321
	49.134*	1523.3	1526.7	3.165
1.942	27.329	1221.6	1222.5	1.973
	54.538*	1146.9	1147.3	2.633
	27.060	1218.9	1223.5	1.963
	54.352*	1146.0	1147.7	2.637
1.693	28.296	974.6	969.7	1.639
	57.129*	894.0	892.3	2.167
	28.517	964.4	968.9	1.634
	57.302*	886.4	891.9	2.155
	31.239	956.2	959.7	2.137
	31.853	957.7	957.7	1.799
	64.108*	878.0	878.2	2.371
1.444	28.074	780.6	774.6	1.306
	56.148*	703.6	698.5	1.690
	27.886	778.2	775.3	1.297
	55.836*	702.1	699.2	1.682
1.286	50.548	615.7	615.9	2.225
	50.595	615.4	615.8	2.228

Table 2. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
1.107	53.342	526.0	529.2	2.021
	55.428	523.0	524.6	2.086
0.9226	74.409	431.6	434.7	2.301
	75.341	431.0	433.1	2.328
0.7474	75.504	403.3	407.3	2.193
	77.632	398.9	403.7	2.231
0.6116	71.874	406.4	407.8	2.112
	70.637	407.2	410.0	2.084
0.4981	56.991	439.8	438.7	1.831
	57.219	438.5	438.2	1.835
0.3752	47.588	465.2	465.4	1.635
	51.519	457.5	456.1	1.734
0.2497	32.099	508.8	508.2	1.246
	26.838	528.7	526.2	1.703
	28.641	518.6	519.8	1.561
0.2119	28.533	516.5	515.8	1.581
	30.518	509.1	509.0	1.411
0.1436	22.164	521.5	519.3	2.239
	23.648	512.1	513.3	2.121
0.09245	15.723	509.0	509.7	2.980
	16.001	501.6	508.3	2.973
0.04885	8.4845	475.3	476.4	3.811
	8.4092	480.4	477.0	3.809
0.001168	5.831	35.4	45.5	3.396
0.001156	5.683	40.5	46.3	3.407
0.001619	7.659	55.2	54.8	4.164

Table 2. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
0.001585	7.678	47.5	52.8	4.040
0.001936	8.992	52.4	59.6	4.348
0.002016	9.810	47.8	57.2	4.411
0.002194	10.706	51.5	58.7	3.654
0.002523	12.445	61.4	60.7	3.354
0.002549	12.282	70.9	62.7	3.408
0.003629	18.103	66.4	67.2	3.357
0.003556	17.368	69.4	68.6	3.333
0.004862	24.360	71.6	72.9	3.391
0.004913	24.435	70.9	73.8	3.437
0.005454	27.329	74.7	75.3	2.869
0.005435	27.060	72.9	75.8	2.870
0.005713	28.296	80.6	77.4	2.365
0.005730	28.517	78.0	77.0	2.353
0.006411	31.853	79.7	79.5	2.588
0.005615	28.074	77.1	76.1	1.851
0.005584	27.886	76.1	76.1	1.841

Dysprosium Perchlorate

4.602	5.2175	7404.8	7418.9	2.356
	10.478*	7374.7	7375.3	3.332
	5.4583	-	7416.4	-
	10.659*	7393.0	7374.0	2.706

Table 2. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
4.317	5.6414	6747.9	6747.7	2.314
	11.280*	6709.6	6703.1	3.255
4.044	5.9287	6111.8	6119.6	2.202
	11.799*	6077.4	6074.5	3.084
	6.0749	6114.2	6118.2	2.256
	12.087*	6077.1	6072.7	3.157
3.537	6.3788	4991.2	4987.3	1.941
	6.2727	4991.7	4988.3	1.926
2.869	10.398	3567.7	3575.6	2.203
	20.128*	3519.9	3522.9	2.985
	9.6409	3582.9	3580.9	2.097
	19.186*	3534.2	3527.1	2.915
2.561	13.498	2980.8	2979.1	2.397
	26.606*	2921.4	2919.7	3.283
	13.508	2975.0	2979.1	2.420
	27.039*	2914.8	2918.1	3.361
2.303	16.039	2513.4	2516.5	2.423
	32.242*	2448.1	2451.6	3.360
	16.232	2516.3	2515.6	2.454
	32.599*	2450.9	2450.5	3.401
2.086	19.316	2152.3	2152.8	2.465
	38.258*	2086.7	2085.6	3.359
	18.638	2156.1	2156.0	2.412
	37.514*	2088.4	2087.7	3.333
1.792	19.400	1728.7	1729.5	2.035
	39.588*	1656.9	1658.9	2.821
	19.070	1731.0	1731.0	1.998
	38.574*	1662.6	1661.7	2.754
1.680	22.096	1572.5	1574.2	2.079
	44.459*	1499.2	1502.3	2.833
	21.991	1579.4	1574.6	2.072
	43.943*	1506.6	1503.7	2.807

Table 2. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
1.456	22.059	1317.5	1315.9	1.743
	21.831	1321.6	1316.9	1.764
	45.171*	1242.1	1242.1	2.434
1.190	23.448	1061.9	1060.0	1.494
	46.767*	987.7	987.9	1.979
	23.619	1060.3	1059.3	1.505
	47.036*	989.6	987.2	1.997
1.069	26.485	952.7	954.9	1.501
	52.545*	879.7	880.7	1.969
	26.601	956.4	954.4	1.537
	54.491*	875.9	876.4	2.057
0.9239	26.664	862.4	860.6	1.392
	54.708*	781.1	782.3	1.849
	26.269	854.6	862.0	1.370
	54.371*	773.8	783.0	1.833
0.7458	38.423	733.2	733.3	1.624
	76.227*	647.6	651.2	2.057
	37.128	740.2	737.1	1.614
	75.236*	656.6	652.9	2.087
0.5885	40.862	671.9	668.9	1.985
	40.237	674.7	670.7	1.965
0.5090	53.171	611.6	615.6	2.333
	53.369	616.4	615.1	2.362
	34.727	665.4	663.6	1.691
	37.908	656.3	654.2	1.813
0.4021	41.910	617.5	615.7	1.884
	46.014	603.9	605.1	2.017
0.2441	31.310	599.5	600.1	1.407
	32.842	596.7	595.2	1.465
0.1632	23.187	586.4	586.5	1.817
	24.461	577.7	581.4	1.703

Table 2. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
0.1045	16.709	556.2	557.9	2.712
	16.799	555.5	557.5	2.701
0.04046	6.6273	484.5	478.7	3.984
	6.5234	483.1	479.6	3.996
0.001048 $\square$	5.218	30.1	43.7	3.599
0.001128	5.641	38.3	44.7	3.518
0.001180	5.929	34.4	45.1	3.336
0.001209	6.075	37.1	45.5	3.415
0.002013	10.398	47.8	52.8	3.245
0.001919	9.641	48.6	53.8	3.156
0.002661	13.498	59.5	59.4	3.563
0.002704	13.508	60.1	61.0	3.640
0.003224	16.039	65.3	64.9	3.640
0.003260	16.232	65.4	65.1	3.684
0.003826	19.316	65.7	67.2	3.648
0.003751	18.638	67.8	68.2	3.612
0.003959	19.400	71.9	70.6	3.056
0.003857	19.070	68.4	69.3	2.986
0.004446	22.096	73.2	71.9	3.077
0.004394	21.991	72.8	71.0	3.051
0.004517	21.831	79.5	74.8	2.638
0.004677	23.448	74.2	72.1	2.159

Table 2. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
0.004704	23.619	70.7	72.1	2.178
0.005255	26.485	72.9	74.1	2.152
0.005449	26.601	80.5	78.1	2.240
0.005471	26.664	81.3	78.3	2.016
0.005437	26.269	80.8	79.0	1.997
0.007623	38.423	85.7	82.1	2.261
0.007524	37.128	83.6	84.1	2.286

Table 3. Calculated heats of dilution for aqueous rare earth solutions at 25°C using the data of Michael Mohs(14).

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
Lanthanum Nitrate				
4.608	30.504	1524.5	1525.7	2.832
	66.374*	1409.6	1412.0	3.469
	30.515	1528.5	1525.7	2.832
	66.178*	1411.7	1412.5	3.469
4.456	28.313	1460.7	1458.1	2.381
	57.472*	1358.1	1357.7	2.916
	28.430	1455.4	1457.5	2.381
	57.275*	1358.7	1358.2	2.916
4.000	48.136	1164.2	1165.7	3.098
	97.180*	1050.5	1051.1	3.794
	48.595	1166.9	1164.3	3.098
	98.149*	1053.3	1049.3	3.794
3.606	25.422	1074.4	1075.8	1.569
	51.065*	976.1	980.2	1.921
	25.341	1075.4	1076.2	1.569
	51.266*	977.7	979.6	1.921
3.239	14.334	988.3	986.3	1.697
	28.837*	904.4	906.8	2.079
	14.334	992.6	986.3	1.697
	28.697*	910.1	907.4	2.079
2.893	19.651	820.3	821.2	1.466
	39.188*	731.6	734.0	1.796
	19.705	825.0	820.9	1.466
	39.038*	735.6	734.6	1.796
2.557	24.020	684.9	686.8	1.519
	47.362*	591.6	595.6	1.861
	23.951	687.3	687.2	1.519
	47.472*	593.8	595.3	1.861

*f=3 for this sample and its corresponding f=2 (unstarred) value is given immediately above it.

Table 3. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
2.092	29.322	543.0	546.6	1.250
	29.268	546.0	546.8	1.250
	34.293	523.0	525.9	1.250
1.960	28.143	532.0	529.2	1.396
	27.552	534.0	531.9	1.396
	35.082	503.0	500.3	1.396
1.694	25.412	514.0	513.0	1.950
	25.492	515.0	512.6	1.950
1.341	26.225	512.0	508.3	2.211
	20.367	541.0	538.3	2.211
	20.385	542.0	538.2	2.211
1.208	30.437	501.0	501.0	1.506
	30.559	499.0	500.5	1.506
1.000	51.840	454.0	456.7	1.715
	51.768	456.0	456.9	1.715
0.8101	59.970	471.0	474.3	2.038
	60.187	473.0	473.7	2.038
0.6397	56.250	526.0	527.2	2.121
	56.490	525.0	526.5	2.121
0.4891	22.184	697.0	692.1	1.832
	52.751	575.0	575.2	1.832
	52.432	575.0	576.1	1.832
0.3598	32.718	666.0	669.4	1.589
	32.149	669.0	671.7	1.589
0.2498	26.998	705.0	700.0	1.423
	27.374	707.0	698.3	1.423
0.1599	26.389	676.0	678.5	1.341
	26.729	676.0	676.9	1.341
	17.447	725.0	726.4	1.341

Table 3. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
0.09897	11.016	715.0	715.9	2.894
	11.350	708.0	713.2	2.894
	15.257	673.0	684.5	2.894
	11.243	705.0	714.1	2.894
0.01702	1.1946	540.0	525.2	10.000
	1.2837	554.0	522.7	10.000
0.009027	0.9860	417.0	415.3	10.000
	0.9807	442.0	415.4	10.000
0.006618 $\square$	30.515	116.8	113.2	3.835
0.006637	30.504	114.9	113.7	3.835
0.005727	28.430	96.7	99.3	3.223
0.005747	28.313	102.6	100.4	3.223
0.009815	48.595	113.6	115.0	4.194
0.009718	48.136	113.7	114.6	4.194
0.005127	25.341	97.7	96.6	2.124
0.005107	25.422	98.3	95.6	2.124
0.002870	14.334	82.5	78.9	2.298
0.002884	14.334	83.9	79.5	2.298
0.003904	19.705	89.4	86.3	1.985
0.003919	19.651	88.7	87.2	1.985
0.004747	23.951	93.5	91.9	2.057
0.004736	24.020	93.3	91.2	2.057

$\square$ Remaining data for this salt are for ΔH_{3-2} values.

Table 3. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
Neodymium Nitrate				
4.582	15.484	1844.1	1846.4	2.046
	37.822*	1744.6	1746.8	2.506
	17.247	1834.4	1835.8	2.046
	38.229*	1745.9	1745.4	2.506
4.144	23.542	1543.3	1539.7	1.980
	45.293*	1461.6	1460.1	2.425
	20.603	1559.8	1554.2	1.980
	42.159*	1470.9	1469.5	2.425
3.618	30.758	1209.7	1211.2	2.110
	59.768*	1122.0	1124.3	2.584
	32.890	1203.7	1203.1	2.110
	62.821*	1116.5	1117.2	2.584
3.394	28.270	1103.1	1101.6	1.849
	57.214*	1010.0	1010.9	2.265
	33.086	1083.8	1082.8	1.849
	61.560*	999.3	1000.6	2.265
3.036	33.954	898.3	900.3	1.613
	63.123*	815.0	817.6	1.975
	33.733	890.8	901.1	1.613
	63.760*	809.3	816.2	1.975
2.662	17.834	811.4	805.1	1.648
	36.289*	727.2	724.6	2.019
	20.476	796.4	790.8	1.648
	37.283*	722.2	721.2	2.019
2.368	16.622	701.9	699.2	2.048
	35.748*	613.1	613.6	2.509
	18.071	699.1	690.9	2.048
	36.433*	616.2	611.3	2.509

Table 3. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
2.033	29.681	533.7	533.0	1.719
	58.064*	445.0	445.9	2.105
	31.014	523.0	527.7	1.719
	58.752*	441.3	444.2	2.105
1.755	25.908	488.0	487.7	2.147
	52.201*	398.7	399.6	2.630
	25.806	492.1	488.1	2.147
	53.949*	395.9	395.0	2.630
1.491	44.769	384.0	385.7	1.530
	30.239	433.0	435.1	1.530
1.250	48.177	367.0	366.3	1.327
	49.182	363.0	363.5	1.327
1.032	53.568	362.0	361.3	1.553
	63.187	336.0	338.1	1.553
	71.470	319.0	320.3	1.553
0.8342	66.945	352.0	352.7	1.677
	62.189	361.0	363.3	1.677
0.6595	47.513	430.0	430.1	1.480
	44.836	439.0	437.8	1.480
0.4908	46.335	470.0	466.4	1.480
	49.745	462.0	456.8	1.480
0.3697	31.450	538.0	537.4	1.365
	27.009	554.0	555.3	1.365
0.2533	22.829	584.0	585.6	1.934
	22.203	585.0	588.7	1.934
0.1639	16.322	607.0	610.0	2.624
	16.040	608.0	611.7	2.624
0.1024	8.5849	628.0	631.4	3.622
	7.2307	638.0	644.4	3.622

Table 3. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
0.04035	3.3526	584.0	573.0	10.000
0.01022	0.8178	435.0	410.2	10.000
0.003823□	17.247	88.5	90.4	2.770
0.003782	15.484	99.5	99.6	2.770
0.004216	20.603	88.9	84.7	2.681
0.004529	23.542	81.7	79.7	2.681
0.006282	32.890	87.2	85.9	2.857
0.005977	30.758	87.7	86.9	2.857
0.006156	33.086	84.5	82.3	2.504
0.005721	28.270	93.1	90.7	2.504
0.006376	33.733	81.5	84.9	2.184
0.006312	33.954	83.3	82.7	2.184
0.003728	20.476	74.2	69.6	2.232
0.003629	17.834	84.2	80.5	2.232
0.003643	18.071	82.9	79.6	2.773
0.003575	16.622	88.8	85.6	2.773
0.005875	31.014	81.7	83.5	2.328
0.005806	29.681	88.7	87.1	2.328
0.005395	25.806	96.2	93.1	2.908
0.005220	25.908	89.3	88.1	2.908

Table 3. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
Gadolinium Nitrate				
4.400	17.564	2363.5	2364.9	2.441
	35.391*	2282.5	2284.4	2.990
	16.451	2372.5	2371.5	2.441
	34.621*	2285.7	2287.2	2.990
3.952	15.785	2019.7	2021.0	1.992
	33.086*	1938.1	1938.3	2.439
	16.370	2022.8	2017.4	1.992
	33.432*	1940.6	1937.0	2.439
3.622	24.069	1722.0	1725.7	2.435
	49.000*	1631.3	1635.8	2.983
	23.300	1731.4	1729.4	2.435
	48.679*	1636.7	1636.8	2.983
3.238	17.741	1481.6	1482.8	1.557
	35.331*	1401.8	1403.6	1.907
	17.189	1483.5	1486.1	1.557
	35.343*	1402.4	1403.5	1.907
2.896	11.580	1293.4	1298.0	1.079
	27.342*	1206.9	1209.5	1.321
	13.757	1288.7	1282.3	1.079
	27.217*	1213.6	1210.0	1.321
2.566	19.351	-	1054.6	-
	44.556*	952.0	953.9	1.483
	19.316	1058.5	1054.8	1.354
	43.745*	956.4	956.4	1.658
2.254	21.178	884.6	889.5	1.140
	43.217*	798.7	802.6	1.396
	19.981	899.3	895.8	1.140
	45.064*	796.8	797.0	1.396
1.967	30.592	731.6	732.2	1.214
	59.413*	643.6	643.3	1.487
	28.026	746.6	742.8	1.214

Table 3. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
	57.517*	649.1	648.0	1.487
1.692	46.581	597.1	596.2	1.512
	98.188*	486.0	484.9	1.852
	49.787	584.5	587.0	1.512
	100.701*	480.9	480.8	1.852
1.440	60.637	508.0	510.5	2.183
	59.444	510.0	513.4	2.183
1.211	77.934	452.0	450.6	2.354
	64.417	480.0	479.4	2.354
1.004	84.824	434.0	434.0	2.536
	77.651	449.0	447.7	2.536
0.8114	67.125	478.0	478.4	2.244
	63.409	487.0	486.8	2.244
0.6417	50.410	534.0	533.5	2.069
	60.591	507.0	507.2	2.069
	55.235	522.0	520.6	2.069
0.4980	43.983	561.0	564.6	1.918
	53.057	536.0	538.6	1.918
0.3597	37.015	596.0	594.0	1.584
	34.893	605.0	601.5	1.584
0.2500	27.144	626.0	625.5	1.464
	21.307	652.0	653.0	1.464
0.1566	13.816	665.0	668.1	2.758
0.09998	12.355	629.0	632.2	3.169
	10.227	647.0	648.7	3.169
0.03951	3.2979	576.0	590.3	10.000
	3.0485	576.0	594.5	10.000
0.003462□	16.451	86.8	84.3	3.305

Table 3. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
0.003539	17.564	81.0	80.5	3.305
0.003343	16.370	82.2	80.4	2.697
0.003309	15.785	81.6	82.7	2.697
0.004868	23.300	94.7	92.6	3.298
0.004900	24.069	90.7	89.8	3.298
0.003534	17.189	81.1	82.5	2.108
0.003533	17.741	79.8	79.3	2.108
0.002722	13.757	75.1	72.3	1.461
0.002734	11.580	86.5	88.5	1.461
0.004374	19.316	102.1	98.4	1.833
0.004506	19.981	102.5	98.8	1.543
0.004322	21.178	85.9	86.9	1.543
0.005752	28.026	97.5	94.8	1.644
0.005941	30.592	88.0	89.0	1.644
0.01007	49.787	103.6	106.2	2.048
0.009819	46.581	111.1	111.3	2.048
Holmium Nitrate				
5.027	13.846	4285.0	4287.3	3.781
	28.751*	4209.0	4205.8	4.630
	14.153	4282.0	4285.2	4.365
	16.614	4260.0	4268.9	4.365

Table 3. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
4.564	12.989	3861.7	3858.6	3.116
	28.687*	3776.1	3771.1	3.817
	13.293	3861.7	3856.4	3.116
	25.827*	3789.7	3784.2	3.817
4.131	16.378	3439.8	3434.5	3.370
	33.710*	3349.8	3349.3	4.127
	17.331	3423.8	3428.6	3.370
	33.074*	3347.4	3351.8	4.127
3.724	16.104	3061.1	3064.9	2.921
	31.192*	2985.8	2988.1	3.578
	16.851	3057.5	3060.2	2.921
	33.501*	2975.6	2978.7	3.578
3.338	26.874	2657.0	2662.8	4.342
	56.340*	2552.3	2559.7	5.317
	28.441	2658.9	2655.7	4.342
	57.487*	2555.1	2556.6	5.317
2.830	18.062	2276.7	2276.5	2.576
	37.933*	2183.4	2185.6	3.155
	19.856	2266.5	2266.2	2.576
	39.589*	2178.9	2179.7	3.155
2.550	24.790	2017.3	2018.0	2.892
	48.414*	1926.6	1928.2	3.542
	24.621	2025.9	2018.9	2.892
	50.723*	1925.2	1921.2	3.542
2.236	21.234	1805.9	1804.8	1.974
	36.881*	1735.5	1735.7	2.418
	19.378	1817.9	1815.1	1.974
	36.651*	1738.5	1736.6	2.418
1.958	39.438	1539.0	1541.5	2.814
	21.013	1620.7	1621.1	1.843
	39.038*	1542.2	1542.9	2.258

Table 3. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
1.685	49.731	1348.0	1347.7	3.349
	19.360	1472.1	1470.0	2.166
	50.581*	1346.8	1345.2	2.298
1.427	36.204	1261.7	1263.2	2.578
	74.511*	1150.2	1153.9	3.157
	37.100	1259.3	1259.9	2.578
	72.403*	1156.6	1158.6	2.734
1.210	31.159	1189.9	1190.8	2.076
	61.890*	1088.8	1091.7	2.543
	32.024	1185.0	1187.2	2.076
	62.016*	1088.0	1091.4	2.543
0.9929	31.562	1113.6	1111.0	1.979
	62.016*	1012.5	1013.3	2.423
	30.802	1114.6	1114.2	1.979
	65.157*	1003.4	1005.4	2.423
0.8020	42.172	1011.6	1012.2	2.200
	77.828*	916.7	916.7	2.695
	45.874	998.3	1000.0	2.200
	79.210*	911.0	913.7	2.695
0.5403	27.363	994.4	991.9	1.502
	52.766*	901.2	901.2	1.840
	26.430	999.0	996.2	1.502
	53.115*	899.7	900.2	1.840
0.4915	23.455	996.3	994.3	1.368
	47.458*	905.0	900.9	1.676
	26.153	985.3	981.3	1.368
	47.845*	901.8	899.7	1.676
0.3598	20.812	950.0	955.5	1.157
	36.349*	883.0	886.1	1.417
	20.958	952.3	954.7	1.157
	36.494*	882.4	885.5	1.417
0.2508	19.802	899.0	897.4	1.327
	19.634	904.0	898.4	1.327

Table 3. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
0.1682	11.499	875.0	876.0	2.582
	11.485	871.0	876.1	2.582
0.09920	6.5434	809.0	813.0	3.564
	6.4974	813.0	813.5	3.564
0.04989	3.8809	693.0	697.7	10.000
	3.1755	700.0	708.9	10.000
0.01578	1.2996	487.0	506.3	10.000
0.002875 $\square$	13.846	76.0	81.6	5.119
0.002583	13.293	72.0	72.2	4.220
0.002869	12.989	85.6	87.4	4.220
0.003307	17.331	76.4	76.8	4.562
0.003371	16.378	90.0	85.3	4.562
0.003350	16.851	81.9	81.5	3.956
0.003119	16.104	75.3	76.8	3.956
0.005749	28.441	103.8	99.1	5.879
0.005634	26.874	104.7	103.0	5.879
0.003959	19.856	87.6	86.5	3.487
0.003793	18.062	93.3	90.9	3.487
0.005072	24.621	100.7	97.6	3.916
0.004841	24.790	90.7	89.8	3.916
0.003665	19.378	79.4	78.5	2.673
0.003688	21.234	70.4	69.1	2.673

Table 3. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
0.003904	21.013	78.5	78.2	2.496
0.003944	50.581	192.2	196.3	3.111
0.005058	19.360	125.3	124.9	2.616
0.004973	72.403	191.4	189.1	3.702
0.007240	37.100	102.7	101.3	3.113
0.007451	36.204	111.5	109.4	3.490
0.006202	32.024	97.0	95.8	2.811
0.006189	31.159	101.1	99.1	2.811
0.006516	30.802	111.2	108.8	2.679
0.006202	31.562	101.1	97.7	2.679
0.007921	45.874	87.3	86.3	2.979
0.007783	42.172	94.9	95.4	2.979
0.005311	26.430	99.3	96.0	2.034
0.005277	27.363	93.2	90.7	2.034
0.004784	26.153	83.5	81.6	1.852
0.004746	23.455	91.3	93.5	1.852
0.003649	20.958	69.9	69.2	1.567
0.003635	20.812	67.0	69.4	1.567
Erbium Nitrate				
5.456	10.278	5005.4	5016.1	3.112
	20.867*	4935.0	4946.6	3.811

Table 3. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
5.179	11.499	4751.4	4742.0	3.317
	23.445*	4676.6	4669.2	4.063
	12.069	4753.9	4737.6	3.317
	23.610*	4677.8	4668.4	4.063
4.848	13.032	4412.7	4412.0	3.432
	26.348*	4332.5	4336.9	4.203
	13.148	4410.1	4411.2	3.432
	26.266*	4334.8	4337.2	4.203
4.452	14.869	4013.5	4013.5	3.518
	29.485*	3933.0	3937.3	4.309
	14.846	4010.3	4013.7	3.518
	30.030*	3928.2	3935.0	4.309
4.014	15.944	3573.9	3575.5	3.314
	31.483*	3492.3	3497.9	4.059
3.703	16.917	3264.5	3262.6	3.241
	33.733*	3181.1	3182.2	3.969
	16.753	3260.5	3263.6	3.241
	33.861*	3177.5	3181.7	3.969
3.288	35.450	2770.0	2770.7	3.434
	17.927	2849.5	2851.6	2.974
	35.402*	2769.8	2770.9	3.642
	17.842	2854.0	2852.1	2.974
	35.438*	2770.4	2770.8	3.642
2.949	37.970	2437.0	2439.5	3.496
	18.888	2524.0	2524.0	2.768
	37.442*	2440.0	2441.4	2.936
	18.602	2528.4	2525.6	3.114
	37.357*	2444.6	2441.7	3.814
2.570	20.052	2180.4	2174.6	2.538
	40.539*	2090.6	2087.6	2.692
	20.530	-	2171.9	-
	40.539*	2097.0	2087.6	2.855

Table 3. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
2.258	22.973	1897.8	1896.9	2.409
	43.639*	1811.8	1815.0	2.951
	23.078	1895.2	1896.4	2.409
	43.441*	1812.1	1815.6	2.951
1.969	24.800	1665.8	1666.7	2.471
	51.710*	1565.3	1569.1	3.026
	24.701	1668.3	1667.1	2.471
	51.725*	1568.2	1569.0	3.026
1.712	31.248	1462.4	1462.9	2.566
	61.434*	1364.2	1367.5	3.143
	31.674	1460.0	1461.2	2.566
	62.284*	1362.9	1365.3	3.143
1.422	32.376	1288.7	1288.6	2.423
	66.929*	1188.4	1184.3	2.967
	32.002	1291.7	1290.1	2.423
	66.635*	1190.1	1185.0	2.967
1.209	28.101	1202.5	1202.4	1.828
	52.882*	1114.7	1116.6	2.239
	28.037	1203.5	1202.7	1.828
	52.867*	1114.3	1116.6	2.239
1.005	42.602	1061.8	1064.7	2.264
	75.864*	973.7	977.0	2.773
	42.042	1066.6	1066.5	2.264
	76.073*	974.3	976.5	2.773
0.8138	29.976	1047.6	1046.3	1.682
	56.295*	957.4	959.1	2.060
0.6428	23.155	1026.8	1026.1	1.336
	44.636*	941.3	941.8	1.636
	23.165	1026.7	1026.0	1.336
	44.449*	943.0	942.4	1.636
0.4909	29.485	951.5	950.7	1.401
	50.737*	874.1	876.9	1.716
	28.079	957.1	956.8	1.401

Table 3. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
	50.325*	876.0	878.1	1.716
0.3516	14.907	972.7	973.1	1.859
	27.405*	903.5	906.1	2.277
	12.341	1000.9	991.0	1.859
	25.990*	917.1	912.5	2.277
0.2546	9.8032	957.9	956.3	2.410
	20.421*	888.0	885.2	2.951
0.1770	17.523	829.0	833.7	1.676
	17.198	833.0	835.6	1.676
0.1011	11.655	751.0	758.2	2.841
	11.635	758.0	758.4	2.841
0.03830	2.9584	635.0	642.9	10.000
	2.8291	637.0	645.2	10.000
0.002087□	10.278	70.4	69.4	4.213
0.002361	12.069	76.1	69.3	4.492
0.002344	11.499	74.8	72.8	4.492
0.002627	13.148	75.3	73.9	4.647
0.002635	13.032	80.2	75.1	4.647
0.003003	14.846	82.1	78.7	4.763
0.002948	14.869	80.5	76.2	4.763
0.003148	15.944	81.6	77.5	4.487
0.003386	16.753	83.0	81.9	4.388
0.003373	16.917	83.4	80.4	4.388
0.003544	17.842	83.6	81.3	4.026

Table 3. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
0.003540	17.927	79.7	80.7	4.026
0.003736	18.602	83.8	83.9	4.217
0.003744	18.888	84.0	82.6	3.343
0.004054	20.052	89.8	86.9	3.065
0.004344	23.078	83.1	80.8	3.262
0.004364	22.973	86.0	82.0	3.262
0.005172	24.701	100.1	98.1	3.345
0.005171	24.800	100.5	97.6	3.345
0.006228	31.674	97.1	95.8	3.475
0.006143	31.248	98.2	95.4	3.475
0.006663	32.002	101.6	105.1	3.281
0.006693	32.376	100.3	104.3	3.281
0.005287	28.037	89.2	86.1	2.476
0.005288	28.101	87.8	85.9	2.476
0.007607	42.042	92.3	90.0	3.066
0.007586	42.602	88.1	87.7	3.066
0.005630	29.976	90.2	87.3	2.277
0.004445	23.165	83.7	83.6	1.809
0.004464	23.155	85.5	84.3	1.809
0.005032	28.079	81.1	78.6	1.897
0.005074	29.485	77.4	73.8	1.897

Table 3. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
0.002599	12.341	83.8	78.5	2.517
0.002741	14.907	69.2	67.0	2.517
0.002042	9.803	69.9	71.1	3.263
Lutetium Nitrate				
6.792	5.7936	7150.0	7171.5	3.525
	5.3917	7190.6	7176.3	3.053
	15.508*	7090.2	7089.7	3.739
5.804	9.1264	6092.5	6095.2	2.986
	16.048*	6049.8	6043.9	3.657
	8.3752	6104.1	6102.1	2.986
	16.573*	6037.6	6040.7	3.657
5.482	7.4857	5744.0	5747.2	3.142
	7.3875	5751.2	5748.2	2.721
	16.048*	5683.8	5680.3	3.333
5.056	8.3694	5248.1	5235.3	2.658
	16.859*	5177.5	5172.0	3.256
4.872	17.148	4930.3	4945.5	5.082
	35.212*	4844.5	4861.6	6.224
4.553	13.293	4561.8	4571.7	3.803
	28.048*	4483.7	4491.4	4.657
	13.935	4556.3	4567.2	3.803
	28.505*	4475.6	4489.4	4.657
4.060	17.065	3912.6	3915.1	3.802
	34.152*	3833.2	3834.7	4.656
	18.139	3898.0	3908.8	3.802
	31.900*	3837.7	3843.4	4.656
3.644	32.707	3306.0	3304.3	3.378
	16.802	3383.2	3380.8	3.158
	31.438*	3312.2	3309.3	3.868

Table 3. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
2.928	14.228	2515.6	2514.8	2.231
	29.463*	2435.5	2435.0	2.732
	15.960	2517.3	2503.5	2.231
	30.151*	2441.3	2432.1	2.366
2.596	47.403	1997.0	2001.4	4.376
	25.110	2080.1	2083.8	3.790
	47.486*	1997.1	2001.1	4.642
2.260	19.678	1778.7	1775.9	1.899
	35.784*	1705.2	1704.4	2.326
	19.616	1774.7	1776.2	1.899
	36.228*	1700.0	1702.8	2.326
2.051	21.041	1585.3	1584.5	1.854
	39.363*	1506.4	1507.6	2.271
	20.539	1580.1	1587.1	1.854
	40.145*	1499.6	1505.0	2.271
1.709	34.059	1269.3	1272.9	2.419
	67.289*	1172.3	1175.8	2.963
	33.466	1273.3	1275.2	2.419
	68.013*	1170.8	1174.1	2.963
1.432	20.485	1176.0	1175.2	1.473
	42.628*	1085.4	1084.6	1.804
	20.304	1175.9	1176.2	1.473
	43.639*	1078.4	1081.3	1.804
1.181	25.735	1046.4	1043.2	1.503
	50.141*	958.9	955.6	1.841
	24.890	1049.4	1047.1	1.503
	49.393*	957.8	957.8	1.841
0.9917	33.051	955.6	954.3	1.751
	65.659*	856.4	857.1	2.145
	33.652	953.8	952.0	1.751
	65.659*	857.4	857.1	2.145

Table 3. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
0.8135	29.528	928.6	927.8	1.565
	59.521*	830.6	831.5	1.917
	31.136	919.2	921.2	1.565
	60.949*	825.2	827.9	1.917
0.6403	25.150	918.1	915.4	1.417
	54.258*	812.6	813.5	1.735
	27.794	905.2	903.5	1.417
	56.130*	808.6	808.5	1.735
0.4881	22.043	901.2	901.4	1.117
	41.719*	820.7	821.9	1.368
	23.785	891.9	892.8	1.117
	42.263*	819.1	820.1	1.368
0.3599	17.090	893.8	894.2	1.750
	32.013*	816.3	822.2	2.143
	13.271	917.0	919.0	2.021
0.2466	18.404	838.0	834.9	1.527
	17.231	842.0	841.7	1.527
	18.430	839.0	834.7	1.527
0.1604	8.5908	833.0	835.3	3.040
	8.8387	833.0	833.0	3.040
	11.022	810.0	814.4	3.040
0.1016	6.4212	760.0	773.6	3.603
	6.9485	764.0	767.9	3.603
0.04795	3.7210	657.0	659.9	10.000
	3.3856	656.0	665.1	10.000
0.008001	0.7894	366.0	387.8	10.000
	0.7742	330.0	388.3	10.000
0.001551□	5.392	100.4	86.7	4.134
0.001657	8.375	66.5	61.5	4.043
0.001605	9.126	42.7	51.3	4.043

Table 3. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
0.001605	7.388	67.4	67.9	3.684
0.001686	8.369	70.6	63.3	3.599
0.003521	17.148	85.8	83.9	6.881
0.002850	13.935	80.7	77.8	5.149
0.002805	13.293	78.1	80.3	5.149
0.003190	18.139	60.3	65.3	5.147
0.003415	17.065	79.4	80.4	5.147
0.003144	16.802	71.0	71.4	4.276
0.003015	15.960	76.0	71.4	2.694
0.002946	14.228	80.1	79.9	3.021
0.004749	25.110	83.0	82.7	5.132
0.003623	19.616	74.7	73.4	2.572
0.003578	19.678	73.5	71.5	2.572
0.004014	20.539	80.5	82.2	2.510
0.003936	21.041	78.9	76.8	2.510
0.006801	33.466	102.5	101.1	3.275
0.006729	34.059	97.0	97.1	3.275
0.004364	20.304	97.5	94.9	1.995
0.004263	20.485	90.6	90.7	1.995
0.004939	24.890	91.6	89.4	2.035
0.005014	25.735	87.5	87.6	2.035

Table 3. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
0.006566	33.652	96.4	94.9	2.371
0.006566	33.051	99.2	97.2	2.371
0.006095	31.136	94.0	93.3	2.120
0.005952	29.528	98.0	96.3	2.120
0.005613	27.794	96.6	95.0	1.918
0.005426	25.150	105.5	101.8	1.918
0.004226	23.785	72.8	72.7	1.513
0.004172	22.043	80.5	79.6	1.513
0.003201	17.090	77.5	72.0	2.369

Lanthanum Perchlorate

4.791	8.9700	7089.5	7100.9	3.800
	18.020*	7036.2	7041.5	4.654
	8.9401	7093.3	7101.1	3.800
	17.944*	7037.8	7041.9	4.654
4.465	7.2469	6347.7	6338.5	2.768
	14.592*	6294.4	6283.1	3.389
	7.4093	6350.9	6336.9	2.768
	14.334*	6301.1	6284.7	3.389
4.093	10.074	5449.5	5465.3	3.987
	23.377*	5368.1	5389.2	4.883
	14.311	5407.4	5436.1	3.987
	26.245*	5353.2	5377.1	4.883
3.581	24.423	4260.7	4275.3	6.031
	47.169*	4186.9	4200.7	7.386
	27.458	4243.8	4262.9	6.031
	50.112*	4179.1	4193.2	7.386

Table 3. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
3.255	12.117	3676.4	3672.6	2.670
	24.000*	3616.5	3608.7	3.270
	11.343	3678.9	3678.1	2.670
	24.572*	3610.2	3606.3	3.270
2.902	17.783	2959.6	2956.4	2.890
	33.432*	2893.2	2890.8	3.540
	15.817	2972.5	2967.2	2.890
	32.376*	2903.1	2894.4	3.540
2.565	18.481	2356.9	2353.1	2.596
	37.970*	2279.0	2276.5	3.179
	18.602	2356.3	2352.4	2.596
	36.784*	2286.2	2280.2	3.179
2.238	38.341	1747.0	1755.3	2.793
	18.680	1826.1	1832.0	3.161
	30.085	1779.1	1782.8	2.738
	58.921*	1700.7	1702.6	3.353
	29.398	1782.3	1785.4	2.738
	60.746*	1696.8	1698.7	3.353
1.982	27.092	1432.3	1438.7	2.281
	53.597*	1355.3	1359.1	2.793
	27.217	1438.0	1438.2	2.281
1.733	31.697	1123.5	1126.7	2.012
	64.096*	1041.2	1041.4	2.134
	31.517	-	1127.3	-
	63.952*	1040.0	1041.7	2.614
1.465	43.705	837.3	834.7	2.101
	90.611*	744.3	740.4	2.574
	39.854	847.0	845.7	2.101
	93.954*	738.9	735.4	2.574
1.176	34.281	670.0	667.5	1.673
	34.258	667.0	667.5	1.673
1.005	41.165	571.0	569.8	1.699
	40.322	573.0	572.3	1.699

Table 3. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
0.8167	33.143	545.0	543.2	1.343
	32.994	544.0	543.7	1.343
0.6448	33.212	521.0	521.6	1.281
	32.160	524.0	525.3	1.281
0.4939	29.441	529.0	530.9	1.592
	26.173	538.0	543.6	1.592
0.3504	26.235	546.0	543.3	1.821
	23.571	556.0	554.5	1.821
0.2500	16.346	588.0	583.6	2.680
	16.233	586.0	584.2	2.680
0.1611	11.635	594.0	590.4	3.216
	11.263	599.0	593.1	3.216
	12.348	585.0	585.5	3.216
0.08912	7.9919	562.0	566.8	3.730
	7.9750	560.0	566.9	3.730
0.03991	3.3636	522.0	521.3	10.000
	3.1684	526.0	524.4	10.000
0.01027	0.8214	378.0	383.7	10.000
0.001794 $\square$	8.940	55.5	59.2	5.145
0.001802	8.970	53.3	59.3	5.145
0.001433	7.409	49.8	52.3	3.747
0.001459	7.247	53.3	55.4	3.747
0.002625	14.311	54.2	59.0	5.398
0.002338	10.074	81.4	76.2	5.398
0.005011	27.458	64.7	69.7	8.165

Table 3. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
0.004717	24.423	73.8	74.7	8.165
0.002457	11.343	68.7	71.8	3.615
0.002400	12.117	59.9	63.9	3.615
0.003238	15.817	69.4	72.9	3.913
0.003343	17.783	66.4	65.6	3.913
0.003678	18.602	70.1	72.2	3.515
0.003797	18.481	77.9	76.6	3.515
0.006075	29.398	85.5	86.7	3.707
0.005892	30.085	78.4	80.2	3.707
0.005360	27.092	77.0	79.6	3.088
0.006410	31.697	82.3	85.3	2.430
0.009395	39.854	108.1	110.3	2.845
0.009061	43.705	93.0	94.4	2.845

Neodymium Perchlorate

4.685	8.6025	6383.0	6381.5	3.643
	18.182*	6320.7	6324.5	4.462
	11.785	6343.7	6359.3	3.643
	20.232*	6300.2	6315.1	4.462
4.509	8.7261	5937.4	5925.4	3.112
	17.523*	5884.4	5872.5	3.812
	8.9760	5932.4	5923.5	3.112
	17.464*	5883.6	5872.7	3.812

Table 3. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
4.075	14.969	4869.2	4878.4	4.232
	29.823*	4803.4	4815.7	5.183
	14.977	4864.9	4878.3	4.232
	29.052*	4809.5	4818.3	5.183
3.625	17.073	3926.5	3933.7	3.965
	34.492*	3859.0	3866.9	4.856
	17.548	3921.5	3931.4	3.965
	34.094*	3858.6	3868.2	4.856
3.223	15.896	3174.3	3168.0	2.823
	30.437*	3110.9	3108.2	3.458
	14.062	3193.0	3177.9	3.260
2.879	14.130	2563.9	2561.5	2.171
	28.580*	2499.6	2498.5	2.659
	13.242	2573.3	2566.6	2.171
	27.889*	2503.9	2500.9	2.659
2.603	18.992	2074.4	2078.6	2.487
	41.204*	1996.6	2001.8	3.046
	19.705	2072.9	2075.4	2.487
	40.437*	1998.7	2003.9	3.046
2.254	20.784	1550.5	1551.2	1.837
	40.183*	1480.0	1485.2	2.250
	20.268	1556.0	1553.5	1.837
	39.640*	1485.8	1486.7	2.250
1.964	27.626	1154.1	1156.7	1.953
	58.706*	1069.2	1073.8	2.392
	29.452	1147.2	1150.3	1.953
	59.737*	1066.2	1071.6	2.392
1.670	33.339	841.8	836.5	1.689
	71.978*	750.3	747.3	2.069
	35.117	834.8	831.0	1.689
	72.642*	748.4	746.2	2.069

Table 3. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
1.444	52.722	609.9	608.7	1.708
	102.941*	524.3	523.6	2.092
	52.722	607.5	608.7	1.708
	107.952*	517.3	517.1	2.092
1.227	49.323	490.0	494.2	1.745
	47.748	499.0	498.0	1.745
1.005	38.963	445.0	443.9	1.321
	41.216	437.0	437.7	1.321
0.7945	46.717	392.0	393.3	1.401
	50.937	382.0	383.3	1.401
0.6390	32.856	431.0	432.8	1.647
	34.928	428.0	426.4	1.647
0.4763	27.731	473.0	467.2	2.002
	26.564	474.0	471.4	2.002
0.3606	23.387	501.0	500.6	2.215
	24.030	495.0	498.1	2.215
0.2496	15.117	549.0	550.7	2.890
	16.185	542.0	545.1	2.890
0.1599	11.149	569.0	566.9	3.360
	10.890	568.0	568.7	3.360
0.1004	6.4161	563.0	572.3	3.889
	6.7808	562.0	569.0	3.889
0.04221	3.6328	517.0	501.0	10.000
	3.1082	497.0	508.2	10.000
0.01050	0.6947	416.0	359.4	10.000
	0.7110	406.0	358.9	10.000
0.002023□	11.785	43.5	44.3	4.932
0.001818	8.602	62.3	57.0	4.932

Table 3. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
0.001746	8.976	48.8	50.7	4.214
0.001752	8.726	53.0	52.9	4.214
0.002905	14.977	55.4	60.0	5.730
0.002982	14.969	65.8	62.7	5.730
0.003409	17.548	62.9	63.2	5.369
0.003449	17.073	67.5	66.8	5.369
0.003044	15.896	63.4	59.8	3.823
0.002789	13.242	69.4	65.7	2.940
0.002858	14.130	64.3	63.0	2.940
0.004044	19.705	74.2	71.5	3.368
0.004120	18.992	77.8	76.8	3.368
0.003964	20.268	70.2	66.8	2.487
0.004018	20.784	70.5	66.0	2.487
0.005974	29.452	81.0	78.7	2.644
0.005871	27.626	84.9	83.0	2.644
0.007264	35.117	86.4	84.9	2.288
0.007198	33.339	91.5	89.2	2.288
0.01080	52.722	90.2	91.6	2.313
0.01029	52.722	85.6	85.1	2.313

Table 3. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
Gadolinium Perchlorate				
4.611	8.4681	6799.0	6801.1	3.973
	8.3175	6807.0	6802.3	3.973
4.205	6.9064	5852.2	5856.2	2.426
	13.631*	5802.1	5807.8	2.971
	6.8225	5862.0	5856.9	2.801
3.827	7.9580	5035.6	5036.6	2.467
	16.176*	4980.8	4983.2	3.021
	8.0826	5040.6	5035.6	2.467
	16.257*	4982.9	4982.8	3.021
3.499	12.180	4352.0	4345.9	3.592
	12.180	4351.9	4345.9	3.111
	23.668*	4289.1	4288.2	3.810
2.891	14.723	3200.0	3194.3	4.063
	14.608	3197.2	3195.0	3.519
	27.720*	3139.7	3136.0	4.309
3.104	17.682	3559.6	3563.4	3.519
	33.513*	3496.6	3500.8	4.309
	17.497	3557.7	3564.4	3.519
	33.443*	3495.4	3501.0	4.309
2.389	21.013	2324.1	2328.1	2.788
	41.409*	2249.4	2257.4	3.415
2.074	24.621	1849.3	1855.0	2.660
	49.365*	1775.1	1778.8	3.258
	24.552	1853.2	1855.3	2.660
	49.351*	1774.2	1778.8	3.258
1.823	29.724	1523.4	1516.7	2.548
	58.049*	1445.6	1439.5	3.121
	29.692	1522.4	1516.8	2.548
	57.866*	1444.1	1439.9	3.121

Table 3. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
1.556	14.846	1299.5	1293.0	1.683
	24.275*	1258.1	1248.7	2.061
	14.907	1293.4	1292.7	1.683
	24.433*	1251.9	1248.0	2.061
	38.900	1198.1	1199.0	1.683
	74.667*	1115.2	1118.2	2.061
	39.075	1194.7	1198.5	1.683
	74.822*	1113.9	1118.0	2.061
1.320	42.107	981.9	982.5	1.961
	89.302*	884.2	886.3	2.402
	41.977	-	982.9	-
	89.246*	884.5	886.4	2.149
	21.884	1052.3	1051.3	1.961
	32.422*	1015.4	1011.6	2.402
1.081	20.702	894.8	893.8	1.332
	32.138*	850.6	849.9	1.632
	20.967	892.8	892.6	1.332
	31.956*	852.9	850.5	1.632
	43.957	809.0	814.8	1.539
	43.957	812.0	814.8	1.539
0.9182	56.010	694.0	701.7	2.238
	56.355	696.0	701.0	2.238
	30.669	767.0	771.1	2.238
	30.980	768.0	770.1	2.238
0.7330	30.492	696.0	701.4	1.459
	30.437	703.0	701.6	1.459
	25.261	717.0	720.7	1.459
	24.800	732.0	722.5	1.459
0.5525	38.465	629.0	629.5	1.503
	38.490	632.0	629.4	1.503
	24.315	680.0	677.8	1.503
	24.384	677.0	677.5	1.503
0.4256	47.665	580.0	580.4	1.748
	47.790	582.0	580.1	1.748
	32.558	625.0	623.7	1.748

Table 3. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
	32.627	625.0	623.4	1.748
0.3275	38.143	589.0	588.1	1.463
	38.155	589.0	588.1	1.463
	27.552	621.0	622.9	1.463
	27.426	625.0	623.4	1.463
0.1982	28.228	578.0	582.9	1.265
	30.305	580.0	575.6	1.265
	28.633	582.0	581.5	1.265
0.1132	14.784	582.0	583.7	2.847
	15.265	570.0	581.0	2.847
	15.571	575.0	579.4	2.847
0.05915	8.3290	526.0	536.1	3.732
	8.3810	535.0	535.7	3.732
	8.6671	525.0	533.4	3.732
0.001363□	6.906	50.1	48.3	3.285
0.001626	8.083	57.7	52.8	3.340
0.001618	7.958	54.8	53.4	3.340
0.002367	12.180	62.8	57.7	4.212
0.002772	14.608	57.5	59.0	4.764
0.003344	17.497	62.3	63.3	4.764
0.003351	17.682	63.0	62.6	4.764
0.004141	21.013	74.7	70.6	3.776
0.004935	24.552	79.0	76.5	3.602
0.004936	24.621	74.2	76.2	3.602
0.005787	29.692	78.3	76.9	3.450

Table 3. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
0.005805	29.724	77.8	77.2	3.450
0.007482	39.075	80.8	80.5	2.278
0.007467	38.900	82.9	80.7	2.278
0.002443	14.907	41.5	44.6	2.278
0.002428	14.846	41.4	44.4	2.278
0.003242	21.884	36.9	39.6	2.656
0.008930	42.107	97.7	96.2	2.656
0.003196	20.967	39.9	42.1	1.804
0.003214	20.702	44.2	43.9	1.804

Erbium Perchlorate

4.627	8.8685	7399.3	7399.4	2.962
	17.514*	7338.0	7348.2	3.628
	8.3348	7400.0	7403.5	2.962
	17.156*	7350.0	7349.9	3.628
4.215	15.817	6396.4	6391.7	4.835
	32.274*	6323.8	6326.1	5.922
	10.824	6431.7	6420.7	4.835
	21.716*	6372.1	6364.4	5.922
	10.883	6435.2	6420.3	4.835
	23.098*	6367.8	6358.7	5.922
	10.272	6446.0	6424.4	5.583
3.413	8.6966	4648.9	4645.9	2.551
	18.207*	4579.9	4590.1	3.125
	8.6554	4651.2	4646.2	2.551
	18.284*	4575.6	4589.7	3.125

Table 3. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
3.086	9.3086	3963.2	3958.7	2.880
	20.458*	3880.7	3897.3	3.527
	9.1930	3956.2	3959.6	2.880
	19.272*	3890.6	3902.5	3.527
	9.2294	3965.0	3959.3	3.325
	14.493	3929.4	3926.2	2.880
	28.794*	3865.8	3865.1	3.527
	14.432	3925.3	3926.6	2.880
	29.074*	3867.6	3864.1	3.527
2.676	16.540	3113.7	3114.6	3.073
	33.397*	3043.8	3049.2	3.763
	16.557	3117.7	3114.6	3.073
	33.281*	3052.0	3049.5	3.763
2.358	36.518	2468.5	2472.3	4.850
	68.145*	2392.9	2399.8	5.940
	36.724	2469.6	2471.7	4.850
	68.096*	2391.8	2399.9	5.940
2.033	39.930	1957.2	1942.8	4.415
	78.925*	1874.7	1861.2	5.407
	40.196	1959.4	1942.1	4.415
	78.997*	1875.2	1861.1	5.407
1.700	32.501	1508.3	1507.6	2.894
	67.191*	1425.9	1424.7	3.545
	32.753	1508.3	1506.8	2.894
	67.273*	1418.7	1424.6	3.545
1.498	44.409	1243.5	1239.5	3.193
	92.641*	1149.5	1148.5	3.910
	44.316	1244.3	1239.8	3.193
	91.968*	1149.0	1149.5	3.910
1.227	53.978	-	958.7	-
	114.426*	867.7	861.1	3.269
	53.802	956.7	959.0	2.985
	115.434*	854.4	859.9	3.655
	53.978	961.6	958.7	2.985
	114.105*	860.6	861.5	3.655

Table 3. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
	53.451	960.0	959.8	3.446
1.055	59.013	815.0	819.3	3.590
	56.912	820.0	823.7	3.590
	57.093	825.0	823.3	3.590
	57.851	819.0	821.7	3.590
	76.668	781.0	786.5	3.590
	76.825	782.0	786.3	3.590
0.8408	80.407	653.0	659.1	3.206
	79.959	656.0	659.8	3.206
	59.413	697.0	697.2	3.206
	59.614	692.0	696.8	3.206
	59.506	696.0	697.1	3.206
0.6626	35.402	681.0	686.3	2.132
	35.426	687.0	686.2	2.132
	35.402	689.0	686.3	2.132
	61.450	618.0	623.3	2.132
	61.450	620.0	623.3	2.132
0.5129	32.879	651.0	653.2	1.566
	32.696	656.0	653.8	1.566
	32.684	655.0	653.8	1.566
	32.971	656.0	652.9	1.566
0.3603	40.145	603.0	598.4	1.669
	40.094	599.0	598.6	1.669
	39.980	599.0	598.9	1.669
	39.930	600.0	599.0	1.669
	33.143	622.0	618.9	1.669
	33.109	620.0	619.0	1.669
0.2307	6.4567	712.7	711.8	2.664
	12.496*	666.9	667.6	3.262
	6.2500	717.1	713.7	2.664
	12.510*	665.4	667.5	3.262
	22.753	615.0	617.5	3.076
	25.020	609.0	608.6	3.076

Table 3. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
0.2029	27.019	588.0	588.7	1.564
	19.598	621.0	618.4	1.564
	28.966	581.0	581.8	1.564
0.1154	14.646	560.0	576.0	2.906
	15.801	552.0	569.9	2.906
0.001716□	8.335	50.0	53.6	4.011
0.001751	8.868	61.3	51.2	4.011
0.002310	10.883	67.4	61.6	6.547
0.002172	10.824	59.6	56.3	6.547
0.003227	15.817	72.6	65.6	6.547
0.001828	8.655	75.6	56.5	3.455
0.001821	8.697	69.0	55.8	3.455
0.002907	14.432	57.7	62.4	3.899
0.002879	14.493	63.6	61.1	3.899
0.001927	9.193	65.6	57.0	3.899
0.002046	9.309	82.5	61.5	3.899
0.003328	16.557	65.7	65.0	4.160
0.003340	16.540	69.9	65.5	4.160
0.006810	36.724	77.8	71.8	6.567
0.006815	36.518	75.6	72.5	6.567
0.007900	40.196	84.2	81.0	5.978
0.007893	39.930	82.5	81.6	5.978

Table 3. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
0.006727	32.753	89.6	82.3	3.919
0.006719	32.501	82.4	82.9	3.919
0.009197	44.316	95.3	90.3	4.323
0.009264	44.409	94.0	91.0	4.323
0.01141	53.978	101.0	97.1	4.041
0.01154	53.802	102.3	99.2	4.041
0.001251	6.250	51.7	46.2	3.606
0.001250	6.457	45.8	44.2	3.606

Lutetium Perchlorate

4.634	11.096	7233.1	7228.7	4.716
	21.874*	7175.9	7173.3	5.776
	11.062	7229.0	7228.9	4.716
	22.212*	7166.4	7171.9	5.776
4.039	14.319	5851.2	5844.5	5.134
	29.225*	5772.3	5780.8	6.288
	14.992	5828.6	5840.9	5.134
	30.714*	5759.0	5775.8	6.288
3.567	12.076	4829.5	4817.2	3.664
	26.657*	4753.1	4749.4	4.487
	12.795	4815.9	4812.8	3.664
	24.621*	4760.6	4757.1	4.487
3.196	12.681	4045.3	4034.3	3.120
	24.493*	3985.1	3978.4	3.822
	14.799	4013.5	4022.3	3.120
	27.479*	3963.4	3967.3	3.822

Table 3. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
2.870	11.202	3392.0	3396.7	2.824
	12.027	3386.9	3391.4	2.445
	24.671*	3327.3	3330.8	2.995
2.529	20.867	2713.7	2718.0	2.991
	38.390*	2653.9	2657.7	3.172
	18.250	-	2729.8	-
	36.132*	2663.0	2664.2	3.885
2.232	16.941	2236.3	2238.3	2.453
	31.764*	2178.9	2179.9	3.005
1.980	17.181	1863.7	1857.6	1.555
	35.713*	1791.3	1788.2	1.905
	17.741	-	1854.9	-
	35.617*	1790.7	1788.4	1.704
1.676	23.561	1431.6	1432.3	1.975
	47.458*	1358.3	1359.5	2.419
	22.307	1436.3	1437.4	1.975
	46.690*	1359.0	1361.4	2.419
1.432	27.741	1152.8	1151.8	1.854
	55.249*	1074.4	1076.8	2.271
	26.988	1153.7	1154.5	1.854
	56.355*	1069.9	1074.5	2.271
1.174	35.653	902.6	903.6	1.721
	64.609*	831.6	835.1	2.108
	32.024	914.3	914.8	1.988
1.006	36.216	792.5	790.4	1.579
	69.789*	713.1	713.9	1.934
	36.192	792.4	790.4	1.579
	71.944*	709.1	710.1	1.934
0.8068	54.716	645.0	645.9	2.487
	53.832	648.0	647.8	2.487
0.6409	51.251	595.0	598.9	2.175
	50.623	599.0	600.3	2.175

Table 3. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
0.4944	36.084	609.0	606.2	1.631
	37.259	607.0	602.8	1.631
0.3586	26.615	614.0	614.5	1.252
	27.783	610.0	610.3	1.252
0.2496	11.683	656.0	660.9	2.944
	13.690	650.0	648.9	2.944
0.1546	9.3269	635.0	634.4	3.466
	8.8209	633.0	638.1	3.466
0.09880	5.7696	603.0	611.0	3.900
	6.3706	601.0	605.2	3.900
0.06717	5.7360	560.0	557.5	10.000
	4.9640	570.0	565.4	10.000
0.009869□	0.9187	363.0	342.6	10.000
0.002221	11.062	62.6	57.0	6.386
0.002187	11.096	57.2	55.3	6.386
0.003071	14.992	69.6	65.0	6.952
0.002922	14.319	78.9	63.7	6.952
0.002462	12.795	55.3	55.8	4.961
0.002666	12.076	76.4	67.7	4.961
0.002748	14.799	50.1	55.0	4.225
0.002449	12.681	60.2	56.0	4.225
0.002467	12.027	59.6	60.6	3.311
0.003839	20.867	59.8	60.3	3.612
0.003176	16.941	57.4	58.4	3.322

Table 3. Continued.

m_i	$m_f \times 10^4$	$\Delta H(\text{exp.})$ Cal/mole	$\Delta H(\text{calc.})$ Cal/mole	σ_i Cal/mole
0.003571	17.181	72.4	69.5	2.106
0.004669	22.307	77.3	76.0	2.674
0.004746	23.561	73.3	72.8	2.674
0.005636	26.988	83.8	80.1	2.510
0.005525	27.741	78.4	75.0	2.510
0.006461	35.653	71.0	68.4	2.331
0.007194	36.192	83.3	80.4	2.138
0.006979	36.216	79.4	76.4	2.138

Table 4. Powers and coefficients for Equations 4.10 and 4.13 -- nitrates.

Salt	j= 2	Upper number: P_j 3	4	Lower number: A_j 5	6	7
$P_1 = 0.50$ and $A_1 = 6990.00$ for all salts.						
La(NO ₃) ₃	1.00 -32256.750	1.25 41877.6139	1.75 -34910.5211	2.00 20602.5901	2.75 -1694.94423	3.25 240.06052
Pr(NO ₃) ₃	1.00 -38190.618	1.25 64583.4396	1.50 -38613.3646	2.00 6386.5588	3.00 -381.46265	3.75 34.517854
Nd(NO ₃) ₃	1.00 -42867.795	1.25 77861.7362	1.50 -50553.4184	2.00 10677.8261	2.75 -2131.75308	3.00 762.84252
Sm(NO ₃) ₃	1.00 -56611.355	1.25 122852.7997	1.50 -99352.3369	2.00 51998.8964	2.25 -31194.7115	2.50 5875.23604
Gd(NO ₃) ₃	1.00 -40307.236	1.25 69831.3558	1.50 -42102.4691	2.00 6742.7600	3.25 -484.16203	3.50 213.06066
Tb(NO ₃) ₃	1.00 -34591.560	1.25 56270.9110	1.50 -31747.6025	2.00 4376.9553	3.75 -136.033881	4.00 68.458381
Dy(NO ₃) ₃	1.00 -37311.223	1.25 67721.7929	1.50 -44607.9683	2.00 10262.1880	2.50 -1695.74648	4.00 9.212981
Ho(NO ₃) ₃	1.00 -37331.209	1.25 67668.4967	1.50 -44314.5013	2.00 9700.1017	2.75 -1998.28716	3.00 716.49916
Er(NO ₃) ₃	1.00 -41318.993	1.25 83725.1907	1.50 -64686.3315	2.00 29628.2407	2.25 -13685.5629	2.75 764.11612

Table 4. Continued.

Salt	Upper number: P_j / Lower number: A_j					
	$j=2$	3	4	5	6	7
$Tm(NO_3)_3$	1.00 -40532.695	1.25 77329.4719	1.50 -53296.0584	2.00 12639.2692	2.75 -2763.43574	3.00 998.78016
$Yb(NO_3)_3$	1.00 -46803.234	1.25 102854.4338	1.50 -86229.2843	2.00 48349.3896	2.25 -29349.2141	2.50 5494.64542
$Lu(NO_3)_3$	1.00 -40512.376	1.25 76029.7792	1.50 -51028.6371	2.00 10994.4242	2.75 -1388.03073	3.25 189.96374

Table 5. Powers and coefficients for Equations 4.10 and 4.13 -- perchlorates.

Salt	j= 2	Upper number: 3	P _j / Lower number: 4	5	A _j 6	7
$P_1 = 0.50$ and $A_1 = 6990.00$ for all salts.						
La(ClO ₄) ₃	1.00 -53930.420	1.25 119602.8009	1.50 -110785.3187	1.75 39847.2599	2.75 -849.29991	4.00 17.608558
Pr(ClO ₄) ₃	0.75 -9866.816	1.25 4762.0196	2.00 -1736.5413	3.25 1487.96831	3.75 -1465.468192	4.00 587.561198
Nd(ClO ₄) ₃	0.75 -9789.311	1.25 4543.8264	2.00 -1569.9242	3.25 1354.35259	3.75 -1330.857723	4.00 532.680189
Sm(ClO ₄) ₃	0.75 -9804.321	1.25 4781.3713	2.00 -1733.9837	3.25 1417.62261	3.75 -1387.953071	4.00 555.814673
Gd(ClO ₄) ₃	0.75 -9422.495	1.25 4341.3987	2.00 -1245.6835	3.25 1005.99537	3.75 -985.614470	4.00 394.371910
Dy(ClO ₄) ₃	0.75 -9989.583	1.25 7097.0994	2.00 -20609.1495	2.25 32196.8356	2.50 -18034.13858	2.75 3504.30275
Er(ClO ₄) ₃	0.75 -10126.464	1.25 7609.3830	2.00 -23931.1872	2.25 37654.2482	2.50 -21236.44333	2.75 4157.84404
Lu(ClO ₄) ₃	0.75 -10064.327	1.25 7102.3011	2.00 -20755.8581	2.25 32350.5938	2.50 -18042.10201	2.75 3484.47710

Table 6. Calculated thermodynamic properties for rare earth nitrates and perchlorates.

molality	ϕ_L (cal/mole)	$d\phi_L/dm^{1/2}$	$-L_1$ (cal/mole)	L_2 (cal/mole)
Lanthanum Nitrate				
0.002870	315.6± 2.3	4836.6±22.4	0.00670±0.00003	445.1± 2.4
0.003904	357.4± 2.0	4555.0±18.7	0.01001±0.00004	499.7± 2.1
0.004736	385.7± 2.1	4366.9±16.4	0.01282±0.00005	535.9± 2.1
0.006618	438.2± 3.8	4021.9±12.4	0.01950±0.00006	601.8± 3.9
0.009027	490.8±10.0	3681.4± 9.0	0.02844±0.00007	665.6±10.0
0.01702	607.6±10.0	2938.8± 4.1	0.05878±0.00008	799.3±10.0
0.09897	927.2± 2.9	889.9± 4.4	0.2496 ±0.0012	1067.2± 3.0
0.1599	982.5± 1.3	437.3± 3.2	0.2518 ±0.0018	1070.0± 1.5
0.2498	1007.2± 1.4	79.0± 3.3	0.0888 ±0.0038	1026.9± 1.6
0.3598	1002.1± 1.6	-164.6± 3.4	-0.3201 ±0.0066	952.7± 1.9
0.4891	977.1± 1.8	-324.4± 2.7	-0.9995 ±0.0084	863.7± 2.1
0.6397	939.5± 2.1	-412.3± 2.2	-1.9003 ±0.0100	774.6± 2.3
0.8101	896.8± 2.0	-428.2± 2.3	-2.813 ±0.015	704.1± 2.3
1.000	856.2± 1.7	-373.0± 2.6	-3.360 ±0.023	669.7± 2.1
1.208	824.7± 1.5	-251.4± 2.5	-3.007 ±0.030	686.6± 2.0
1.341	812.8± 2.2	-150.4± 2.3	-2.104 ±0.032	725.7± 2.6
1.694	812.9± 1.9	167.2± 2.1	3.320 ±0.041	921.7± 2.4
1.960	841.9± 1.4	424.5± 2.3	10.493 ±0.058	1139.1± 2.1
2.092	864.5± 1.3	551.0± 2.4	15.018 ±0.066	1263.0± 2.2
2.557	980.4± 1.7	963.9± 2.2	35.503 ±0.081	1751.1± 2.4
2.893	1091.7± 1.6	1217.4± 2.5	53.96 ±0.11	2127.0± 2.7
3.239	1223.1± 1.9	1438.3± 3.8	75.52 ±0.20	2517.4± 3.9
3.606	1376.0± 1.8	1640.7± 4.4	101.20 ±0.27	2933.8± 4.5
4.000	1552.2± 3.4	1849.5± 4.1	133.28 ±0.30	3401.7± 5.4
4.456	1772.3± 2.6	2136.8±15.6	181.0 ±1.3	4027.6±16.7
4.608	1850.7± 3.1	2256.9±23.2	201.1 ±2.1	4273.0±25.1

Table 6. Continued.

molality	ϕ_L (cal/mole)	$d\phi_L/dm^{1/2}$	$-L_1$ (cal/mole)	L_2 (cal/mole)
Praseodymium Nitrate				
0.002552	286.7 $\pm$ 2.5	4659.9 $\pm$ 23.0	0.00541 $\pm$ 0.00003	404.4 $\pm$ 2.6
0.003810	336.9 $\pm$ 3.4	4306.4 $\pm$ 18.7	0.00912 $\pm$ 0.00004	469.8 $\pm$ 3.4
0.006468	412.4 $\pm$ 2.9	3787.7 $\pm$ 13.0	0.01775 $\pm$ 0.00006	564.8 $\pm$ 3.0
0.008527	455.8 $\pm$ 1.9	3495.9 $\pm$ 10.2	0.02479 $\pm$ 0.00007	617.2 $\pm$ 1.9
0.01927	595.7 $\pm$ 4.3	2574.6 $\pm$ 4.8	0.06206 $\pm$ 0.00012	774.4 $\pm$ 4.3
0.05127	767.6 $\pm$ 3.6	1452.2 $\pm$ 6.0	0.15188 $\pm$ 0.00062	932.1 $\pm$ 3.7
0.09997	864.8 $\pm$ 2.7	770.0 $\pm$ 5.3	0.2192 $\pm$ 0.0015	986.6 $\pm$ 2.8
0.1693	915.2 $\pm$ 1.8	322.2 $\pm$ 3.7	0.2022 $\pm$ 0.0023	981.5 $\pm$ 2.0
0.2534	931.2 $\pm$ 2.8	43.8 $\pm$ 3.2	0.0503 $\pm$ 0.0037	942.2 $\pm$ 2.9
0.3582	925.6 $\pm$ 2.6	-145.9 $\pm$ 3.3	-0.2819 $\pm$ 0.0065	882.0 $\pm$ 2.8
0.5006	901.9 $\pm$ 1.3	-275.9 $\pm$ 3.2	-0.880 $\pm$ 0.010	804.3 $\pm$ 1.7
0.6430	873.1 $\pm$ 1.4	-324.7 $\pm$ 2.8	-1.508 $\pm$ 0.013	743.0 $\pm$ 1.8
0.9174	823.8 $\pm$ 1.4	-281.8 $\pm$ 2.4	-2.231 $\pm$ 0.019	688.9 $\pm$ 1.8
1.106	801.6 $\pm$ 1.5	-182.7 $\pm$ 2.2	-1.914 $\pm$ 0.023	705.6 $\pm$ 1.9
1.226	793.7 $\pm$ 1.6	-99.0 $\pm$ 2.1	-1.210 $\pm$ 0.026	738.9 $\pm$ 1.9
1.448	792.7 $\pm$ 1.6	85.2 $\pm$ 1.8	1.337 $\pm$ 0.029	843.9 $\pm$ 1.9
1.684	810.9 $\pm$ 1.8	307.6 $\pm$ 1.8	6.055 $\pm$ 0.035	1010.5 $\pm$ 2.1
1.922	848.6 $\pm$ 1.9	544.8 $\pm$ 2.0	13.078 $\pm$ 0.047	1226.3 $\pm$ 2.3
2.200	914.7 $\pm$ 1.5	820.8 $\pm$ 2.2	24.134 $\pm$ 0.066	1523.5 $\pm$ 2.2
2.564	1031.5 $\pm$ 1.6	1158.9 $\pm$ 2.3	42.864 $\pm$ 0.084	1959.4 $\pm$ 2.4
2.978	1196.7 $\pm$ 1.6	1494.2 $\pm$ 2.4	69.15 $\pm$ 0.11	2485.8 $\pm$ 2.6
3.444	1412.0 $\pm$ 2.3	1808.8 $\pm$ 3.8	104.12 $\pm$ 0.22	3090.3 $\pm$ 4.2
3.618	1498.3 $\pm$ 2.3	1913.9 $\pm$ 4.4	118.64 $\pm$ 0.27	3318.5 $\pm$ 4.8
4.002	1697.9 $\pm$ 2.9	2140.1 $\pm$ 4.7	154.36 $\pm$ 0.34	3838.7 $\pm$ 5.5
4.465	1955.3 $\pm$ 3.2	2448.0 $\pm$ 5.0	208.08 $\pm$ 0.42	4541.8 $\pm$ 6.2
4.833	2177.0 $\pm$ 2.3	2774.7 $\pm$ 14.1	265.6 $\pm$ 1.4	5227.0 $\pm$ 15.7

Table 6. Continued.

molality	ϕ_L (cal/mole)	$d\phi_L/dm^{1/2}$	$-L_1$ (cal/mole)	L_2 (cal/mole)
4.990	2278.1 $\pm$ 1.9	2950.2 $\pm$ 20.9	296.2 $\pm$ 2.1	5573.1 $\pm$ 23.4
Neodymium Nitrate				
0.003643	336.4 $\pm$ 2.8	4246.9 $\pm$ 26.6	0.00841 $\pm$ 0.00005	464.6 $\pm$ 2.9
0.004529	365.1 $\pm$ 2.7	4017.0 $\pm$ 22.8	0.01103 $\pm$ 0.00006	500.3 $\pm$ 2.8
0.006376	413.1 $\pm$ 2.2	3638.7 $\pm$ 16.9	0.01669 $\pm$ 0.00008	558.3 $\pm$ 2.3
0.01022	484.4 $\pm$ 10.0	3089.7 $\pm$ 10.3	0.02875 $\pm$ 0.00010	640.5 $\pm$ 10.0
0.04035	702.0 $\pm$ 10.0	1478.3 $\pm$ 8.9	0.10793 $\pm$ 0.00065	850.4 $\pm$ 10.0
0.1024	818.3 $\pm$ 3.6	589.1 $\pm$ 5.6	0.1739 $\pm$ 0.0017	912.6 $\pm$ 3.7
0.1639	852.8 $\pm$ 2.6	249.6 $\pm$ 3.9	0.1492 $\pm$ 0.0023	903.4 $\pm$ 2.7
0.2533	864.2 $\pm$ 1.9	0.0 $\pm$ 4.9	0.0000 $\pm$ 0.0056	864.2 $\pm$ 2.3
0.3697	854.7 $\pm$ 1.4	-168.3 $\pm$ 5.3	-0.341 $\pm$ 0.011	803.5 $\pm$ 2.1
0.4908	834.6 $\pm$ 1.5	-257.8 $\pm$ 4.4	-0.798 $\pm$ 0.014	744.3 $\pm$ 2.1
0.6595	802.9 $\pm$ 1.5	-298.6 $\pm$ 2.8	-1.440 $\pm$ 0.014	681.6 $\pm$ 1.9
0.8342	773.5 $\pm$ 1.7	-270.3 $\pm$ 2.3	-1.855 $\pm$ 0.016	650.1 $\pm$ 2.0
1.032	750.1 $\pm$ 1.5	-176.2 $\pm$ 2.7	-1.664 $\pm$ 0.026	660.6 $\pm$ 2.1
1.250	739.6 $\pm$ 1.3	-18.7 $\pm$ 2.9	-0.235 $\pm$ 0.037	729.1 $\pm$ 2.1
1.491	748.4 $\pm$ 1.5	197.9 $\pm$ 2.8	3.245 $\pm$ 0.046	869.2 $\pm$ 2.3
1.755	782.3 $\pm$ 2.4	462.5 $\pm$ 2.5	9.685 $\pm$ 0.053	1088.6 $\pm$ 2.9
2.033	843.4 $\pm$ 1.9	750.1 $\pm$ 2.4	19.586 $\pm$ 0.064	1378.2 $\pm$ 2.6
2.368	947.1 $\pm$ 2.3	1086.2 $\pm$ 2.4	35.652 $\pm$ 0.080	1782.8 $\pm$ 2.9
2.662	1060.5 $\pm$ 1.8	1358.4 $\pm$ 2.5	53.144 $\pm$ 0.099	2168.7 $\pm$ 2.8
3.036	1228.3 $\pm$ 1.8	1665.6 $\pm$ 3.3	79.37 $\pm$ 0.16	2679.4 $\pm$ 3.4
3.394	1407.5 $\pm$ 2.1	1919.8 $\pm$ 4.3	108.13 $\pm$ 0.24	3175.9 $\pm$ 4.4
3.618	1526.7 $\pm$ 2.3	2063.0 $\pm$ 4.4	127.89 $\pm$ 0.27	3488.8 $\pm$ 4.8
4.144	1823.2 $\pm$ 2.2	2378.6 $\pm$ 5.8	180.75 $\pm$ 0.44	4244.3 $\pm$ 6.3
4.582	2087.0 $\pm$ 2.3	2661.3 $\pm$ 19.1	235.1 $\pm$ 1.7	4935.3 $\pm$ 20.5

Table 6. Continued.

molality	ϕ_L (cal/mole)	$d\phi_L/dm^{1/2}$	$-L_1$ (cal/mole)	L_2 (cal/mole)
Samarium Nitrate				
0.002974	281.3± 2.4	3860.8±27.0	0.00564±0.00004	386.5± 2.5
0.003746	306.2± 2.4	3627.8±22.6	0.00749±0.00005	417.3± 2.5
0.005218	344.3± 2.6	3280.1±16.9	0.01114±0.00006	462.8± 2.7
0.006387	368.6± 2.0	3061.5±13.9	0.01408±0.00006	491.0± 2.0
0.007381	386.5± 4.6	2903.0±12.1	0.01658±0.00007	511.2± 4.6
0.04669	614.8± 4.2	965.4± 9.0	0.08773±0.00082	719.1± 4.3
0.09923	678.0± 3.3	377.4± 4.7	0.1063 ±0.0013	737.4± 3.4
0.1495	695.5± 3.0	127.8± 4.8	0.0666 ±0.0025	720.2± 3.1
0.2655	692.5± 2.2	-147.4± 6.1	-0.1817 ±0.0075	654.5± 2.7
0.3450	678.2± 1.7	-243.3± 5.6	-0.444 ±0.010	606.8± 2.4
0.4402	657.0± 1.3	-309.0± 4.6	-0.813 ±0.012	554.5± 2.0
0.6532	608.7± 1.7	-335.6± 3.4	-1.596 ±0.016	473.1± 2.2
0.8045	580.8± 1.5	-285.2± 3.3	-1.854 ±0.022	452.9± 2.1
0.9781	559.1± 1.9	-177.9± 3.1	-1.550 ±0.027	471.1± 2.4
1.124	550.5± 2.1	-57.5± 2.7	-0.617 ±0.029	520.0± 2.5
1.428	562.4± 2.1	251.4± 2.1	3.863 ±0.032	712.7± 2.4
1.647	595.6± 1.3	502.8± 2.4	9.572 ±0.046	918.2± 2.0
1.935	667.9± 2.0	846.3± 3.0	20.514 ±0.072	1256.4± 2.9
2.125	731.9± 1.8	1073.2± 3.0	29.944 ±0.085	1514.1± 2.9
2.457	870.6± 1.7	1455.4± 2.7	50.487 ±0.094	2011.2± 2.8
2.778	1032.3± 1.6	1799.2± 2.8	75.04 ±0.12	2531.7± 2.8
3.228	1294.0± 2.0	2227.5± 4.0	116.35 ±0.21	3295.0± 4.1
3.461	1442.2± 2.1	2424.5± 4.2	140.59 ±0.24	3697.2± 4.4
3.827	1688.6± 2.0	2704.0± 4.8	182.36 ±0.32	4333.5± 5.1
4.284	2013.4± 2.0	3012.3±15.3	240.6 ±1.2	5130.9±16.0

Table 6. Continued.

molality	ϕ_L (cal/mole)	$d\phi_L/dm^{1/2}$	$-L_1$ (cal/mole)	L_2 (cal/mole)
Gadolinium Nitrate				
0.002722	294.2 $\pm$ 1.5	4542.8 $\pm$ 23.2	0.00581 $\pm$ 0.00003	412.7 $\pm$ 1.6
0.003539	326.5 $\pm$ 3.3	4301.3 $\pm$ 20.1	0.00816 $\pm$ 0.00004	454.5 $\pm$ 3.4
0.004900	370.0 $\pm$ 3.3	3982.2 $\pm$ 16.4	0.01230 $\pm$ 0.00005	509.4 $\pm$ 3.3
0.01007	478.7 $\pm$ 2.0	3209.2 $\pm$ 9.1	0.02921 $\pm$ 0.00008	639.7 $\pm$ 2.1
0.03951	708.8 $\pm$ 10.0	1653.2 $\pm$ 6.4	0.11695 $\pm$ 0.00045	873.1 $\pm$ 10.0
0.09998	843.9 $\pm$ 3.2	757.1 $\pm$ 4.8	0.2156 $\pm$ 0.0014	963.6 $\pm$ 3.3
0.1566	889.9 $\pm$ 2.8	425.6 $\pm$ 3.6	0.2376 $\pm$ 0.0020	974.1 $\pm$ 2.8
0.2500	919.1 $\pm$ 1.5	156.1 $\pm$ 4.2	0.1757 $\pm$ 0.0047	958.1 $\pm$ 1.8
0.3597	926.1 $\pm$ 1.6	-3.1 $\pm$ 4.7	-0.0060 $\pm$ 0.0091	925.1 $\pm$ 2.1
0.4980	919.9 $\pm$ 1.9	-103.4 $\pm$ 4.2	-0.327 $\pm$ 0.013	883.4 $\pm$ 2.4
0.6417	907.8 $\pm$ 2.1	-140.5 $\pm$ 3.3	-0.650 $\pm$ 0.015	851.6 $\pm$ 2.4
0.8114	894.3 $\pm$ 2.2	-121.9 $\pm$ 2.5	-0.802 $\pm$ 0.017	839.3 $\pm$ 2.5
1.004	885.6 $\pm$ 2.5	-36.5 $\pm$ 2.4	-0.331 $\pm$ 0.021	867.4 $\pm$ 2.8
1.211	889.0 $\pm$ 2.3	115.5 $\pm$ 2.6	1.386 $\pm$ 0.031	952.5 $\pm$ 2.8
1.440	911.0 $\pm$ 2.2	338.4 $\pm$ 2.8	5.267 $\pm$ 0.044	1114.0 $\pm$ 2.8
1.692	959.2 $\pm$ 1.7	629.0 $\pm$ 3.0	12.471 $\pm$ 0.059	1368.3 $\pm$ 2.6
1.967	1040.5 $\pm$ 1.3	976.5 $\pm$ 2.9	24.265 $\pm$ 0.073	1725.2 $\pm$ 2.5
2.254	1155.2 $\pm$ 1.3	1349.1 $\pm$ 2.5	41.122 $\pm$ 0.077	2167.9 $\pm$ 2.3
2.566	1310.6 $\pm$ 1.5	1743.1 $\pm$ 2.1	64.540 $\pm$ 0.080	2706.8 $\pm$ 2.3
2.896	1504.1 $\pm$ 1.2	2129.0 $\pm$ 2.8	94.51 $\pm$ 0.13	3315.7 $\pm$ 2.7
3.238	1729.7 $\pm$ 1.7	2483.9 $\pm$ 3.9	130.37 $\pm$ 0.21	3964.5 $\pm$ 3.9
3.622	2005.3 $\pm$ 2.7	2825.7 $\pm$ 3.9	175.45 $\pm$ 0.24	4694.2 $\pm$ 4.6
3.952	2255.9 $\pm$ 2.2	3079.8 $\pm$ 6.1	217.95 $\pm$ 0.43	5317.1 $\pm$ 6.5
4.400	2610.9 $\pm$ 2.7	3395.6 $\pm$ 23.1	282.3 $\pm$ 1.9	6172.2 $\pm$ 24.4

Table 6. Continued.

molality	ϕ_L (cal/mole)	$d\phi_L/dm^{1/2}$	$-L_1$ (cal/mole)	L_2 (cal/mole)
Terbium Nitrate				
0.001552	232.1± 2.3	5133.6±25.8	0.00283±0.00001	333.2± 2.4
0.002648	291.7± 3.3	4757.0±20.5	0.00584±0.00003	414.1± 3.3
0.003712	335.4± 2.4	4488.3±17.0	0.00914±0.00003	472.2± 2.4
0.005043	379.4± 1.8	4224.1±13.8	0.01363±0.00004	529.4± 1.9
0.006390	416.1± 3.2	4007.2±11.4	0.01844±0.00005	576.3± 3.2
0.008076	454.8± 2.8	3782.5± 9.1	0.02473±0.00006	624.7± 2.8
0.008706	467.6± 3.0	3708.5± 8.4	0.02713±0.00006	640.6± 3.0
0.03454	736.2± 4.0	2242.4± 5.4	0.12964±0.00032	944.6± 4.1
0.09473	940.2± 2.5	1219.9± 4.6	0.3204 ±0.0012	1128.0± 2.6
0.1574	1028.7± 1.8	801.5± 2.9	0.4509 ±0.0016	1187.7± 1.9
0.2350	1086.8± 1.5	535.7± 3.1	0.5498 ±0.0032	1216.6± 1.7
0.3571	1134.3± 1.7	326.3± 3.9	0.6273 ±0.0075	1231.8± 2.0
0.4661	1157.8± 1.5	234.5± 3.7	0.672 ±0.011	1237.9± 1.9
0.6748	1185.3± 2.0	180.7± 2.5	0.903 ±0.013	1259.6± 2.3
0.8602	1205.8± 2.2	216.1± 2.2	1.553 ±0.016	1306.0± 2.4
1.045	1230.1± 2.3	306.6± 2.4	2.951 ±0.023	1386.8± 2.6
1.209	1258.1± 2.2	422.9± 2.5	5.068 ±0.030	1490.7± 2.6
1.535	1336.8± 2.0	727.6± 2.3	12.465 ±0.040	1787.5± 2.5
1.752	1408.5± 1.6	968.8± 2.5	20.245 ±0.052	2049.7± 2.3
2.020	1518.0± 2.5	1287.5± 3.0	33.290 ±0.077	2432.9± 3.3
2.210	1609.6± 2.0	1520.0± 3.2	44.973 ±0.096	2739.4± 3.1
2.384	1703.4± 1.8	1733.4± 3.3	57.49 ±0.11	3041.8± 3.1
3.193	2235.1± 2.2	2639.5± 3.6	135.67 ±0.18	4593.4± 3.9
3.625	2568.0± 2.6	3049.2± 5.6	189.56 ±0.35	5470.7± 5.9
3.925	2813.6± 2.6	3314.4± 5.3	232.14 ±0.37	6096.7± 5.8
4.323	3156.1± 2.3	3673.4± 9.8	297.46 ±0.79	6975.2±10.4

Table 6. Continued.

molality	Δ_L (cal/mole)	$d\Delta_L/dm^{1/2}$	$-L_1$ (cal/mole)	L_2 (cal/mole)
4.539	3350.1 $\pm$ 1.8	3888.9 $\pm$ 20.1	338.8 $\pm$ 1.8	7493.0 $\pm$ 21.5
Dysprosium Nitrate				
0.001704	242.2 $\pm$ 2.9	5056.7 $\pm$ 30.8	0.00320 $\pm$ 0.00002	346.6 $\pm$ 3.0
0.002917	304.0 $\pm$ 3.2	4665.0 $\pm$ 23.8	0.00662 $\pm$ 0.00003	430.0 $\pm$ 3.3
0.003518	328.4 $\pm$ 2.6	4515.5 $\pm$ 21.3	0.00849 $\pm$ 0.00004	462.3 $\pm$ 2.7
0.004633	366.8 $\pm$ 2.9	4284.6 $\pm$ 17.6	0.01217 $\pm$ 0.00005	512.7 $\pm$ 3.0
0.006307	413.9 $\pm$ 2.9	4010.4 $\pm$ 13.6	0.01810 $\pm$ 0.00006	573.2 $\pm$ 2.9
0.03919	767.2 $\pm$ 3.8	2199.9 $\pm$ 5.9	0.15372 $\pm$ 0.00042	985.0 $\pm$ 3.9
0.09093	950.7 $\pm$ 2.5	1416.7 $\pm$ 4.9	0.3499 $\pm$ 0.0012	1164.3 $\pm$ 2.6
0.1615	1068.5 $\pm$ 1.4	964.8 $\pm$ 3.0	0.5642 $\pm$ 0.0017	1262.4 $\pm$ 1.5
0.2513	1149.1 $\pm$ 1.7	676.4 $\pm$ 3.3	0.7678 $\pm$ 0.0038	1318.6 $\pm$ 1.9
0.3622	1206.8 $\pm$ 1.5	487.8 $\pm$ 3.7	0.9578 $\pm$ 0.0072	1353.6 $\pm$ 1.8
0.4885	1248.5 $\pm$ 2.0	382.5 $\pm$ 3.2	1.1765 $\pm$ 0.0097	1382.2 $\pm$ 2.3
0.6627	1289.6 $\pm$ 2.2	347.6 $\pm$ 2.3	1.689 $\pm$ 0.011	1431.1 $\pm$ 2.4
0.8056	1319.8 $\pm$ 2.3	382.7 $\pm$ 2.1	2.492 $\pm$ 0.014	1491.5 $\pm$ 2.5
0.9848	1360.3 $\pm$ 2.1	483.3 $\pm$ 2.4	4.254 $\pm$ 0.021	1600.1 $\pm$ 2.4
1.215	1423.2 $\pm$ 2.2	676.5 $\pm$ 2.6	8.157 $\pm$ 0.031	1796.0 $\pm$ 2.6
1.440	1500.7 $\pm$ 2.3	911.3 $\pm$ 2.5	14.192 $\pm$ 0.038	2047.5 $\pm$ 2.7
1.705	1612.7 $\pm$ 2.4	1216.4 $\pm$ 2.4	24.400 $\pm$ 0.048	2406.9 $\pm$ 2.8
1.960	1741.5 $\pm$ 2.2	1520.3 $\pm$ 2.5	37.589 $\pm$ 0.062	2805.8 $\pm$ 2.8
2.274	1925.1 $\pm$ 2.1	1886.2 $\pm$ 2.7	58.262 $\pm$ 0.082	3347.2 $\pm$ 2.9
2.587	2131.9 $\pm$ 2.6	2228.3 $\pm$ 2.6	83.529 $\pm$ 0.098	3924.0 $\pm$ 3.4
2.917	2370.2 $\pm$ 2.9	2556.6 $\pm$ 2.9	114.76 $\pm$ 0.13	4553.6 $\pm$ 3.8
3.249	2625.6 $\pm$ 2.6	2854.7 $\pm$ 3.9	150.57 $\pm$ 0.20	5198.3 $\pm$ 4.3
3.592	2904.2 $\pm$ 3.0	3142.3 $\pm$ 4.9	192.71 $\pm$ 0.30	5882.0 $\pm$ 5.5
4.038	3284.3 $\pm$ 2.2	3518.0 $\pm$ 4.8	257.18 $\pm$ 0.35	6819.1 $\pm$ 5.3
4.502	3703.1 $\pm$ 2.4	3975.8 $\pm$ 11.5	342.06 $\pm$ 0.99	7920.9 $\pm$ 12.4

Table 6. Continued.

molality	ϕ_L (cal/mole)	$d\phi_L/dm^{1/2}$	$-L_1$ (cal/mole)	L_2 (cal/mole)
4.738	3929.6 $\pm$ 2.2	4265.5 $\pm$ 21.1	396.3 $\pm$ 2.0	8572.0 $\pm$ 23.1
Holmium Nitrate				
0.002583	295.0 $\pm$ 4.2	4821.7 $\pm$ 29.0	0.00570 $\pm$ 0.00003	417.5 $\pm$ 4.3
0.003665	340.4 $\pm$ 2.7	4531.5 $\pm$ 23.4	0.00906 $\pm$ 0.00005	477.6 $\pm$ 2.8
0.004841	380.3 $\pm$ 3.9	4284.9 $\pm$ 19.0	0.01300 $\pm$ 0.00006	529.3 $\pm$ 4.0
0.006516	426.4 $\pm$ 2.7	4007.7 $\pm$ 14.6	0.01899 $\pm$ 0.00007	588.2 $\pm$ 2.7
0.007921	458.8 $\pm$ 3.0	3818.4 $\pm$ 12.0	0.02425 $\pm$ 0.00008	628.7 $\pm$ 3.0
0.01578	585.2 $\pm$ 10.0	3119.4 $\pm$ 6.4	0.05570 $\pm$ 0.00011	781.2 $\pm$ 10.0
0.04989	826.9 $\pm$ 10.0	1952.9 $\pm$ 7.8	0.19603 $\pm$ 0.00078	1045.0 $\pm$ 10.0
0.09920	975.7 $\pm$ 3.6	1349.6 $\pm$ 5.3	0.3798 $\pm$ 0.0015	1188.3 $\pm$ 3.7
0.1682	1084.6 $\pm$ 2.6	967.9 $\pm$ 3.6	0.6014 $\pm$ 0.0022	1283.0 $\pm$ 2.7
0.2508	1161.0 $\pm$ 1.3	734.3 $\pm$ 4.4	0.8307 $\pm$ 0.0050	1344.9 $\pm$ 1.7
0.3598	1225.0 $\pm$ 1.3	572.8 $\pm$ 4.7	1.1136 $\pm$ 0.0091	1396.8 $\pm$ 1.9
0.4915	1278.1 $\pm$ 1.5	487.2 $\pm$ 3.8	1.512 $\pm$ 0.012	1448.8 $\pm$ 2.0
0.5403	1294.4 $\pm$ 1.7	475.1 $\pm$ 3.4	1.700 $\pm$ 0.012	1469.0 $\pm$ 2.1
0.8020	1372.5 $\pm$ 2.4	529.1 $\pm$ 2.2	3.423 $\pm$ 0.014	1609.4 $\pm$ 2.6
0.9929	1431.7 $\pm$ 2.2	656.6 $\pm$ 2.5	5.852 $\pm$ 0.023	1758.9 $\pm$ 2.5
1.210	1509.6 $\pm$ 2.3	858.9 $\pm$ 2.8	10.297 $\pm$ 0.033	1982.0 $\pm$ 2.8
1.427	1601.8 $\pm$ 2.8	1099.9 $\pm$ 2.6	16.889 $\pm$ 0.040	2258.8 $\pm$ 3.2
1.685	1731.5 $\pm$ 2.6	1413.8 $\pm$ 2.6	27.855 $\pm$ 0.051	2649.1 $\pm$ 3.1
1.958	1891.7 $\pm$ 2.3	1756.2 $\pm$ 2.8	43.343 $\pm$ 0.070	3120.5 $\pm$ 3.0
2.236	2076.8 $\pm$ 2.2	2097.9 $\pm$ 3.2	63.184 $\pm$ 0.095	3645.3 $\pm$ 3.2
2.550	2308.2 $\pm$ 3.2	2459.8 $\pm$ 3.2	90.22 $\pm$ 0.12	4272.2 $\pm$ 4.1
2.830	2530.9 $\pm$ 2.9	2752.9 $\pm$ 3.1	118.05 $\pm$ 0.13	4846.4 $\pm$ 3.9
3.338	2962.9 $\pm$ 4.8	3204.7 $\pm$ 4.2	176.05 $\pm$ 0.23	5890.4 $\pm$ 6.1
3.724	3306.8 $\pm$ 3.3	3484.3 $\pm$ 5.3	225.55 $\pm$ 0.35	6668.8 $\pm$ 6.1

Table 6. Continued.

molality	ϕ_L (cal/mole)	$d\phi_L/dm^{1/2}$	$-L_1$ (cal/mole)	L_2 (cal/mole)
4.131	3677.8 $\pm$ 3.8	3735.9 $\pm$ 5.8	282.55 $\pm$ 0.44	7474.4 $\pm$ 7.0
4.564	4078.6 $\pm$ 3.5	3982.4 $\pm$ 10.3	349.76 $\pm$ 0.90	8332.5 $\pm$ 11.5
5.027	4514.1 $\pm$ 4.3	4264.6 $\pm$ 28.1	433.0 $\pm$ 2.9	9294.9 $\pm$ 31.8

Erbium Nitrate

0.002599	298.6 $\pm$ 2.5	4785.5 $\pm$ 33.1	0.00571 $\pm$ 0.00004	420.6 $\pm$ 2.6
0.003544	338.3 $\pm$ 4.0	4516.0 $\pm$ 27.3	0.00858 $\pm$ 0.00005	472.8 $\pm$ 4.1
0.005032	388.0 $\pm$ 1.9	4193.0 $\pm$ 20.8	0.01348 $\pm$ 0.00007	536.7 $\pm$ 2.0
0.006228	420.6 $\pm$ 3.5	3988.4 $\pm$ 17.0	0.01766 $\pm$ 0.00008	578.0 $\pm$ 3.5
0.007607	452.9 $\pm$ 3.1	3791.8 $\pm$ 13.8	0.02266 $\pm$ 0.00008	618.3 $\pm$ 3.1
0.03830	763.7 $\pm$ 10.0	2167.4 $\pm$ 8.5	0.14633 $\pm$ 0.00057	975.8 $\pm$ 10.0
0.1011	971.4 $\pm$ 2.8	1326.5 $\pm$ 6.1	0.3841 $\pm$ 0.0018	1182.3 $\pm$ 3.0
0.1770	1085.8 $\pm$ 1.7	930.1 $\pm$ 3.7	0.6239 $\pm$ 0.0025	1281.4 $\pm$ 1.8
0.2546	1154.2 $\pm$ 2.7	714.9 $\pm$ 3.9	0.8273 $\pm$ 0.0046	1334.5 $\pm$ 2.9
0.3516	1210.2 $\pm$ 2.1	563.7 $\pm$ 4.3	1.0586 $\pm$ 0.0080	1377.3 $\pm$ 2.4
0.4909	1265.0 $\pm$ 1.6	472.0 $\pm$ 3.9	1.462 $\pm$ 0.012	1430.4 $\pm$ 2.1
0.6428	1312.2 $\pm$ 1.5	476.1 $\pm$ 3.1	2.210 $\pm$ 0.014	1503.1 $\pm$ 1.9
0.8138	1363.8 $\pm$ 1.9	566.3 $\pm$ 2.5	3.745 $\pm$ 0.016	1619.2 $\pm$ 2.2
1.005	1428.7 $\pm$ 2.5	738.8 $\pm$ 2.3	6.705 $\pm$ 0.021	1799.0 $\pm$ 2.8
1.209	1511.4 $\pm$ 2.0	976.8 $\pm$ 2.2	11.696 $\pm$ 0.027	2048.4 $\pm$ 2.4
1.422	1614.9 $\pm$ 2.7	1260.0 $\pm$ 2.2	19.245 $\pm$ 0.034	2366.2 $\pm$ 3.0
1.712	1784.3 $\pm$ 2.8	1669.8 $\pm$ 2.4	33.693 $\pm$ 0.049	2876.8 $\pm$ 3.3
1.969	1959.7 $\pm$ 2.8	2032.9 $\pm$ 2.7	50.595 $\pm$ 0.066	3386.0 $\pm$ 3.3
2.258	2181.2 $\pm$ 2.7	2421.7 $\pm$ 2.8	74.014 $\pm$ 0.087	4000.7 $\pm$ 3.4
2.570	2443.8 $\pm$ 2.7	2803.6 $\pm$ 2.8	104.05 $\pm$ 0.10	4691.1 $\pm$ 3.5
2.949	2787.1 $\pm$ 3.2	3203.0 $\pm$ 2.8	146.11 $\pm$ 0.13	5537.2 $\pm$ 4.0
3.288	3109.1 $\pm$ 3.3	3496.9 $\pm$ 3.5	187.80 $\pm$ 0.19	6279.5 $\pm$ 4.6

Table 6. Continued.

molality	ϕ_L (cal/mole)	$d\phi_L/dm^{1/2}$	$-L_1$ (cal/mole)	L_2 (cal/mole)
3.703	3513.6 $\pm$ 3.6	3780.1 $\pm$ 4.7	242.63 $\pm$ 0.30	7150.7 $\pm$ 5.8
4.014	3819.7 $\pm$ 3.7	3945.1 $\pm$ 5.2	285.78 $\pm$ 0.38	7771.7 $\pm$ 6.4
4.452	4249.8 $\pm$ 3.9	4126.9 $\pm$ 5.1	349.20 $\pm$ 0.43	8603.6 $\pm$ 6.7
4.848	4635.1 $\pm$ 3.8	4262.6 $\pm$ 8.0	409.86 $\pm$ 0.77	9327.8 $\pm$ 9.6
5.179	4954.2 $\pm$ 3.7	4373.8 $\pm$ 15.9	464.3 $\pm$ 1.7	9931.0 $\pm$ 18.4
5.456	5220.0 $\pm$ 3.5	4477.5 $\pm$ 26.5	514.0 $\pm$ 3.0	10449.3 $\pm$ 31.2

Thulium Nitrate

0.002067	264.8 $\pm$ 5.7	4875.4 $\pm$ 25.0	0.00413 $\pm$ 0.00002	375.6 $\pm$ 5.7
0.002549	288.9 $\pm$ 3.7	4709.5 $\pm$ 22.7	0.00546 $\pm$ 0.00003	407.8 $\pm$ 3.8
0.003578	331.5 $\pm$ 4.5	4424.3 $\pm$ 18.8	0.00853 $\pm$ 0.00004	463.8 $\pm$ 4.6
0.004852	373.6 $\pm$ 1.9	4151.7 $\pm$ 15.3	0.01264 $\pm$ 0.00005	518.2 $\pm$ 2.0
0.006422	415.8 $\pm$ 3.7	3888.2 $\pm$ 12.2	0.01803 $\pm$ 0.00006	571.6 $\pm$ 3.8
0.03459	725.9 $\pm$ 4.2	2203.0 $\pm$ 4.9	0.12768 $\pm$ 0.00028	930.8 $\pm$ 4.2
0.09131	926.2 $\pm$ 2.9	1343.3 $\pm$ 4.8	0.3339 $\pm$ 0.0012	1129.1 $\pm$ 3.0
0.1617	1038.3 $\pm$ 2.0	931.5 $\pm$ 2.9	0.5458 $\pm$ 0.0017	1225.6 $\pm$ 2.0
0.2144	1089.4 $\pm$ 2.9	757.4 $\pm$ 2.5	0.6772 $\pm$ 0.0022	1264.8 $\pm$ 3.0
0.3602	1173.8 $\pm$ 1.8	502.0 $\pm$ 2.7	0.9777 $\pm$ 0.0053	1324.5 $\pm$ 2.0
0.4799	1216.0 $\pm$ 1.5	421.7 $\pm$ 2.6	1.2628 $\pm$ 0.0077	1362.1 $\pm$ 1.8
0.6164	1254.2 $\pm$ 1.6	416.1 $\pm$ 2.2	1.8141 $\pm$ 0.0095	1417.5 $\pm$ 1.8
0.8194	1309.4 $\pm$ 1.6	526.9 $\pm$ 1.8	3.520 $\pm$ 0.012	1547.9 $\pm$ 1.8
0.9978	1366.6 $\pm$ 1.9	707.8 $\pm$ 1.8	6.354 $\pm$ 0.017	1720.1 $\pm$ 2.1
1.210	1452.0 $\pm$ 2.4	992.5 $\pm$ 1.9	11.907 $\pm$ 0.023	1998.0 $\pm$ 2.6
1.445	1571.3 $\pm$ 2.2	1360.4 $\pm$ 1.8	21.289 $\pm$ 0.027	2389.0 $\pm$ 2.5
1.696	1728.6 $\pm$ 3.1	1783.8 $\pm$ 1.6	35.506 $\pm$ 0.033	2890.4 $\pm$ 3.2
1.961	1925.1 $\pm$ 3.0	2233.4 $\pm$ 1.9	55.250 $\pm$ 0.047	3488.9 $\pm$ 3.2
2.249	2169.9 $\pm$ 3.3	2700.3 $\pm$ 2.3	82.033 $\pm$ 0.071	4194.7 $\pm$ 3.7

Table 6. Continued.

molality	ϕ_L (cal/mole)	$d\phi_L/dm^{1/2}$	$-L_1$ (cal/mole)	L_2 (cal/mole)
2.558	2462.2± 3.0	3154.6± 2.7	116.261 ±0.098	4985.0± 3.7
2.906	2818.3± 3.3	3590.6± 2.7	160.26 ±0.12	5879.1± 4.0
3.246	3183.4± 3.6	3931.7± 2.5	207.16 ±0.13	6725.5± 4.3
3.765	3755.3± 4.1	4300.5± 3.4	282.97 ±0.22	7927.4± 5.3
3.997	4012.5± 3.8	4416.0± 4.1	317.89 ±0.29	8426.9± 5.6
4.412	4467.1± 4.0	4570.0± 5.1	381.45 ±0.42	9266.5± 6.7
5.016	5115.8± 3.5	4755.9± 5.2	481.23 ±0.52	10441.4± 6.8
5.499	5627.6± 4.1	4970.8± 9.8	577.4 ±1.1	11455.9±12.2
6.028	6196.5± 4.6	5397.5±26.3	719.6 ±3.5	12822.7±32.6

Ytterbium Nitrate

0.001567	227.0± 3.5	4863.4±32.8	0.00272±0.00002	323.2± 3.6
0.002535	277.4± 3.9	4506.9±26.2	0.00518±0.00003	390.8± 3.9
0.003947	331.3± 3.8	4147.7±20.0	0.00926±0.00004	461.6± 3.8
0.004523	349.4± 1.8	4031.8±18.1	0.01105±0.00005	484.9± 1.9
0.006378	398.3± 2.9	3729.8±13.5	0.01711±0.00006	547.2± 2.9
0.08900	895.5± 2.7	1384.7± 4.6	0.3312 ±0.0011	1102.1± 2.8
0.1596	1012.0± 1.3	946.3± 2.7	0.5435 ±0.0015	1201.1± 1.4
0.2334	1079.8± 1.5	685.5± 2.6	0.6964 ±0.0027	1245.4± 1.6
0.3732	1148.8± 1.4	420.8± 3.0	0.8643 ±0.0062	1277.3± 1.7
0.4975	1183.4± 1.8	326.9± 2.7	1.0335 ±0.0085	1298.7± 2.0
0.6894	1223.6± 2.1	344.1± 1.9	1.7740 ±0.0098	1366.4± 2.2
0.8362	1256.5± 2.2	449.4± 1.7	3.095 ±0.012	1461.9± 2.3
1.015	1306.9± 2.2	651.6± 1.9	5.999 ±0.018	1635.1± 2.4
1.211	1380.3± 2.3	938.6± 2.2	11.267 ±0.026	1896.8± 2.6
1.461	1504.0± 2.4	1363.4± 2.3	21.684 ±0.037	2328.0± 2.8
1.687	1645.2± 2.8	1776.4± 2.3	35.056 ±0.045	2798.8± 3.1

Table 6. Continued.

molality	ϕ_L (cal/mole)	$d\phi_L/dm^{1/2}$	$-L_1$ (cal/mole)	L_2 (cal/mole)
1.963	1852.6 $\pm$ 2.9	2287.8 $\pm$ 2.1	56.665 $\pm$ 0.053	3455.2 $\pm$ 3.3
2.249	2103.9 $\pm$ 2.9	2801.9 $\pm$ 2.1	85.135 $\pm$ 0.065	4204.9 $\pm$ 3.3
2.552	2402.8 $\pm$ 2.9	3305.8 $\pm$ 2.2	121.412 $\pm$ 0.079	5043.4 $\pm$ 3.4
3.226	3153.1 $\pm$ 3.0	4216.4 $\pm$ 2.0	220.08 $\pm$ 0.11	6939.8 $\pm$ 3.5
3.576	3570.6 $\pm$ 3.1	4559.0 $\pm$ 2.1	277.75 $\pm$ 0.13	7881.4 $\pm$ 3.7
3.994	4076.1 $\pm$ 2.9	4848.5 $\pm$ 2.8	348.56 $\pm$ 0.20	8920.8 $\pm$ 4.0
4.445	4620.1 $\pm$ 2.9	5025.7 $\pm$ 3.8	424.28 $\pm$ 0.32	9918.2 $\pm$ 4.9
4.816	5055.9 $\pm$ 2.8	5077.0 $\pm$ 4.4	483.33 $\pm$ 0.42	10626.7 $\pm$ 5.6
5.306	5608.4 $\pm$ 2.7	5037.1 $\pm$ 4.3	554.64 $\pm$ 0.48	11410.2 $\pm$ 5.7
5.761	6090.3 $\pm$ 2.9	4917.4 $\pm$ 4.6	612.54 $\pm$ 0.57	11991.8 $\pm$ 6.2
6.650	6938.4 $\pm$ 2.8	4570.9 $\pm$ 18.2	706.1 $\pm$ 2.8	12832.0 $\pm$ 23.6

Lutetium Nitrate

0.001605	238.8 $\pm$ 4.0	5069.0 $\pm$ 26.9	0.00294 $\pm$ 0.00002	340.3 $\pm$ 4.1
0.002850	303.3 $\pm$ 5.1	4612.7 $\pm$ 21.1	0.00632 $\pm$ 0.00003	426.4 $\pm$ 5.2
0.003623	333.9 $\pm$ 2.6	4403.9 $\pm$ 18.6	0.00865 $\pm$ 0.00004	466.4 $\pm$ 2.6
0.004939	376.9 $\pm$ 2.0	4119.1 $\pm$ 15.3	0.01288 $\pm$ 0.00005	521.6 $\pm$ 2.1
0.006566	419.6 $\pm$ 2.4	3844.6 $\pm$ 12.3	0.01843 $\pm$ 0.00006	575.4 $\pm$ 2.4
0.008001	451.2 $\pm$ 10.0	3647.9 $\pm$ 10.4	0.02352 $\pm$ 0.00007	614.3 $\pm$ 10.0
0.04795	787.0 $\pm$ 10.0	1829.1 $\pm$ 5.2	0.17299 $\pm$ 0.00050	987.3 $\pm$ 10.0
0.1016	934.6 $\pm$ 3.6	1190.1 $\pm$ 4.5	0.3472 $\pm$ 0.0013	1124.2 $\pm$ 3.7
0.1604	1017.8 $\pm$ 3.0	865.6 $\pm$ 3.1	0.5009 $\pm$ 0.0018	1191.1 $\pm$ 3.1
0.2466	1087.5 $\pm$ 1.5	603.2 $\pm$ 2.6	0.6653 $\pm$ 0.0028	1237.3 $\pm$ 1.7
0.3599	1139.3 $\pm$ 2.0	413.5 $\pm$ 2.9	0.8042 $\pm$ 0.0057	1263.4 $\pm$ 2.2
0.4881	1174.4 $\pm$ 1.2	309.3 $\pm$ 2.9	0.9500 $\pm$ 0.0088	1282.4 $\pm$ 1.6
0.6403	1203.9 $\pm$ 1.6	286.2 $\pm$ 2.3	1.321 $\pm$ 0.011	1318.4 $\pm$ 1.8
0.8135	1235.9 $\pm$ 1.7	360.1 $\pm$ 1.7	2.380 $\pm$ 0.011	1398.3 $\pm$ 1.9

Table 6. Continued.

molality	ϕ_L (cal/mole)	$d\phi_L/dm^{1/2}$	$-L_1$ (cal/mole)	L_2 (cal/mole)
0.9917	1276.6 $\pm$ 1.9	522.3 $\pm$ 1.6	4.647 $\pm$ 0.014	1536.7 $\pm$ 2.1
1.181	1334.6 $\pm$ 1.7	768.1 $\pm$ 1.8	8.880 $\pm$ 0.021	1751.9 $\pm$ 1.9
1.432	1440.4 $\pm$ 1.6	1177.2 $\pm$ 2.0	18.171 $\pm$ 0.031	2144.8 $\pm$ 2.0
1.709	1598.5 $\pm$ 2.7	1696.8 $\pm$ 2.0	34.148 $\pm$ 0.039	2707.6 $\pm$ 3.0
2.051	1852.0 $\pm$ 2.1	2378.1 $\pm$ 1.9	62.922 $\pm$ 0.050	3555.0 $\pm$ 2.5
2.260	2036.1 $\pm$ 2.1	2792.5 $\pm$ 2.1	85.460 $\pm$ 0.063	4135.1 $\pm$ 2.6
2.596	2371.5 $\pm$ 4.3	3425.0 $\pm$ 2.5	129.043 $\pm$ 0.093	5130.7 $\pm$ 4.7
2.928	2742.1 $\pm$ 2.4	3983.8 $\pm$ 2.7	179.79 $\pm$ 0.12	6150.4 $\pm$ 3.3
3.644	3624.9 $\pm$ 3.5	4886.3 $\pm$ 2.3	306.17 $\pm$ 0.14	8288.8 $\pm$ 4.1
4.060	4161.0 $\pm$ 4.2	5204.4 $\pm$ 2.7	383.51 $\pm$ 0.20	9404.3 $\pm$ 5.0
4.553	4792.8 $\pm$ 4.2	5399.7 $\pm$ 4.4	472.53 $\pm$ 0.39	10553.6 $\pm$ 6.3
4.872	5191.3 $\pm$ 5.6	5438.4 $\pm$ 5.5	526.81 $\pm$ 0.54	11193.4 $\pm$ 8.3
5.056	5415.9 $\pm$ 3.0	5436.5 $\pm$ 6.0	556.73 $\pm$ 0.61	11528.1 $\pm$ 7.3
5.482	5918.6 $\pm$ 3.1	5386.4 $\pm$ 6.1	622.76 $\pm$ 0.71	12224.3 $\pm$ 7.8
5.804	6281.8 $\pm$ 3.3	5330.3 $\pm$ 5.8	671.36 $\pm$ 0.73	12702.5 $\pm$ 7.7
6.792	7324.8 $\pm$ 3.4	5341.0 $\pm$ 22.8	851.6 $\pm$ 3.6	14284.5 $\pm$ 30.0

Lanthanum Perchlorate

0.001794	235.4 $\pm$ 5.1	4479.1 $\pm$ 39.9	0.00307 $\pm$ 0.00003	330.3 $\pm$ 5.2
0.002625	273.6 $\pm$ 5.4	4138.8 $\pm$ 33.4	0.00501 $\pm$ 0.00004	379.6 $\pm$ 5.5
0.003678	311.1 $\pm$ 3.5	3815.6 $\pm$ 27.5	0.00767 $\pm$ 0.00006	426.8 $\pm$ 3.6
0.005011	348.1 $\pm$ 8.2	3504.7 $\pm$ 22.3	0.01120 $\pm$ 0.00007	472.2 $\pm$ 8.2
0.006410	379.4 $\pm$ 2.4	3249.2 $\pm$ 18.2	0.01502 $\pm$ 0.00008	509.5 $\pm$ 2.5
0.009061	425.7 $\pm$ 2.8	2881.7 $\pm$ 13.1	0.02239 $\pm$ 0.00010	562.9 $\pm$ 2.9
0.01027	443.0 $\pm$ 10.0	2747.5 $\pm$ 11.5	0.02576 $\pm$ 0.00011	582.3 $\pm$ 10.0
0.03991	635.8 $\pm$ 10.0	1362.0 $\pm$ 9.0	0.09782 $\pm$ 0.00064	771.9 $\pm$ 10.0
0.08912	734.7 $\pm$ 3.7	713.4 $\pm$ 7.6	0.1710 $\pm$ 0.0018	841.2 $\pm$ 3.9

Table 6. Continued.

molality	ϕ_L (cal/mole)	$d\phi_L/dm^{1/2}$	$-L_1$ (cal/mole)	L_2 (cal/mole)
0.1611	787.5 $\pm$ 3.2	346.1 $\pm$ 4.9	0.2016 $\pm$ 0.0028	857.0 $\pm$ 3.4
0.2500	810.3 $\pm$ 2.7	134.2 $\pm$ 4.6	0.1511 $\pm$ 0.0052	843.9 $\pm$ 2.9
0.3504	816.9 $\pm$ 1.8	22.4 $\pm$ 4.9	0.0419 $\pm$ 0.0092	823.6 $\pm$ 2.3
0.4939	816.9 $\pm$ 1.6	-0.3 $\pm$ 4.5	-0.001 $\pm$ 0.014	816.8 $\pm$ 2.2
0.6448	821.0 $\pm$ 1.3	103.1 $\pm$ 3.7	0.481 $\pm$ 0.017	862.4 $\pm$ 2.0
0.8167	842.4 $\pm$ 1.3	344.8 $\pm$ 3.1	2.292 $\pm$ 0.020	998.2 $\pm$ 1.9
1.005	894.1 $\pm$ 1.7	726.8 $\pm$ 2.8	6.596 $\pm$ 0.025	1258.4 $\pm$ 2.2
1.176	970.4 $\pm$ 1.7	1153.4 $\pm$ 2.6	13.250 $\pm$ 0.029	1595.8 $\pm$ 2.2
1.465	1166.1 $\pm$ 2.3	1988.3 $\pm$ 2.4	31.758 $\pm$ 0.039	2369.4 $\pm$ 2.8
1.733	1420.8 $\pm$ 2.3	2831.4 $\pm$ 2.8	58.186 $\pm$ 0.057	3284.5 $\pm$ 2.9
1.982	1715.7 $\pm$ 2.4	3630.5 $\pm$ 3.2	91.252 $\pm$ 0.081	4271.3 $\pm$ 3.3
2.238	2071.2 $\pm$ 3.0	4437.6 $\pm$ 3.4	133.83 $\pm$ 0.10	5390.5 $\pm$ 4.0
2.565	2591.3 $\pm$ 2.9	5415.3 $\pm$ 3.3	200.39 $\pm$ 0.12	6927.8 $\pm$ 3.9
2.902	3190.8 $\pm$ 3.2	6338.8 $\pm$ 3.8	282.27 $\pm$ 0.17	8590.0 $\pm$ 4.6
3.255	3873.0 $\pm$ 3.0	7210.8 $\pm$ 5.4	381.44 $\pm$ 0.29	10377.8 $\pm$ 5.7
3.581	4541.4 $\pm$ 6.7	7944.4 $\pm$ 6.4	484.93 $\pm$ 0.39	12058.2 $\pm$ 9.1
4.093	5650.8 $\pm$ 4.4	9032.6 $\pm$ 6.2	673.74 $\pm$ 0.46	14787.9 $\pm$ 7.7
4.465	6499.6 $\pm$ 3.1	9861.5 $\pm$ 15.6	838.1 $\pm$ 1.3	16918.6 $\pm$ 16.8
4.791	7277.3 $\pm$ 4.2	10692.1 $\pm$ 35.8	1010.0 $\pm$ 3.4	18978.9 $\pm$ 39.4

Praseodymium Perchlorate

0.000835	153.8 $\pm$ 2.6	4521.5 $\pm$ 30.7	0.00098 $\pm$ 0.00001	219.1 $\pm$ 2.6
0.001553	199.2 $\pm$ 2.8	4135.4 $\pm$ 25.9	0.00228 $\pm$ 0.00001	280.7 $\pm$ 2.9
0.002464	239.8 $\pm$ 3.1	3815.7 $\pm$ 22.1	0.00420 $\pm$ 0.00002	334.5 $\pm$ 3.2
0.003816	284.1 $\pm$ 2.6	3486.3 $\pm$ 18.2	0.00740 $\pm$ 0.00004	391.8 $\pm$ 2.7
0.005234	319.6 $\pm$ 2.8	3232.9 $\pm$ 15.4	0.01103 $\pm$ 0.00005	436.5 $\pm$ 2.9
0.006793	351.0 $\pm$ 2.8	3014.4 $\pm$ 13.1	0.01520 $\pm$ 0.00007	475.3 $\pm$ 2.9

Table 6. Continued.

molality	ϕ_L (cal/mole)	$d\phi_L/dm^{1/2}$	$-L_1$ (cal/mole)	L_2 (cal/mole)
0.008726	383.0 $\pm$ 2.6	2797.3 $\pm$ 10.9	0.02054 $\pm$ 0.00008	513.6 $\pm$ 2.7
0.01003	401.4 $\pm$ 1.8	2673.6 $\pm$ 9.7	0.02419 $\pm$ 0.00009	535.3 $\pm$ 1.9
0.01025	404.3 $\pm$ 1.9	2654.0 $\pm$ 9.5	0.02481 $\pm$ 0.00009	538.7 $\pm$ 1.9
0.04174	602.8 $\pm$ 4.0	1342.8 $\pm$ 3.4	0.10313 $\pm$ 0.00026	740.0 $\pm$ 4.0
0.09976	705.9 $\pm$ 3.1	580.6 $\pm$ 4.5	0.1648 $\pm$ 0.0013	797.6 $\pm$ 3.2
0.1608	739.6 $\pm$ 2.4	236.4 $\pm$ 3.6	0.1374 $\pm$ 0.0021	787.0 $\pm$ 2.5
0.2564	749.8 $\pm$ 1.5	-16.3 $\pm$ 2.6	-0.0190 $\pm$ 0.0030	745.7 $\pm$ 1.6
0.3820	740.1 $\pm$ 1.4	-135.3 $\pm$ 2.7	-0.2878 $\pm$ 0.0058	698.3 $\pm$ 1.7
0.5042	727.0 $\pm$ 1.5	-134.0 $\pm$ 2.9	-0.4322 $\pm$ 0.0093	679.4 $\pm$ 1.8
0.7096	718.1 $\pm$ 1.6	33.3 $\pm$ 2.3	0.179 $\pm$ 0.012	732.1 $\pm$ 1.9
0.9529	746.4 $\pm$ 1.9	432.1 $\pm$ 1.9	3.620 $\pm$ 0.016	957.3 $\pm$ 2.1
1.119	796.2 $\pm$ 1.5	802.8 $\pm$ 2.2	8.563 $\pm$ 0.024	1220.9 $\pm$ 1.9
1.305	884.0 $\pm$ 1.5	1290.3 $\pm$ 2.6	17.333 $\pm$ 0.035	1621.1 $\pm$ 2.1
1.521	1028.9 $\pm$ 2.1	1923.2 $\pm$ 2.7	32.487 $\pm$ 0.046	2214.7 $\pm$ 2.7
1.773	1256.3 $\pm$ 2.3	2717.0 $\pm$ 2.6	57.773 $\pm$ 0.055	3065.1 $\pm$ 2.9
1.966	1470.2 $\pm$ 2.3	3336.7 $\pm$ 2.6	82.872 $\pm$ 0.064	3809.7 $\pm$ 2.9
2.150	1702.1 $\pm$ 2.1	3915.8 $\pm$ 2.7	111.181 $\pm$ 0.076	4572.9 $\pm$ 2.8
2.508	2225.2 $\pm$ 2.3	4980.1 $\pm$ 2.9	178.21 $\pm$ 0.10	6168.9 $\pm$ 3.2
2.930	2933.6 $\pm$ 2.4	6077.1 $\pm$ 2.4	274.54 $\pm$ 0.11	8134.7 $\pm$ 3.1
3.398	3803.6 $\pm$ 2.2	7150.6 $\pm$ 3.8	403.40 $\pm$ 0.22	10393.9 $\pm$ 4.1
3.862	4741.8 $\pm$ 2.2	8306.1 $\pm$ 6.1	567.80 $\pm$ 0.42	12903.2 $\pm$ 6.4
4.255	5615.9 $\pm$ 2.2	9688.9 $\pm$ 5.5	766.12 $\pm$ 0.44	15609.3 $\pm$ 6.1
4.695	6741.8 $\pm$ 2.0	12194.4 $\pm$ 20.6	1117.6 $\pm$ 1.9	19953.8 $\pm$ 22.4

Neodymium Perchlorate

0.001746	217.6 $\pm$ 4.2	4202.1 $\pm$ 31.4	0.00276 $\pm$ 0.00002	305.4 $\pm$ 4.3
0.002789	261.9 $\pm$ 2.9	3849.0 $\pm$ 26.2	0.00511 $\pm$ 0.00003	363.6 $\pm$ 3.0

Table 6. Continued.

molality	ϕ_L (cal/mole)	$d\phi_L/dm^{1/2}$	$-L_1$ (cal/mole)	L_2 (cal/mole)
0.003449	284.2± 5.4	3678.5±23.8	0.00671±0.00004	392.2± 5.4
0.004120	303.9± 3.4	3531.1±21.8	0.00841±0.00005	417.2± 3.4
0.005871	345.8± 2.6	3225.0±17.6	0.01307±0.00007	469.4± 2.7
0.007264	372.8± 2.3	3033.3±15.2	0.01692±0.00008	502.0± 2.4
0.01029	419.3± 2.3	2708.2±11.3	0.02548±0.00011	556.7± 2.4
0.04221	620.6±10.0	1319.9± 5.6	0.10311±0.00044	756.2±10.0
0.1004	719.5± 3.9	535.8± 6.8	0.1535 ±0.0019	804.4± 4.0
0.1599	748.8± 3.4	195.1± 5.2	0.1124 ±0.0030	787.8± 3.5
0.2496	754.9± 2.9	-48.1± 3.4	-0.0540 ±0.0038	742.9± 3.0
0.3606	743.2± 2.2	-165.0± 3.7	-0.3219 ±0.0072	693.6± 2.5
0.4763	727.2± 2.0	-179.4± 4.4	-0.531 ±0.013	665.3± 2.5
0.6390	711.6± 1.6	-83.3± 4.3	-0.383 ±0.020	678.3± 2.4
0.7945	711.8± 1.4	105.4± 3.5	0.672 ±0.022	758.8± 2.1
1.005	743.0± 1.3	483.4± 2.6	4.387 ±0.024	985.3± 1.8
1.227	819.8± 1.8	1005.5± 2.6	12.310 ±0.031	1376.7± 2.3
1.444	941.6± 1.9	1606.3± 2.9	25.108 ±0.046	1906.8± 2.6
1.670	1117.6± 1.9	2293.0± 3.2	44.575 ±0.062	2599.2± 2.8
1.964	1417.8± 2.2	3224.4± 3.3	79.942 ±0.083	3677.2± 3.2
2.254	1785.0± 2.0	4128.5± 3.4	125.85 ±0.11	4884.1± 3.3
2.603	2304.4± 2.8	5136.4± 3.6	194.31 ±0.13	6447.9± 4.0
2.879	2762.7± 2.4	5850.8± 4.1	257.45 ±0.18	7726.4± 4.2
3.223	3378.8± 3.2	6651.8± 5.9	346.69 ±0.31	9349.7± 6.2
3.625	4149.8± 4.4	7553.6± 7.8	469.60 ±0.49	11340.6± 8.7
4.075	5081.9± 4.7	8779.4± 7.0	650.54 ±0.52	13943.3± 8.5
4.509	6089.1± 3.5	10612.7±25.8	915.3 ±2.2	17356.8±27.6
4.685	6545.6± 4.0	11671.4±43.3	1066.1 ±4.0	19176.9±47.0

Table 6. Continued.

molality	ϕ_L (cal/mole)	$d\phi_L/dm^{1/2}$	$-L_1$ (cal/mole)	L_2 (cal/mole)
Samarium Perchlorate				
0.001156	178.7 $\pm$ 3.4	4383.2 $\pm$ 28.5	0.00155 $\pm$ 0.00001	253.2 $\pm$ 3.4
0.001619	205.3 $\pm$ 4.2	4163.3 $\pm$ 25.7	0.00244 $\pm$ 0.00002	289.1 $\pm$ 4.2
0.002523	245.3 $\pm$ 3.3	3850.6 $\pm$ 21.8	0.00440 $\pm$ 0.00002	342.0 $\pm$ 3.4
0.003629	282.5 $\pm$ 3.4	3574.9 $\pm$ 18.5	0.00704 $\pm$ 0.00004	390.1 $\pm$ 3.4
0.004913	316.5 $\pm$ 3.4	3332.0 $\pm$ 15.6	0.01034 $\pm$ 0.00005	433.3 $\pm$ 3.5
0.006411	348.6 $\pm$ 2.6	3109.3 $\pm$ 13.1	0.01438 $\pm$ 0.00006	473.1 $\pm$ 2.6
0.04885	634.7 $\pm$ 3.8	1241.2 $\pm$ 3.8	0.12073 $\pm$ 0.00037	771.9 $\pm$ 3.8
0.09245	713.3 $\pm$ 3.0	694.8 $\pm$ 4.4	0.1759 $\pm$ 0.0011	819.0 $\pm$ 3.0
0.1436	752.6 $\pm$ 2.2	374.7 $\pm$ 3.5	0.1837 $\pm$ 0.0017	823.6 $\pm$ 2.3
0.2119	773.2 $\pm$ 1.5	149.0 $\pm$ 2.6	0.1309 $\pm$ 0.0023	807.5 $\pm$ 1.6
0.2497	777.5 $\pm$ 1.5	73.9 $\pm$ 2.5	0.0830 $\pm$ 0.0028	796.0 $\pm$ 1.6
0.3752	777.8 $\pm$ 1.7	-45.9 $\pm$ 3.2	-0.0951 $\pm$ 0.0067	763.8 $\pm$ 2.0
0.4981	772.7 $\pm$ 1.8	-50.3 $\pm$ 3.3	-0.159 $\pm$ 0.011	754.9 $\pm$ 2.2
0.6116	770.8 $\pm$ 2.1	9.9 $\pm$ 2.9	0.043 $\pm$ 0.012	774.7 $\pm$ 2.4
0.7474	776.7 $\pm$ 2.2	146.0 $\pm$ 2.1	0.850 $\pm$ 0.012	839.8 $\pm$ 2.4
0.9226	802.3 $\pm$ 2.3	408.5 $\pm$ 1.9	3.261 $\pm$ 0.016	998.5 $\pm$ 2.5
1.107	855.6 $\pm$ 2.0	773.5 $\pm$ 2.7	8.116 $\pm$ 0.028	1262.6 $\pm$ 2.5
1.286	935.9 $\pm$ 2.2	1198.6 $\pm$ 3.3	15.750 $\pm$ 0.043	1615.5 $\pm$ 2.9
1.444	1030.8 $\pm$ 1.5	1616.8 $\pm$ 3.5	25.279 $\pm$ 0.055	2002.3 $\pm$ 2.6
1.693	1226.4 $\pm$ 2.0	2330.8 $\pm$ 3.3	46.269 $\pm$ 0.065	2742.9 $\pm$ 2.9
1.942	1475.6 $\pm$ 2.3	3073.9 $\pm$ 3.0	74.964 $\pm$ 0.073	3617.7 $\pm$ 3.1
2.244	1842.7 $\pm$ 2.7	3964.4 $\pm$ 3.1	120.073 $\pm$ 0.094	4812.3 $\pm$ 3.6
2.560	2290.6 $\pm$ 2.7	4837.8 $\pm$ 3.3	178.45 $\pm$ 0.12	6160.6 $\pm$ 3.8
3.051	3091.1 $\pm$ 2.7	6051.0 $\pm$ 3.7	290.50 $\pm$ 0.18	8376.0 $\pm$ 4.2
3.433	3779.2 $\pm$ 2.8	6930.4 $\pm$ 5.8	397.10 $\pm$ 0.33	10199.7 $\pm$ 6.0
4.006	4916.9 $\pm$ 3.4	8511.7 $\pm$ 6.7	614.65 $\pm$ 0.48	13434.6 $\pm$ 7.5

Table 6. Continued.

molality	ϕ_L (cal/mole)	$d\phi_L/dm^{1/2}$	$-L_1$ (cal/mole)	L_2 (cal/mole)
4.324	5627.9 $\pm$ 3.2	9812.3 $\pm$ 10.5	794.63 $\pm$ 0.85	15829.5 $\pm$ 11.4
4.640	6426.0 $\pm$ 2.7	11671.4 $\pm$ 30.6	1050.8 $\pm$ 2.8	18996.6 $\pm$ 33.1

Gadolinium Perchlorate

0.001363	192.6 $\pm$ 3.3	4355.5 $\pm$ 19.9	0.00197 $\pm$ 0.00001	273.0 $\pm$ 3.3
0.001618	206.8 $\pm$ 3.3	4247.0 $\pm$ 18.8	0.00249 $\pm$ 0.00001	292.2 $\pm$ 3.4
0.002443	244.6 $\pm$ 2.3	3970.0 $\pm$ 16.3	0.00432 $\pm$ 0.00002	342.7 $\pm$ 2.3
0.003351	277.2 $\pm$ 4.8	3742.8 $\pm$ 14.2	0.00654 $\pm$ 0.00002	385.5 $\pm$ 4.8
0.004935	321.6 $\pm$ 3.6	3446.8 $\pm$ 11.7	0.01076 $\pm$ 0.00004	442.7 $\pm$ 3.6
0.007467	374.5 $\pm$ 2.3	3109.7 $\pm$ 8.9	0.01807 $\pm$ 0.00005	508.9 $\pm$ 2.3
0.008930	399.1 $\pm$ 2.7	2957.9 $\pm$ 7.8	0.02249 $\pm$ 0.00006	538.8 $\pm$ 2.7
0.05915	692.7 $\pm$ 3.7	1251.4 $\pm$ 3.3	0.16216 $\pm$ 0.00043	844.8 $\pm$ 3.8
0.1132	783.0 $\pm$ 2.8	731.1 $\pm$ 3.3	0.2508 $\pm$ 0.0011	906.0 $\pm$ 2.9
0.1982	842.0 $\pm$ 1.3	392.3 $\pm$ 2.5	0.3118 $\pm$ 0.0020	929.4 $\pm$ 1.4
0.3275	879.5 $\pm$ 1.5	233.5 $\pm$ 2.4	0.3942 $\pm$ 0.0040	946.4 $\pm$ 1.6
0.4256	897.7 $\pm$ 1.8	232.4 $\pm$ 2.4	0.5813 $\pm$ 0.0060	973.6 $\pm$ 1.9
0.5525	921.9 $\pm$ 1.5	313.7 $\pm$ 2.1	1.1606 $\pm$ 0.0078	1038.5 $\pm$ 1.7
0.7330	968.6 $\pm$ 1.5	536.7 $\pm$ 1.6	3.0339 $\pm$ 0.0093	1198.4 $\pm$ 1.6
0.9182	1038.9 $\pm$ 2.2	861.0 $\pm$ 1.7	6.824 $\pm$ 0.014	1451.4 $\pm$ 2.4
1.081	1122.7 $\pm$ 1.5	1207.5 $\pm$ 2.0	12.224 $\pm$ 0.020	1750.4 $\pm$ 1.8
1.320	1285.3 $\pm$ 2.2	1793.8 $\pm$ 2.3	24.505 $\pm$ 0.031	2315.8 $\pm$ 2.5
1.556	1492.7 $\pm$ 1.9	2433.8 $\pm$ 2.5	42.550 $\pm$ 0.044	3010.6 $\pm$ 2.4
1.823	1781.2 $\pm$ 2.8	3193.1 $\pm$ 3.1	70.795 $\pm$ 0.068	3936.8 $\pm$ 3.5
2.074	2100.3 $\pm$ 3.0	3909.1 $\pm$ 3.6	105.173 $\pm$ 0.098	4915.2 $\pm$ 3.9
2.389	2558.3 $\pm$ 3.1	4773.5 $\pm$ 3.7	158.77 $\pm$ 0.12	6247.3 $\pm$ 4.2
2.891	3393.3 $\pm$ 4.0	6014.7 $\pm$ 3.6	266.32 $\pm$ 0.16	8506.7 $\pm$ 5.0
3.104	3778.0 $\pm$ 3.9	6491.1 $\pm$ 4.9	319.75 $\pm$ 0.24	9496.1 $\pm$ 5.8

Table 6. Continued.

molality	Δ_L (cal/mole)	$d\Delta_L/dm^{1/2}$	$-L_1$ (cal/mole)	L_2 (cal/mole)
3.499	4529.7 $\pm$ 3.5	7340.3 $\pm$ 7.9	432.76 $\pm$ 0.47	11395.0 $\pm$ 8.2
3.827	5190.0 $\pm$ 2.7	8088.6 $\pm$ 8.7	545.47 $\pm$ 0.59	13101.8 $\pm$ 8.9
4.205	6000.4 $\pm$ 2.7	9151.9 $\pm$ 14.0	710.8 $\pm$ 1.1	15383.9 $\pm$ 14.6
4.611	6958.6 $\pm$ 4.0	10789.4 $\pm$ 45.3	962.3 $\pm$ 4.0	18542.8 $\pm$ 48.8

Dysprosium Perchlorate

0.001048	168.1 $\pm$ 3.6	4370.7 $\pm$ 43.4	0.00134 $\pm$ 0.00001	238.9 $\pm$ 3.7
0.001919	215.9 $\pm$ 3.2	3993.2 $\pm$ 33.7	0.00302 $\pm$ 0.00003	303.3 $\pm$ 3.2
0.002661	246.1 $\pm$ 3.6	3771.9 $\pm$ 28.3	0.00466 $\pm$ 0.00004	343.3 $\pm$ 3.6
0.003751	281.3 $\pm$ 3.6	3526.7 $\pm$ 22.8	0.00730 $\pm$ 0.00005	389.3 $\pm$ 3.7
0.004704	306.6 $\pm$ 2.2	3358.6 $\pm$ 19.3	0.00976 $\pm$ 0.00006	421.7 $\pm$ 2.3
0.007524	364.1 $\pm$ 2.3	2994.1 $\pm$ 12.5	0.01760 $\pm$ 0.00007	494.0 $\pm$ 2.3
0.04046	616.2 $\pm$ 4.0	1598.5 $\pm$ 6.3	0.11718 $\pm$ 0.00046	777.0 $\pm$ 4.0
0.1045	762.0 $\pm$ 2.7	866.2 $\pm$ 4.1	0.2636 $\pm$ 0.0013	902.0 $\pm$ 2.8
0.1632	819.6 $\pm$ 1.8	582.8 $\pm$ 3.2	0.3460 $\pm$ 0.0019	937.3 $\pm$ 1.9
0.2441	862.6 $\pm$ 1.4	392.1 $\pm$ 3.6	0.4260 $\pm$ 0.0039	959.5 $\pm$ 1.7
0.4021	909.2 $\pm$ 1.9	316.0 $\pm$ 3.2	0.7257 $\pm$ 0.0074	1009.4 $\pm$ 2.2
0.5090	936.5 $\pm$ 2.0	385.2 $\pm$ 2.5	1.2600 $\pm$ 0.0081	1073.9 $\pm$ 2.2
0.5885	959.5 $\pm$ 2.0	477.8 $\pm$ 2.1	1.9430 $\pm$ 0.0087	1142.8 $\pm$ 2.1
0.7458	1017.1 $\pm$ 1.8	736.8 $\pm$ 2.3	4.275 $\pm$ 0.013	1335.3 $\pm$ 2.1
0.9239	1106.7 $\pm$ 1.6	1117.9 $\pm$ 2.7	8.942 $\pm$ 0.021	1643.9 $\pm$ 2.1
1.069	1200.4 $\pm$ 1.8	1475.7 $\pm$ 2.7	14.684 $\pm$ 0.027	1963.1 $\pm$ 2.3
1.190	1293.9 $\pm$ 1.7	1800.0 $\pm$ 2.6	21.053 $\pm$ 0.030	2275.8 $\pm$ 2.2
1.456	1544.3 $\pm$ 2.0	2555.9 $\pm$ 2.2	40.432 $\pm$ 0.034	3086.1 $\pm$ 2.4
1.680	1802.8 $\pm$ 2.4	3221.9 $\pm$ 2.2	63.190 $\pm$ 0.044	3890.7 $\pm$ 2.8
1.792	1946.4 $\pm$ 2.4	3556.3 $\pm$ 2.3	76.817 $\pm$ 0.051	4326.4 $\pm$ 2.9
2.086	2369.3 $\pm$ 2.9	4433.7 $\pm$ 2.6	120.367 $\pm$ 0.071	5571.5 $\pm$ 3.4

Table 6. Continued.

molality	ϕ_L (cal/mole)	$d\phi_L/dm^{1/2}$	$-L_1$ (cal/mole)	L_2 (cal/mole)
2.303	2717.1± 2.9	5063.1± 2.6	159.445 ±0.081	6559.3± 3.5
2.561	3165.8± 2.9	5783.5± 2.6	213.572 ±0.097	7793.9± 3.6
2.869	3742.9± 2.5	6592.6± 3.5	288.53 ±0.15	9325.9± 3.9
3.537	5123.3± 1.9	8149.0± 5.8	488.33 ±0.35	12786.4± 5.8
4.044	6251.6± 2.7	9151.1± 5.7	670.48 ±0.42	15453.5± 6.3
4.317	6876.8± 2.8	9635.5±12.1	778.40 ±0.97	16886.4±12.8
4.602	7543.3± 2.8	10112.3±25.7	899.1 ±2.3	18389.5±27.7

Erbium Perchlorate

0.001250	186.5± 3.6	4343.9±46.3	0.00173±0.00002	263.3± 3.7
0.001716	212.2± 4.0	4129.5±40.7	0.00264±0.00003	297.7± 4.1
0.002310	238.9± 6.5	3917.8±35.5	0.00392±0.00004	333.0± 6.6
0.003340	275.6± 4.2	3642.0±29.0	0.00633±0.00005	380.9± 4.2
0.006719	356.6± 3.9	3083.5±17.3	0.01530±0.00009	483.0± 4.0
0.007900	377.5± 6.0	2948.7±14.8	0.01865±0.00009	508.5± 6.0
0.01141	427.5± 4.0	2637.5±10.1	0.02896±0.00011	568.4± 4.1
0.1154	775.5± 2.9	778.8± 5.4	0.2750 ±0.0019	907.8± 3.0
0.2029	842.0± 1.6	453.5± 4.4	0.3734 ±0.0036	944.1± 1.8
0.2307	854.6± 3.0	396.2± 4.3	0.3955 ±0.0043	949.8± 3.2
0.3603	893.4± 1.7	280.0± 4.3	0.5454 ±0.0084	977.4± 2.1
0.5129	927.6± 1.6	339.0± 3.8	1.122 ±0.013	1049.0± 2.1
0.6626	968.8± 2.1	524.5± 3.4	2.548 ±0.016	1182.3± 2.5
0.8408	1038.7± 3.2	857.4± 3.0	5.955 ±0.021	1431.8± 3.5
1.055	1159.9± 3.6	1367.1± 2.8	13.344 ±0.027	1861.9± 3.9
1.227	1288.3± 3.3	1833.6± 2.8	22.448 ±0.034	2303.8± 3.7
1.498	1546.3± 3.5	2628.4± 3.3	43.408 ±0.055	3154.8± 4.1
1.700	1780.6± 3.2	3243.5± 3.8	64.760 ±0.076	3895.1± 4.1

Table 6. Continued.

molality	ϕ_L (cal/mole)	$d\phi_L/dm^{1/2}$	$-L_1$ (cal/mole)	L_2 (cal/mole)
2.033	2237.5 $\pm$ 4.9	4258.8 $\pm$ 3.9	111.20 $\pm$ 0.10	5273.6 $\pm$ 5.7
2.358	2757.2 $\pm$ 5.4	5216.2 $\pm$ 3.5	170.13 $\pm$ 0.11	6762.1 $\pm$ 6.0
2.676	3324.5 $\pm$ 3.4	6098.1 $\pm$ 3.9	240.46 $\pm$ 0.15	8312.3 $\pm$ 4.7
3.086	4124.7 $\pm$ 3.2	7138.7 $\pm$ 6.3	348.60 $\pm$ 0.31	10395.0 $\pm$ 6.4
3.413	4806.7 $\pm$ 2.8	7889.6 $\pm$ 7.6	448.10 $\pm$ 0.43	12094.4 $\pm$ 7.6
4.215	6595.4 $\pm$ 5.4	9490.0 $\pm$ 9.9	739.74 $\pm$ 0.77	16337.1 $\pm$ 11.5
4.627	7561.9 $\pm$ 3.3	10236.5 $\pm$ 32.4	917.7 $\pm$ 2.9	18571.4 $\pm$ 35.0

Lutetium Perchlorate

0.002467	250.0 $\pm$ 3.3	3911.1 $\pm$ 39.2	0.00432 $\pm$ 0.00004	347.2 $\pm$ 3.4
0.003571	288.0 $\pm$ 2.1	3617.9 $\pm$ 30.2	0.00696 $\pm$ 0.00006	396.1 $\pm$ 2.3
0.004746	319.9 $\pm$ 2.7	3383.2 $\pm$ 23.6	0.00996 $\pm$ 0.00007	436.4 $\pm$ 2.8
0.006461	357.3 $\pm$ 2.3	3120.6 $\pm$ 17.2	0.01460 $\pm$ 0.00008	482.7 $\pm$ 2.4
0.007194	370.9 $\pm$ 2.1	3027.5 $\pm$ 15.1	0.01664 $\pm$ 0.00008	499.3 $\pm$ 2.2
0.009869	412.8 $\pm$ 10.0	2749.9 $\pm$ 10.4	0.02429 $\pm$ 0.00009	549.4 $\pm$ 10.0
0.06717	696.8 $\pm$ 10.0	1102.9 $\pm$ 9.9	0.1729 $\pm$ 0.0015	839.7 $\pm$ 10.1
0.09880	749.5 $\pm$ 3.9	821.5 $\pm$ 6.6	0.2298 $\pm$ 0.0018	878.6 $\pm$ 4.0
0.1546	802.3 $\pm$ 3.5	537.1 $\pm$ 4.4	0.2941 $\pm$ 0.0024	907.9 $\pm$ 3.6
0.2496	845.9 $\pm$ 2.9	308.0 $\pm$ 6.7	0.3460 $\pm$ 0.0076	922.8 $\pm$ 3.4
0.3586	871.3 $\pm$ 1.3	224.1 $\pm$ 7.1	0.433 $\pm$ 0.014	938.4 $\pm$ 2.5
0.4944	895.7 $\pm$ 1.6	265.6 $\pm$ 5.4	0.832 $\pm$ 0.017	989.0 $\pm$ 2.5
0.6409	928.5 $\pm$ 2.2	428.8 $\pm$ 3.3	1.982 $\pm$ 0.015	1100.1 $\pm$ 2.5
0.8068	983.4 $\pm$ 2.5	717.1 $\pm$ 2.7	4.681 $\pm$ 0.018	1305.5 $\pm$ 2.8
1.006	1080.8 $\pm$ 1.8	1165.0 $\pm$ 3.4	10.589 $\pm$ 0.031	1665.0 $\pm$ 2.5
1.174	1191.7 $\pm$ 1.9	1602.3 $\pm$ 3.7	18.359 $\pm$ 0.042	2059.7 $\pm$ 2.8
1.432	1413.4 $\pm$ 2.1	2339.2 $\pm$ 3.5	36.108 $\pm$ 0.054	2813.1 $\pm$ 2.9
1.676	1677.9 $\pm$ 2.2	3073.9 $\pm$ 3.4	60.077 $\pm$ 0.066	3667.6 $\pm$ 3.1

Table 6. Continued.

molality	ϕ_L (cal/mole)	$d\phi_L/dm^{1/2}$	$-L_1$ (cal/mole)	L_2 (cal/mole)
1.980	2075.1 $\pm$ 1.7	3998.7 $\pm$ 3.5	100.353 $\pm$ 0.087	4888.4 $\pm$ 3.0
2.232	2454.9 $\pm$ 2.7	4749.4 $\pm$ 3.3	142.657 $\pm$ 0.099	6002.7 $\pm$ 3.7
2.529	2953.0 $\pm$ 3.3	5596.1 $\pm$ 3.2	202.73 $\pm$ 0.11	7402.6 $\pm$ 4.2
2.870	3581.2 $\pm$ 2.8	6501.9 $\pm$ 4.7	284.76 $\pm$ 0.21	9088.6 $\pm$ 4.9
3.196	4227.3 $\pm$ 3.5	7294.7 $\pm$ 7.2	375.43 $\pm$ 0.37	10747.8 $\pm$ 7.3
3.567	5005.0 $\pm$ 4.1	8112.0 $\pm$ 8.7	492.26 $\pm$ 0.53	12665.4 $\pm$ 9.1
4.039	6043.9 $\pm$ 5.7	9040.5 $\pm$ 8.4	661.03 $\pm$ 0.61	15128.4 $\pm$ 10.2
4.634	7411.9 $\pm$ 5.3	10099.1 $\pm$ 38.7	907.5 $\pm$ 3.5	18282.0 $\pm$ 42.0

Figure 5. Relative apparent molal heat contents of 1-3 rare earth nitrate solutions at 25°C

Figure 6. Relative partial molal heat contents of water in 1-3 rare earth nitrate solutions at 25°C

Figure 7. Relative partial molal heat contents of the solute in 1-3 rare earth nitrate solutions at 25°C

Figure 8. Relative apparent molal heat contents of 1-3 rare earth perchlorate solutions at 25°C

Figure 9. Relative partial molal heat contents of water in 1-3 rare earth perchlorate solutions at 25°C

Figure 10. Relative partial molal heat contents of the solute in 1-3 rare earth perchlorate solutions at 25°C

either Equation 4.10 or Equation 4.13 to represent the ΔH_{i-f} and ϕ_L values for the salt.

C. Calculated Thermodynamic Properties

The relative apparent molal heat content of a salt can be calculated using Equation 4.10. The $\bar{L}_1$ and $\bar{L}_2$ values for the solutions can be calculated using equations developed in Section A of Chapter 2. The values for the relative apparent molal heat content, the slope with respect to $m^{1/2}$, the relative partial molal heat content of the solvent and the relative partial molal heat content of the solute were calculated from the equation parameters given in Table 4 and 5 and are presented in Table 6 for all of the salts. The properties were calculated at experimentally used molalities in order to be able to calculate error values for the derivative properties.

The above listed properties were also graphed as a function of concentration in Figures 5-7 for the nitrates and Figures 8-10 for the perchlorates.

No simple analytical method exists that can assign error values for derivative properties when the error in the parent functions is known. Therefore, in order to obtain an estimate of the accuracy of the derivative equation, a stochastic (random variable) computer method was developed and implemented for properties based on relative apparent molal heat

content data.

The error limits given for the relative apparent molal heat contents in Table 6 correspond to the standard deviation values used in Equation 4.5 and are derived from the average weight factor of all of the ΔH_{1-f} values obtained for one m_i value.

The error limits given for the slope of the apparent molal heat contents with respect to $m^{1/2}$ were obtained by the following method. A standard computer routine, called GAUSS (94) was used to randomly shift each ΔH_{1-f} value used in a fit to a new normally distributed value. This was done in such a way that if the shift was repeated a large number of times, the shifted values would have a Gaussian distribution with the experimental ΔH_{1-f} value as the mean value of the distribution and with the variance value equal to the value predicted by the weighting factor used for that experimental ΔH_{1-f} point. All of the experimental ΔH_{1-f} values obtained for each salt were shifted in the same manner and this new set of normally shifted ΔH_{1-f} values was fitted to an equation with the same set of powers that reflected the effects of the shifts. Repeating this process on the original experimental values 400 times produced a set of 400 fitted equations of the form given in Equation 4.13. Using these 400 equations, slope values were calculated at experimentally used molalities. The standard deviation of the slope values

at a given molality was used as the error limit given in Table 6 for the slope values. 400 equations were sufficient to reproduce the standard deviation of the slope to 2 significant figures, independently of the random numbers generated in the computer program.

Using the standard deviation error limits given for the relative apparent molal heat content values and the slope values, standard propagation of error equations yielded error limits for the rest of the properties in the table.

D. Analysis of Data Treatment

The scatter that exists in the individual experimental points is, in general, characterized in Tables 2 and 3 by the σ_i values, which are equal to standard deviation values within the accuracy limits for the values. These error values must be combined with a second source of error when considering the standard deviation errors for the fitting equations. Since only four readings of ΔH_{1-f} values were usually taken for a given molality, significant deviation of the mean value from the true value can occur, both from systematic errors that occur throughout any single experimental run, and from the inability of four points to represent a Gaussian distribution about the mean value. As a result, the standard deviation values for the fits will include both the scatter of the ΔH values about their mean value, and also the difference between the mean value and the value indicated by the fitted

equation. In the rare earth nitrates, the standard deviation ranged from 2.4 cal/mole to 4.8 cal/mole, while the rare earth perchlorates had standard deviations from 3.7 to 5.7 calories. The larger standard deviations for the perchlorates reflects the fact that smaller sample sizes were used to measure the large ΔH values for these salts.

The smaller sample sizes that were used to measure high concentration ΔH values also contributed to a larger error value for the two or three highest concentrations for each salt. At almost all concentrations, the deviation of any fitted value is within 0.2% of the ΔH_{1-f} value, and this is correctly reflected by the σ_i value. In the case of the ΔH_{1-f} values for the two or three highest concentration solutions of some of the salts, the data in Table 2 and 3 indicates that a value of 10 to 15 cal/mole is a more realistic value for the standard deviation. Besides the effect of small sample size, another important source of error existed for the saturated solutions. Since the saturated solutions were exposed to temperatures of less than 25.0°C during the early parts of the experimental runs, the solutions in the bulbs would be supersaturated, and could crystallize out at some time before a break was carried out. Then during a break when the heat of dilution was being measured, the heat effect being measured could be affected in one of two ways. First, if the bulb being broken held crystals at the time, the mea-

sured heat value would be for a mixture of crystallized salt and solution, yielding an incorrect value for a pure saturated solution. Second, if other unbroken bulbs in the calorimeter held crystals, these crystals may dissolve back into the solution as the temperature of the calorimeter goes up during a break, and thus absorbing heat in the process.

Any attempt to use the fitting equation as a smoothing function in the region of highest concentration was not possible because the fitting equation loses accuracy in the representation of data at the endpoints of the data. The form of equation used here was very flexible in this region, and as a result, the deviation of the fitted equation from the experimental points was smaller than the data warranted. Therefore, at the highest concentration m_1 values for a salt, a standard deviation value for the fitting process of 15 cal/mole should be assumed, while in the region of the next two lower m_1 values, 10 cal/mole would be more realistic.

Below the low concentration limit of ΔH values, the error that occurs was minimized by the use of the theoretical slope value as the first coefficient in the fitting equation. Since the ϕ_L values change quickly in the vicinity of infinite dilution, the behavior of the fitting equations can best be studied by comparing the average slope values, $\bar{P}_i$, generated from the fitting equation, against $\bar{P}_i$ points obtained from experimental data using Equation 2.36, as discussed in

Chapter 2.

$$\bar{P}_i = -\Delta H_{3-2} / (m_2^{1/2} - m_3^{1/2}) \quad (2.36)$$

The $\bar{P}_i$ points for six salts are plotted in Figures 11-16. The scatter and deviations in the $\bar{P}_i$ data points below 0.04 $m^{1/2}$ has previously been reported and discussed by Pepple (13) for the calorimeter used in this project. In this work this scatter and deviation occurred when small sample sizes yielded large experimental heat measurements and are definitely systematic errors associated with the calorimeter. The sources of error in the heat measurements of saturated solutions also accounted for some of the deviations of the lower $\bar{P}_i$ points.

Substitution of Equation 4.13 with the proper subscripts for ΔH_{3-2} , into Equation 2.36 yields the equation for $\bar{P}_i$ for the polynomial equation used in this work.

$$\bar{P}_i = \sum_{j=1}^7 A_j \frac{(m_3^{1/2} - m_2^{1/2})}{(m_3^{1/2} - m_2^{1/2})} \quad (4.14)$$

Under the experimental procedures followed in this work, m_3 was almost always about equal to twice the value of m_2 . Using this relationship and solving the $\bar{P}_i$ equation for the mean square root molality, $\bar{m}^{1/2} = (m_2^{1/2} + m_3^{1/2})/2$, the working equation for $\bar{P}_i$ is derived as in Equation 4.15.

$$\bar{P}_i = \sum_{j=1}^7 A_j \frac{(2^{p_j-1})(2^{2p_j-1})}{(2^{1/2}-1)(2^{1/2}+1)} \frac{\bar{m}^{1/2}}{2^{p_j-1}} \quad (4.15)$$

These curves are also plotted for the six particular salts in Figures 11-16.

From these figures, it is evident that the $\bar{P}_i$ equation represents the data well within the limits set by the scatter in the data. The extrapolation from the lowest $\bar{P}_i$ points to infinite dilution is smooth, but represents a possible source of error for apparent molal heat content values. For the perchlorates, a sudden upturn in the $\bar{P}_i$ equation is evident below $0.01m^{1/2}$. This sudden upturn is probably caused by the usual errors in the terms of the polynomial at concentrations outside the range of experimentally measured points. In the equation used in this work, the first coefficient is fixed at a theoretical value, and thus, only higher terms contribute to the sudden upturn. This sort of error exists for all attempts to extrapolate to infinite dilution. If experimental points could have been obtained at these low concentrations, most of the error would be eliminated by a better fit of the coefficients to the data. For Figures 11-16, the area under the $\bar{P}_i$ equation and between any two molality values is a good approximation to the ΔH value between the two concentration values. (It is a good approximation, but not a perfect one, because the $\bar{P}_i$ equation for the dilution scheme used in this work ($m_3=2m_2$) is not exactly the same as the slope equation but is within 100 slope units of the value give by the slope

Figure 11. $\bar{P}_i$ data for praseodymium nitrate solutions at 25°C

Figure 12. $\bar{P}_i$ data for samarium nitrate solutions at 25°C

Figure 13. $\bar{P}_i$ data for lutetium nitrate solutions at 25°C

Figure 14. $\bar{\alpha}_i$ data for praseodymium perchlorate solutions at 25°C

Figure 15. $\bar{P}_i$ data for samarium perchlorate solutions at 25°C

Figure 16. $\bar{\eta}_i$ data for lutetium perchlorate solutions at 25°C

equation at $0.1 \text{ m}^{1/2}$ and proportionately less as the concentration approaches infinite dilution.) Since the extrapolation error occurs below experimental points, using different extrapolation equations will yield different areas which represents an almost constant shift in ϕ_L values at higher molality values. Using the difference in area between the $\bar{P}_i$ equation used in this work and other possible curves in the dilute region, this extrapolation error can be estimated as about +5 calories with a limit of about +10 cal/mole from the values listed in Table 6. The extrapolation error discussed above is one reason why fitting equations with common powers in their low powered terms were chosen whenever possible. The terms with powers less than 1.50 are important in determining the slope of the slope line at concentrations where the extrapolation errors occur. Because of this, an error of ± 5 cal/mole can be assumed when comparing ϕ_L equation values for two salts if different powers were used in the lower terms, as is usually the case with salts of different anions.

In summary, the experimental heat of dilution values have a scatter of about 0.2% for repeat measurements of the same values, and a scatter of about 0.4% when compared to the data smoothing empirical equation.

The following systematic errors can also be expected in the data. The uncertainty in the molality value for the salt solution is about 0.1% across the concentration scale. The

standardization of the calorimeter, as discussed in Chapter 3, indicates that the systematic error due to the equipment can be expected to be about 0.25%. The extrapolation error for the ϕ_L data is about 0.5% for ϕ_L values in the midrange of the concentration scale. The extrapolation error in ϕ_L will not directly contribute to the error in the slope values, but systematic errors in the derivative equations should be no greater than 0.5%. As a result, the errors in the ϕ_L , $\bar{L}_1$, and $\bar{L}_2$ values should be no greater than 1%, and the probable error is about 0.7%. For the ϕ_L and $\bar{L}_2$ data the probable error corresponds to a value of about 7 calories for values not close to the endpoints of the concentration range studied.

V. DISCUSSION

A. Polynomial Fitted Equation

In this work, the heats of dilution between various sets of initial and final concentrations were measured for nine rare earth nitrate and perchlorate solutions. The data for these salts, and the data for nitrate and perchlorate salts obtained by Mohs (14) were fitted to seven coefficient equations utilizing powers of molality that were multiples of 0.25. The first term in each equation contains molality to the one-half power, since this was found to produce lower standard deviations for the fit when included, rather than when left out of any form of fitting equation checked in this work. The coefficient of the $m^{1/2}$ term was fixed at a value predicted by the Debye-Huckel equation and this resulted in fits that were no less precise than if this coefficient had instead been determined by the fitting process.

The rest of the terms of the fitting equation consisted of six coefficients calculated to yield minimum chi square statistics for various multiple powers of $m^{1/4}$. This contrasts strongly with various procedures in the literature (47,48,77,79), where the forms of the heat content equation were derived from an expanded form of the Debye-Huckel equation. The reason for the change of method is that the equations in this work were developed to apply over the entire concentration range that the solution exists, while retaining

a mathematical form that is concise and convenient to use. While heat content equations for ϕ_L at lower concentrations have been based on Debye-Huckel considerations, they also have been simplified in most cases for mathematical convenience, and have had empirical terms included to extend the usefulness of their form into higher concentrations. Owen and Brinkley (47) set the temperature derivative of the Debye-Huckel mean distance of approach parameter equal to zero in order to simplify their equation, while avoiding the difficulty of obtaining a value for the temperature dependent parameter. At the same time, they added a linear term to the equation to extend the usefulness of their equation into higher concentrations. Jones and Wood (78) added an empirical term to the Owen-Brinkley equation that had a dependence in concentration to the 1.5 power for similar reasons, and Gibbard (79) developed a similar equation with 3 or 4 empirical terms with integer powers of concentration. These procedures yield equations which are too complicated to be convenient to use mathematically, even with simplifications, and their forms include parameters which cannot be related meaningfully to conditions in the solution over most of the concentration range where data can be collected. Further problems are encountered when these equations need to be differentiated to obtain partial molal quantities. The equation forms used in this work avoid these problems with no loss in

fitting accuracy when compared to the fitting accuracies of other methods. At the same time, these equation forms are able to represent the data to the limits of accuracy found in the original data.

One of the principal uses of the fitted equation for the heat content data is to extrapolate the experimental results to infinite dilution. For this reason, previous workers have included the theoretical equation for apparent molal heat contents in the equation used to extrapolate the data, since the Debye-Huckel equation should apply in very dilute solutions. The ability of the 7 term fitted equation to extrapolate to infinite dilution is shown in Figures 11 through 16. The particular details of the construction and the error analysis of these figures has been discussed in Chapter 4. The errors in the extrapolations are no greater than systematic errors obtained by other methods of extrapolation, and the 7 term fitted equation provides a consistent method of extrapolation that minimizes differences in extrapolation errors among most of the salts considered in this work.

The use of multiples of 0.25 as powers of concentration for heat content fitting equations is without precedent in the literature. Its use in this work was initiated directly as a result of a search for an equation form that could fit the data over the entire concentration range within experimental error. The fitting procedure did indicate the need

for a term in the square root of concentration, and this term exists in most forms of equation developed from modern theoretical studies, but no theory exists to explain the occurrence of most higher multiples of 0.25 as powers of concentration. Any theory that could explain the theoretical dependence of heat properties on an extended series of quarter powers would need to take into consideration all of the different processes that occur in the solution over the wide range of concentration covered by the fitting equation. Because of all of the possible hydration, solvation, and complexing processes that come into equilibrium in the solution at various concentrations, no simple rigorous theory to explain the 0.25 power multiples can be expected.

B. Interpretation of Heat Data

The apparent molal heat content, ϕ_L , the apparent partial molal heat contents for the solute, $\bar{L}_2$, and the solvent, $\bar{L}_1$, are shown in Figures 5 through 7 for the nitrates and in Figures 8 through 10 for the perchlorates. The first two properties listed above are also plotted as a function of atomic number for both the nitrates and perchlorates in Figures 17 through 20. For Figures 17 through 20 the properties are plotted at $0.25m^{1/2}$ increments from $0.25m^{1/2}$ to $2.00m^{1/2}$.

Combining data from the work of Pepple (13) with the data in this work, six sets of data for salts with common cations are available that were obtained by the same experi-

mental techniques and have about the same degree of accuracy. These six sets of data are for Nd, Sm, Gd, Dy, Er, and Lu cations, with Cl, NO₃, and ClO₄ anions being used to make up the salts. The data for the chlorides was refitted to a 7-term-or-less equation of the form used for ϕ_L properties of the nitrates and perchlorates. Plots of ϕ_L , $\bar{L}_1$, and $\bar{L}_2$ as a function of the square root of molality for each of the six cations compared are given in Figures 21 through 38. As discussed in Chapter 4, the differences in equation forms for rare earth salts with different anions may introduce an error of ± 10 calories between the salt equations.

The behavior of ϕ_L , $\bar{L}_1$, and $\bar{L}_2$ at concentrations of less than $0.1m^{1/2}$ will be dominated by the electrostatic effects, and the expanded form of the Debye-Huckel equation will apply in this region. The positive curvature of the equation will be determined by the value of the mean distance of closest approach parameter, a , used in the expanded form of the Debye-Huckel equation. Mohs (14) has discussed the behavior of La(NO₃)₃ and La(ClO₄)₃ heat properties in this region. He fitted an Owen-Brinkley equation, in which the mean distance of closest approach was allowed to vary, to his extrapolated experimental data equations for these two salts. The former salt could be fitted fairly well in the dilute region if the value of the mean distance of closest approach parameter is set at about $4A$. The perchlorate salts could be fitted well

Figure 17. ϕ_L values of nitrate solutions vs. atomic number at various concentrations in $m^{1/2}$ at 25°C

Figure 18. $\bar{L}_2$ values of the solute in nitrate solutions at various concentrations in $m^{1/2}$ at 25°C

Figure 19. ϕ_L values of perchlorate solutions vs. atomic number at various concentrations in $m^{1/2}$ at 25°C

Figure 20. $\bar{L}_2$ values of the solute in perchlorate solutions at various concentrations in $m^{1/2}$ at 25°C

Figure 21. Relative apparent molal heat contents for neodymium salt solutions at 25°C

Figure 22. Relative partial molal heat contents of solvent for neodymium salt solutions at 25°C

Figure 23. Relative partial molal heat contents of solute for neodymium salt solutions at 25°C

Figure 24. Relative apparent molal heat contents for samarium salt solutions at 25°C

Figure 25. Relative partial molal heat contents of solvent for samarium salt solutions at 25°C

Figure 26. Relative partial molal heat contents of solute for samarium salt solutions at 25°C

Figure 27. Relative apparent molal heat contents for gadolinium salt solutions at 25°C

Figure 28. Relative partial molal heat contents of solvent for gadolinium salt solutions at 25°C

Figure 29. Relative partial molal heat contents of solute for gadolinium salt solutions at 25°C

Figure 30. Relative apparent molal heat contents for dysprosium salt solutions at 25°C

Figure 31. Relative partial molal heat contents of solvent for dysprosium salt solutions at 25°C

Figure 32. Relative partial molal heat contents of solute for dysprosium salt solutions at 25°C

Figure 33. Relative apparent molal heat contents for erbium salt solutions at 25°C

Figure 34. Relative partial molal heat contents of solvent for erbium salt solutions at 25°C

Figure 35. Relative partial molal heat contents of solute for erbium salt solutions at 25°C

Figure 36. Relative apparent molal heat contents for lutetium salt solutions at 25°C

Figure 37. Relative partial molal heat contents of solvent for lutetium salt solutions at 25°C

Figure 38. Relative partial molal heat contents of solute for lutetium salt solutions at 25°C

using a value of 7A. The same parameters can be used for Nd salts with the same anions, which have similar ϕ_L values at low concentrations. Spedding and coworkers (12,95) have listed the values of mean distance of closest approach, based on various transport and thermodynamic properties, for various rare earth chlorides as being about 6A. In Figure 21, the ϕ_L values of NdCl_3 approach those of $\text{Nd}(\text{NO}_3)_3$ as concentration decreases toward very dilute values. The curvature of the chloride heat content equation would thus seem to correspond to a value of 4A. At the same time, nitrates, such as $\text{Sm}(\text{NO}_3)_3$, shown in Figure 24, shows a limiting slope corresponding to 4A but with a very significant downturn of the experimental data equation near $0.1\text{m}^{1/2}$. This situation suggests that there are sources of heat for solutions in this concentration range which are not electrostatic in nature, and are not therefore included in the Debye-Huckel theorem. This precludes the possibility of assigning accurate mean distance of approach parameter values on the basis of heat data.

The non-electrostatic effects become more strongly manifested at higher concentrations. Several authors (96,97,98) have measured the experimental stability constants of mononitrate complexes of the rare earths at an ionic strength of 1.00. Although the values change for solutions at different ionic strengths, the trends across the series for these sta-

bility constants correlates closely with the non-electrostatic deviations of the nitrate heat data in this work. There is also a correlation that can be noticed between the trend in the values of $\bar{\phi}_L$ across the series in Figure 17 at values of $m^{1/2}$ less than or equal to 1.25, and the heats of formation of rare earth mono-EDTA, mono-diglycolate and dipicolinate complexes measured by Grenthe (99). While the trends are similar, drawing conclusions for the trend is risky, unless a lot of other data collaborates the similarities.

At higher concentrations ($m^{1/2} > 1.25$), the nitrate solution $\bar{\phi}_L$ values start to rise sharply similar to the way they do for salts with other anions. This can be inferred as due to disruption of outer spheres of hydration, and the formation of complexes of the cation with more than one anion. The $\bar{L}_1$ values given in Figure 9 for the perchlorates, remain within 50 calories per mole of each other at all concentrations. This would be indicative of the fact that the solvent plays about the same role in the structure for all of the perchlorates. At the same time, the $\bar{L}_1$ values for the nitrates show wide deviation for different cations in Figure 6, and wide deviation from the other common cation solutions as shown, for example, in Figure 22.

The most significant pattern of behavior for the perchlorates occurs as a function of atomic number, as displayed

in Figure 19. This pattern of behavior has also been observed for the heat properties of the chlorides (13) and in other properties as well (15,17,19). The downward trend at each end of the series is the result of energy stabilization that occurs as the size of the cation decreases and the size of the total hydration sphere increases around it in response to the increased charge density. The increase that occurs between approximately neodymium and terbium is attributed to a change in the inner hydration sphere where 9 solvent molecules exist for the salts at the left end of the series and 8 solvent molecules exist in the series at the right. In the middle region, the ions exist in equilibrium between the two forms. For the perchlorates this two series effect has a maximum spread of 1000 calories in the ϕ_L data across the series and remains fairly constant above $1.0m^{1/2}$.

The existence of the different inner spheres at each end of the series has recently been confirmed by x-ray scattering studies of aqueous rare earth solutions. Martin (100) has found that the inner coordination sphere contains 9 waters in concentrated $PrCl_3$ solutions, while it is 8 in concentrated $ErCl_3$, $TbCl_3$, and $Dy(ClO_4)_3$ solutions. He also found that it is 8 for $ErCl_3$ solutions near $0.8m$.

The behavior of the perchlorates between $0.50m^{1/2}$ and $1.5m^{1/2}$ is not easily correlated with any pattern of microscopic behavior. Evidence for bond formation between various

cations and perchlorate ions in solution has been reported which has been interpreted in terms of a weak rare earth mono-perchlorate complex (101,102). A weak ion pair for ferric ions and perchlorate ions has also been postulated (103). Attempts to observe the interaction between rare earth cations and perchlorate ions spectroscopically were indecisive. P. Krumholz (104) reported that there was no evidence discernible for complexes at low concentrations on the basis of molar absorptivities of solution species in the visible region. M. M. Jones and coworkers (105) examined rare earth perchlorate solutions with Raman spectra techniques and reported that if any ion associations exist they must be very weak.

At high concentrations, the only other effect observed is the increase in heat content most likely due to changes in outer sphere complexes of the cations and anions.

Attempts to explain the difference in heat values between rare earth chlorides and perchlorates at intermediate concentrations is also inconclusive. Where stability constants for rare earth or transuranium cations with nitrate, chloride and perchlorate anions have been measured (96,106,107), results indicate a small stability constant for the chlorides and the perchlorates. In Figure 22 and the $\bar{L}_1$ graphs that follow, the $\bar{L}_1$ data indicates that the heat content of the solvent is very similar for the perchlorate and

chloride solutions. The chloride ϕ_L values show the same two series effect as a function of atomic number as was observed for the perchlorates, but with a higher heat content.

This higher heat content for the chlorides begins to be apparent at concentrations of about $0.05m^{1/2}$. If the mean distance of closest approach parameters listed by Spedding and coworkers (12,95) are used in an Owen-Brinkley type of heat content equation that is compared to experimental heat content curves, different behavior is observed for the chlorides than for the perchlorates. For the chlorides, the experimental heat content equations deviate toward larger ϕ_L values than predicted by the Owen-Brinkley equation, while for the perchlorates, the experimental heat content curve deviates toward smaller ϕ_L values as concentration increases. This difference remains fairly constant across the atomic number series with the two series effect remaining small compared to the heat content difference between chlorides and perchlorates, implying that this effect is not mainly dependent on the cation. The difference in behavior between the chloride and the perchlorate is thus most likely due to differences in anion interactions for the different salts. At the same time, the heat data is not sensitive enough to distinguish whether the anion is involved with the cation as in weak ion pairs or whether it is totally independent of the cation.

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