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SOME THERMODYNAMIC PROPERTIES OF AQUEOUS RARE-EARTH CHLORIDE SOLUTIONS

by

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I. INTRODUCTION

During the past several decades a large number of research workers have been occupied with the task of elucidating the complex nature of electrolytic solutions, and in doing so several approaches intended to clarify solution phenomena were developed. Foremost among these methods is the systematic study of solution properties employing the methods of classical thermodynamics.

Classical thermodynamics is an invaluable tool with which it is possible to evaluate properties of a system under equilibrium conditions. The relationship of a system's initial state to that of some future state can be deduced exactly from the first and second laws of thermodynamics. However, the prediction of these properties depends on a complete knowledge of the initial state and evades any reference as to how the future state was arrived at or to the rate at which this state was achieved.

Experimentally the thermodynamic approach is limited to the measurements of macroscopic observables; no assumptions need to be made about the microscopic structure of the system. The theoretical interpretation and derivation of thermodynamic quantities, which require a knowledge of the individual particles that constitute a system, is left to the study of quantum and statistical mechanics.

A complete theoretical explanation of electrolytic solution properties must take into account the interactions among the various ionic species and the solvent molecules. The complexity of the mathematical formulation of such a theory is immediately realized when factors which affect the behavior of a solution are known. For instance the ionic size and charge, which contribute to long-range interionic forces acting in the solution, and short-range interactions of ions and solvent molecules resulting in ion solvation and ion association are several factors that must be considered. Variation of concentration, temperature, pressure and dielectric constant of the solvent further complicate any attempt to derive a suitable relation which will predict solution properties.

A theory, considering interionic forces, proposed by Debye and Hückel (1) has won general acceptance as the correct theoretical interpretation of extremely dilute electrolytic solutions. Attempts have been made to extend its validity to solutions of higher concentrations but without much success. It has been realized that in more concentrated solutions the electrostatic interionic forces are no longer the predominating factor; short-range effects due to ion-ion and ion-solvent interactions begin to manifest themselves and in some cases overshadow the electrostatic effects.

Aqueous solutions containing 1-1 valence type electrolytes have been extensively investigated; however studies of polyvalent electrolytes in solution have been mainly restricted to 1-2, 2-1 and 2-2 valent types. While the properties of very dilute uni-uni valent electrolytic solutions have been successfully predicted by the Debye-Hückel theory, the solutions of polyvalent electrolytes show greater deviation from the theory, and in some cases show no agreement at all. The greater deviation is attributed to the fact that many polyvalent electrolytes tend to hydrolyze and associate more readily, even in very dilute solutions.

Studies of higher valence type electrolytes have been fragmentary, probably because of their undesirable properties exhibited in solution. The hydrolysis reactions, the degree of ionic solvation and the amount of ionic association make any theoretical account of such solutions a formidable task. Investigations of these solutions, however, are valuable because they provide a strenuous test for any theory which takes into account charge effects of the ions.

Of all the tri-valent and tetra-valent cation systems the lanthanide elements are a natural choice for experimental studies. In combination with most strong acids they form soluble salts; dissolved in water they dissociate into the tri-valent rare-earth cations and the anions of the strong acid. Relative to other tri-valent and tetra-valent cations in solution the rare-earth ions tend to hydrolyze less because of their greater basicity, and hence, present a simpler picture of their aqueous chemistry.

As the atomic number increases in the series from lanthanum to lutetium, the additional electrons fill the 4f orbital which is well shielded by closed orbitals surrounding it. The chemical properties are unaffected by these inner electron changes because of the shielding. As the nuclear charge increases with atomic number the electron orbitals are attracted inward, resulting in a gradual decrease in atomic radius, which is known as the "Lanthanide Contraction". Thus the rare earths also offer a system for studying the effect of changing ionic size on solution properties.

Until recently the rare earths, due to their chemical similarities, were not available in the amount and the purity needed for extensive experimental study. The separation of kilogram quantities of spectroscopic pure rare earths has been accomplished through ion exchange techniques (2, 3, 4, 5) at the Ames Laboratory of the Atomic Energy Commission. As a result, the investigation of solution properties of rare-earth salts was initiated at this laboratory as a part of an extensive program to study the physical and chemical properties of rare-earth metals and their compounds. Thus far investigations have been carried out on conductances, transference numbers, activity coefficients, solubilities, partial molal volumes and partial molal compressibilities (6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17) for various rare-earth salts. The heats of solution of some rare-earth metals and their chlorides (18, 19, 20) and the heats of dilution of several rare-earth nitrates and chlorides (21) have also been determined. This work has been reviewed up to 1957 by Spedding and Atkinson (22).

Changes in energy are closely associated with alterations of the microscopic structure of a solution. Thus the separation of ionic species when a solution is diluted or solvent dissociation due to hydrolysis of electrolytes result in changes of energy. In solutions of incompletely dissociated electrolytes the ionic dissociation will affect the thermal properties. Ionic association and solvation also affect the energy and are a function of the concentration. It would be ideal if certain electrolytes were found where each of these effects could be studied independently. Unfortunately such groups do not exist; so at best, solutions in which one or two of these effects predominate need to be studied systematically in order to obtain a clear understanding of their role in determining solution properties.

Measurements of the heats of dilution of rare-earth salts offer one way in which these effects may be studied. Usually the heats of dilution are expressed in terms of the related thermodynamic property, ϕ_L, the relative apparent molal heat content. Hence, any thermal effects, which accompany energy changes in solutions, are reflected in the relative apparent molal heat content.

In extremely dilute solutions the rare-earth salts are assumed to be completely dissociated, and the electrical interactions between the ions account for the observed deviations from ideal behavior. The values for ϕ_L in this concentration region are correctly predicted by the Debye-Hückel theory. However, as the concentration increases ionic association and changes in ionic solvation become important, and are noted in the ϕ_L values which begin to deviate from the theoretical predictions.

It would be advantageous, then, to obtain thermal data of electrolytic solutions in a concentration region where their values begin to deviate from the theoretical predictions. This work is concerned with the measurements of heats of dilution of some rare-earth chlorides. The relative apparent molal heat contents are determined from the heats of dilution and compared with existing heat of solution data.

II. HISTORICAL REVIEW

As calorimetric investigations changed from rather crude to more exact determinations of energy quantities, calorimeters have become more complex. Their design and construction not only depend upon the particular chemical or physical process to be studied, but also on the degree of accuracy that is required. Thus numerous types of calorimaters have been built to meet these needs ever since thermal measurements first began. An extensive survey of the field of calorimetry is beyond the scope of this thesis. More complete treatments are given by White (23), for the general theory; Rossini (24), for bomb calorimetry; Sturtevant (25), for applications to organic chemistry; and Swietoslawski (26), for microcalorimetry. A general review concerning that part of the field encountered in this research will be discussed, namely, adiabatic differential calorimetry as applied to the measurements of heats of dilution.

Person (27) and later Richards (28) originally founded the basis of adiabatic calorimetry. The essential feature of the adiabatic calorimeter is the elimination of the thermal head between the calorimeter and its surroundings. In many other calorimeters the presence of a thermal head requires the calculation of the thermal leakage to or from the calorimeter using Newton's law of cooling.

The main advantages of the adiabatic method are: (1) errors due to the thermal leakage modulus and the deviation of the heat exchange from Newton's law are reduced; (2) the maintenance of a small thermal head reduces convection in the air gap above the calorimeter liquid, which does not follow Newton's cooling law; and (3) measurements of small quantities of heat and processes of long duration are handled more effectively. In these cases the thermal leakage in non-adiabatic calorimeters may be larger than the measured quantity of heat; this would necessitate a very accurate determination of the leakage.

In 1926 Bjerrum (29) initiated a great deal of interest in the thermal properties of dilute electrolytic solutions when he showed that the relative heat contents, and hence the heats of dilution, could be derived from the Debye-Hückel theory. In order to bear out his claims Bjerrum used the data of Richards and Rowe (30, 31), but did not find any agreement with the theory. Richards and Rowe used an adiabatic calorimeter to measure the heats of dilution of several 1-1 valence type electrolytes down to a concentration of 0.139 molal. Adiabatic conditions were maintained to within a few hundredths of a degree, and the temperature was measured with a Beckmann thermometer.

Nernst and Orthmann (32) employed a non-adiabatic differential calorimeter, and succeeded in measuring heats of dilution down to a concentration of 0.1 molar and in some cases as low as 0.03 molar. Temperature measurements were made with a 20 junction iron-constantan thermopile, which had a sensitivity of 0.121 calories per millimeter deflection of a galvanometer. Later Nernst and Orthmann (33) repeated this work using an improved differential calorimeter with an insulated jacket. The size of their thermopile was increased to 100 junctions having a sensitivity of 3.18×10^{-3} calories per millimeter galvanometer deflection. The concentration range was extended to 0.004 molar, and the data obtained were in qualitative agreement with the Debye-Hückel theory.

Modification of the Joule (34) and Pfaundler (35) twin calorimeter technique by Richards and Gucker (36) marked the beginning of accurate thermal measurements in dilute solutions. The twin calorimeter essentially consists of two calorimeter containers as nearly identical in construction as possible, and having heaters of equal resistances connected in series. If both containers change temperature at nearly the same rate during an experiment, the thermal leakages of the containers will approximately be equal. Thus by calibrating the calorimeter by suitable rating periods any error due to thermal leakage can accurately be determined. Richards and Gucker applied the adiabatic method to the twin calorimeters when they measured the heat capacities of several solutions and virtually eliminated the need for heat leak determinations.

The first accurate heats of dilution measurements employing an adiabatically jacketed twin calorimeter were conducted by Lange and Messner (37). The calorimeter consists of a two liter Dewar flask partitioned into two equal parts by a 1000 to 1500 junction iron-constantan thermopile. Temperature differences between the two halves of 2×10^{-7} degrees can be measured using a high sensitivity galvanometer, giving the system a sensitivity of 2×10^{-4} calories per millimeter galvanometer deflection. The adiabatic jacket is maintained to within 0.001° C. of the calorimeter temperature. The heats of dilution of several 1-1, 1-2, and 2-2 valence type electrolytes were measured to a concentration of 1×10^{-5} molal; however, only qualitative agreement with the limiting values of the Debye-Hückel theory was obtained. A complete description of the apparatus and dilution experiments is given by Lange and Robinson (38).

Differences between the experimental limiting slopes obtained by Lange and those predicted by theory were due largely to the difficulty in reading the slopes from plots of heats of dilution versus the square root of the concentration. It was not until the adaptation of the chord-area method of Young and Vogel (39) that better agreement with theory was obtained. In 1936 Young and Groenier (40) applied this method to the sodium chloride data of Gulbransen and Robinson (41), and obtained limiting slopes which agreed within five per cent of the theoretical. Later Young and Seligmann (42) treated the heat of dilution data of a number of 1-1 and 1-2 valence type electrolytes, and found good agreement with theory. However, the existing data for 2-2 valence type electrolytes did not lead to the predicted limiting values.

Wallace and Robinson (43) measured the heats of dilution of sodium sulfate, and using a slight modification of the chord-area method obtained good agreement with limiting values predicted by theory. Using existing data for 2-2 valence type electrolytes Robinson and Wallace (44) applied their modified method to find ϕ_L values. Although no attempt had been made to derive the limiting value, the authors felt that better agreement with the Debye-Hückel limiting law existed than previously reported. A detailed account of this method will be given in the theory section.

Another modification of the twin calorimeter for heat of dilution measurements was developed by Gucker et al. (45). Their apparatus essentially consists of two identically made containers enclosed in a jacket which is submerged in a water bath. Adiabatic conditions are maintained between the bath and containers by means of two control thermals connected in series. A 60 junction copper-constantan thermopile fits into a thin well in the side of each container and is connected to a semi-automatic recording potentiometer and a highly sensitive galvanometer. The system has a sensitivity of 6 x 10^{-4} calories per millimeter deflection of the galvanometer. The main advantages of this calorimeter are the reduction of heat conduction between the containers and the utilization of an automatic device for maintaining adiabatic control. The apparatus has been used mainly for heat of dilution measurements of nonelectrolytic solutions.

Recently Lange(46) has summarized the heats of dilution data and the limiting slopes for the various valence type electrolytes. While there is general agreement with theory for the majority of salts containing a uni-valent ion, the 2-2, 2-3 and 2-4 valence type electrolytes give values several times larger than predicted. The 3-3 valence type electrolytes that have been investigated show a value eight times smaller than the expected value. However, it should be noted that hydrolysis and ionic association may become important factors influencing the heats of dilution of higher valence type electrolytes even in dilute solutions. This may be a reason for the poor agreement between theory and experiment.

III. THEORY

A. General Thermodynamics

Thermodynamic systems are completely described in terms of their thermodynamic coordinates. For systems of constant mass and composition in unvaried external fields these coordinates are pressure, volume and temperature when only pressure-volume work is considered. Only two of the three variables are independent, that is, any coordinate is a function of the remaining two. However, such systems in which the compositions of their components vary are not described by two of these coordinates alone; additional ones are needed to specify its state. The masses, or more usually the numbers of moles, of each component serve as the supplementary coordinates.

In general, thermodynamic quantities are divided into two groups: extensive and intensive. An extensive quantity depends on the mass in such a way that if the system is reduced to half its original mass then the value of the extensive quantity is also halved; those quantities which remain unchanged are intensive. Thus volume and the numbers of moles are extensive while temperature and pressure are intensive.

If the change of any extensive quantity depends solely on its value in the initial and final states and not on the manner in which the final state was achieved, then the quantity is called a thermodynamic function. These functions possess two important mathematical properties. First, their differentials are exact, that is, their definite integral has a unique value which depends only on the limits of the integral and not on the path of integration. Second, thermodynamic functions are homogeneous of degree one. A function, $G(x_1, x_2, \ldots, x_m)$, is homogeneous if

$$G(kx_1, kx_2, \ldots, kx_m) = k^nG(x_1, x_2, \ldots, x_m), \qquad \text{(III-1)}$$

where k is a positive constant; n is a number indicating the degree of homogeneity and $x_1, x_2, \ldots, x_m$ are the variables.

There are various methods employed by the chemist to determine energy changes in chemical systems. One of the earliest and most direct is measuring the heat evolved or absorbed during a chemical reaction and relating it to changes in energy.

The first law of thermodynamics states that an increase in the internal energy of a system, of constant mass and composition, is equal to the heat absorbed by the system plus the work done on the system by the surroundings. Mathematically, the first law is expressed as

$$\Delta E = q - w, \qquad \text{(III-2)}$$

where ΔE is the change in the internal energy; q is the heat absorbed or evolved; and w is the work performed on or by the system. By convention q is positive when heat is absorbed and negative when it is evolved by the system. Work done by the system on the surroundings is taken as positive and is considered negative when done on the system. From observation the internal energy is found to be a thermodynamic function; however, heat and work are not.

During a process where all work other than pressure-volume work is excluded the first law becomes

$$\Delta E = q - PdV, \qquad \text{(III-3)}$$

where P is the pressure and V is the volume. When the process is also conducted at constant volume, the PdV term in equation III-3 vanishes and

$$\Delta E = q_v, \qquad \text{(III-4)}$$

where q_v is the quantity of heat at constant volume. If the same process were done at constant pressure instead of constant volume, then

$$\Delta E = q_p - PdV \qquad \text{(III-5)}$$

where q_p is the quantity of heat at constant pressure. Equation III-5 may also be stated as

$$E_f - E_i = q_p - P(V_f - V_i), \qquad \text{(III-6)}$$

where the subscripts i and f refer to the initial and final states of the system respectively. If equation III-6 is rearranged, then

$$q_p = (E_f + PV_f) - (E_i + PV_i). \qquad \text{(III-7)}$$

The amount of thermal energy at constant pressure, therefore, measures directly the change in the quantity (E + PV) in passing from the initial to the final state. It is convenient at this point to define a quantity H, the enthalpy, as

$$H = E + PV, \qquad \text{(III-8)}$$

so that equation III-7 becomes

$$q_p = H_f - H_i = \Delta H. \qquad \text{(III-9)}$$

Clearly, H is also a thermodynamic function since it is characterized by E, P and V which depend only on the state of the system and not on the manner in which it was achieved.

B. Partial Molal Heat Contents

1. Definitions and properties

If G is any extensive thermodynamic property, then the partial molal quantity of G is

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,\, P,\, n_j} = \overline{G}_i, \qquad \text{(III-10)}$$

where n_j represents all the components except the i-th component. $\overline{G}_i$ refers to the increase in total G when one mole of component i is added to an infinite amount of a solution at constant temperature and pressure with all other components held constant.

An important property of homogeneous thermodynamic functions is related to partial molal quantities by the use of Euler's theorem. At constant temperature and pressure any extensive thermodynamic property is only a function of the numbers of moles of the components. Hence,

$$G(n_1, n_2, \ldots, n_m) = n_1\left(\frac{\partial G}{\partial n_1}\right)_{n_j} + n_2\left(\frac{\partial G}{\partial n_2}\right)_{n_j} + \ldots + n_m\left(\frac{\partial G}{\partial n_m}\right)_{n_j}. \qquad \text{(III-11)}$$

The following discussion of thermodynamic relationships will be restricted to systems of two components since these were the systems encountered in this work. Equation III-11 then reduces to

$$G(n_1, n_2) = n_1\overline{G}_1 + n_2\overline{G}_2. \qquad \text{(III-12)}$$

Another useful quantity is the apparent molal quantity, ϕ_G, which is defined as

$$\phi_G = \frac{G - n_1\overline{G}_1^o}{n_2}. \qquad \text{(III-13)}$$

where $\overline{G}_1^o$ is the partial molal quantity in an arbitrary reference state.

In view of equations III-12 and III-13 the enthalpies may be stated as

$$H(n_1, n_2) = n_1\overline{H}_1 + n_2\overline{H}_2, \tag{III-14}$$

and

$$H(n_1, n_2) = n_1\overline{H}_1^o + n_2\phi_H. \tag{III-15}$$

Since no absolute values for the enthalpy can be determined, it is convenient to define the relative enthalpy as

$$L = H - H^o, \tag{III-16}$$

where H^o is the enthalpy in some arbitrarily chosen reference state, usually infinite dilution. The term L is commonly referred to as the apparent molal heat content.

Equations III-14 and III-15 then become

$$L(n_1, n_2) = n_1\overline{L}_1 + n_2\overline{L}_2, \tag{III-17}$$

and

$$L(n_1, n_2) = n_1\overline{L}_1^o + n_2\phi_L. \tag{III-18}$$

However,

$$\overline{L}_1^o = \overline{H}_1^o - \overline{H}_1^o = 0, \tag{III-19}$$

so that equation III-18 becomes

$$L(n_1, n_2) = n_2\phi_L. \qquad \text{(III-20)}$$

2. Evaluation of partial molal heat contents

Any infintesimal change in L at constant temperature and pressure may be represented as

$$dL(n_1, n_2) = \left(\frac{\partial L}{\partial n_1}\right)_{n_2} dn_1 + \left(\frac{\partial L}{\partial n_2}\right)_{n_1} dn_2$$

$$= \bar{L}_1 dn_1 + \bar{L}_2 dn_2. \qquad \text{(III-21)}$$

If the total differential of equation III-17 is found, then

$$dL(n_1, n_2) = n_1 d\bar{L}_1 + \bar{L}_1 dn_1 + n_2 d\bar{L}_2 + \bar{L}_2 dn_2. \qquad \text{(III-22)}$$

Equating equations III-21 and III-22

$$n_1 d\bar{L}_1 + n_2 d\bar{L}_2 = 0. \qquad \text{(III-23)}$$

Thus if one relative partial molal heat content is known, equation III-23 can be integrated to find the other.

The evaluation of the relative partial molal heat contents from the apparent molal heat content is somewhat simpler. If equation III-20 is differentiated with respect to n_2 holding n_1 fixed, then

$$\left(\frac{\partial L}{\partial n_2}\right)_{n_1} = \bar{L}_2 = n_2\left(\frac{\partial \phi_L}{\partial n_2}\right)_{n_1} + \phi_L. \qquad \text{(III-24)}$$

Combining equations III-17 and III-20

$$n_2\phi_L = n_1\bar{L}_1 + n_2\bar{L}_2, \qquad \text{(III-25)}$$

and on rearrangement

$$\bar{L}_1 = \frac{n_2}{n_1}(\phi_L - \bar{L}_2). \qquad \text{(III-26)}$$

Substituting the value for $\bar{L}_2$ from equation III-24 into equation III-26

$$\bar{L}_1 = \frac{-n_2^2}{n_1}\left(\frac{\partial\phi_L}{\partial n_2}\right)_{n_1}. \qquad \text{(III-27)}$$

3. Relation of partial molal heat contents to heats of dilution

When a solution of n_1 moles of solvent and n_2 moles of solute is mixed with n_1^* moles of pure solvent, at constant temperature and pressure, the resulting heat effect, q, is equal to ΔH_{dil}, the heat of dilution. This enthalpy change is the difference between the enthalpy of the system in its final and initial states.

The enthalpy in the initial and final states of the system are:

$$H^i = n_1\bar{H}_1 + n_2\bar{H}_2 + n_1^*\bar{H}_1^o, \qquad \text{(III-28)}$$

and

$$H^{f} = (n_1 + n_1^*)\bar{H}_1' + n_2\bar{H}_2', \qquad \text{(III-29)}$$

respectively. Thus,

$$q = \Delta H_{dil} = H^{f} - H^{i} \qquad \text{(III-30)}$$

or using equations III-28 and III-29

$$\Delta H_{dil} = (n_1 + n_1^*)\bar{H}_1' + n_2\bar{H}_2' - n_1\bar{H}_1 - n_2\bar{H}_2 - n_1^*\bar{H}_1^{o}. \qquad \text{(III-31)}$$

By adding and subtracting $n_1\bar{H}_1^{o}$ and $n_2\bar{H}_2^{o}$, and in view of equation III-16, the right side of equation III-31 becomes

$$\Delta H_{dil} = (n_1 + n_1^*)\bar{L}_1' + n_2\bar{L}_2' - n_1\bar{L}_1 - n_2\bar{L}_2, \qquad \text{(III-32)}$$

or from equation III-25

$$\Delta H_{dil} = n_2\phi_L' - n_2\phi_L. \qquad \text{(III-33)}$$

Usually heats of dilution are determined per mole of solute, hence, both sides of equation III-33 are divided by n_2 so that

$$\Delta H_D = \phi_L' - \phi_L, \qquad \text{(III-34)}$$

where ΔH_D is the heat of dilution per mole. The enthalpy change for a dilution process then may be determined by finding the difference between the relative apparent molal heat contents of the initial and final solutions.

4. Relation of partial molal heat contents to heats of solution

If n_2 moles of pure substance are dissolved into n_1 moles of pure solvent, at constant temperature and pressure, the observed heat is the integral heat of solution, ΔH_{sol}. The enthalpy of the system prior to mixing is

$$H^i = n_1 H_1^\bullet + n_2 H_2^\bullet, \qquad \text{(III-35)}$$

where $H_1^\bullet$ and $H_2^\bullet$ are the enthalpies of pure solvent and solute respectively. The enthalpy of the system in its final state is

$$H^f = n_1 \overline{H}_1 + n_2 \overline{H}_2. \qquad \text{(III-36)}$$

The enthalpy change can then be represented as

$$\begin{aligned}\Delta H_{sol} &= H^f - H^i \\ &= n_1 \overline{H}_1 + n_2 \overline{H}_2 - n_1 H_1^\bullet - n_2 H_2^\bullet, \qquad \text{(III-37)}\end{aligned}$$

or by adding and subtracting $n_1 \overline{H}_1^o$ and $n_2 \overline{H}_2^o$ as before, equation III-37 becomes

$$\begin{aligned}\Delta H_{sol} &= n_1(\overline{H}_1 - \overline{H}_1^o) + n_2(\overline{H}_2 - \overline{H}_2^o) \\ &\quad - n_1(H_1^\bullet - \overline{H}_1^o) - n_2(H_2^\bullet - \overline{H}_2^o). \qquad \text{(III-38)}\end{aligned}$$

Since the infinitely dilute solution is the chosen reference state, then

$$\underline{H}_1^{\bullet} = \bar{H}_1^{o}. \qquad \text{(III-39)}$$

Hence, equation III-38 becomes

$$\Delta H_{sol} = n_1\bar{L}_1 + n_2\bar{L}_2 - n_2L_2^{\bullet} \qquad \text{(III-40)}$$

where $L_2^{\bullet}$ is the integral heat of solution at infinite dilution. Using equation III-25

$$\Delta H_{sol} = n_2\phi_L - n_2L_2^{\bullet}. \qquad \text{(III-41)}$$

Usually the heats of solution are determined per mole of solute, hence, equation III-41 becomes

$$\Delta H_S = \phi_L - L_2^{\bullet}, \qquad \text{(III-42)}$$

where ΔH_S is the integral heat of solution per mole of solute.

5. Experimental determination of partial molal heat contents

When a solution of molality m_1, containing n_2' moles of salt, is diluted into pure water, it will give a solution of molality m_2. The heat associated with the dilution is $q_1 - q_0$, where q_1 is the total observed heat and q_0 is the heat generated when the sample holder filled with the solution was opened. If a second solution of molality m_1, containing n_2'' moles of salt, is added to the solution of molality m_2, then a final solution of molality m_3 is obtained; the heat associated with this dilution is $q_2 - q_0$.

From equations III-30 and III-33 q_1 and q_2 may be related to the apparent molal heat contents, i.e.,

$$-(q_1 - q_0) = n_2'\left[\phi_{L(m_2)} - \phi_{L(m_1)}\right], \tag{III-43}$$

and

$$-(q_2 - q_0) = n_2'\left[\phi_{L(m_3)} - \phi_{L(m_2)}\right] + n_2''\left[\phi_{L(m_3)} - \phi_{L(m_1)}\right]. \tag{III-44}$$

The heat quantities are negative because heat was evolved during the dilution processes.

The heats of dilution per mole as given in equation III-34 are

$$\Delta H_{1,2} = \phi_{L(m_2)} - \phi_{L(m_1)}, \tag{III-45}$$

$$\Delta H_{1,3} = \phi_{L(m_3)} - \phi_{L(m_1)}, \tag{III-46}$$

$$\Delta H_{3,2} = \phi_{L(m_2)} - \phi_{L(m_3)}, \tag{III-47}$$

where $\Delta H_{i,k}$ is the heat absorbed when a solution of concentration m_i is diluted to concentration m_k. The quantities

$\Delta H_{1,2}$ and $\Delta H_{1,3}$ are referred to as "long chord dilutions" and $\Delta H_{3,2}$ as a "short chord dilution".

The long chord dilutions may be found by substituting equations III-45, III-46 and III-47 into equations III-43 and III-44. Hence,

$$\Delta H_{1,2} = - \frac{q_1 - q_0}{n_2'}, \tag{III-48}$$

$$\Delta H_{1,3} = - \frac{q_1 + q_2 - 2q_0}{n_2' + n_2''}, \tag{III-49}$$

The short chord dilution may be found by subtracting equation III-49 from equation III-48, i.e.,

$$\Delta H_{3,2} = \Delta H_{1,2} - \Delta H_{1,3}. \tag{III-50}$$

Following the method of Young and his associates (39, 40, 42) and its modification by Wallace and Robinson (43, 44), ϕ_L as a function of $m^{1/2}$ was determined from the various thermal quantities discussed above.

Experimentally it is possible to determine the average slope of ϕ_L versus $m^{1/2}$ between two concentrations. The average slope, $\overline{P}_i$, is found to be

$$\overline{P}_i = \frac{\Delta \phi_L}{\Delta m_i^{1/2}}, \tag{III-51}$$

where the index i refers to a particular solution of concentration m_1. Using equation III-47

$$\overline{P}_i = \frac{\Delta H_{3,2}}{\Delta m_i^{1/2}}. \qquad \text{(III-52)}$$

The true slope at a given concentration would be, in general, a function of $m^{1/2}$, that is,

$$\frac{d\phi_L}{dm^{1/2}} = S = S^o + Bm^{1/2} + Cm \ldots \qquad \text{(III-53)}$$

From equation III-53

$$\Delta\phi_L = \int_{(m_{2,i})^{1/2}}^{(m_{3,i})^{1/2}} S dm^{1/2}, \qquad \text{(III-54)}$$

over the concentration range of $(m_{3,i})^{1/2}$ to $(m_{2,i})^{1/2}$. Substituting equation III-54 into equation III-51

$$\overline{P}_i = \frac{\displaystyle\int_{(m_{2,i})^{1/2}}^{(m_{3,i})^{1/2}} S dm^{1/2}}{(m_{3,i})^{1/2} - (m_{2,i})^{1/2}} \qquad \text{(III-55)}$$

or, neglecting terms higher than Cm,

$$\overline{P}_i = S^o + Bx_i + \frac{C}{3}\left[4x_i - (m_{2,i})^{1/2} (m_{3,i})^{1/2}\right], \qquad \text{(III-56)}$$

where $x_i = \frac{1}{2}\left[(m_{2,i})^{1/2} + (m_{3,i})^{1/2}\right]$.

The value of S at a concentration x_i is

$$P_i = S^o + Bx_i + Cx_i^2. \qquad \text{(III-57)}$$

The difference between equations III-56 and III-57 is

$$P_i - \overline{P}_i = -C \frac{\delta_i^2}{12}, \qquad \text{(III-58)}$$

where $\delta_i = (m_{3,i})^{1/2} - (m_{2,i})^{1/2}$, and

$$\overline{P}_i = S^o + Bx_i + C(x_i^2 + \frac{\delta_i^2}{12}). \qquad \text{(III-59)}$$

If only a two parameter equation is needed to represent S, then $\overline{P}_i = P_i$ and

$$\overline{P}_i = S^o + Bx_i. \qquad \text{(III-60)}$$

Various dilutions were performed and the quantities $\Delta H_{1,2}$, $\Delta H_{1,3}$ and $\Delta H_{3,2}$ were calculated by means of equations III-48, III-49 and III-50. Equation III-52 was then used to determine $\overline{P}_i$. Since several determinations using solutions of the same concentration were carried out, it was possible to obtain averaged values for $\Delta H_{1,2}$, $\Delta H_{1,3}$ and $\overline{P}_i$.

An empirical equation by the method of weighted least squares was obtained using the average $\overline{P}_i$ values. The empirical equation was in the form of either equation

III-59 or III-60 whichever happened to fit the data best. The details of the dilution processes and the application of the least squares will be given in the section on experimental procedure.

The constants found by the least squares method were substituted into equation III-53 which was integrated to give ϕ_L as a function of $m^{1/2}$ for the dilute concentration range. Using this equation the values for $\phi_{L(m_2)}$ and $\phi_{L(m_3)}$ were found for each dilution experiment and were substituted, with the average values of $\Delta H_{1,2}$ and $\Delta H_{1,3}$, into equations III-45 and III-46. In this way two values of $\phi_{L(m_1)}$, which should be identical, could be calculated. Usually it was found that the values did not coincide; if this was the case, an average was determined. When all the values of $\phi_{L(m_1)}$, $\phi_{L(m_2)}$ and $\phi_{L(m_3)}$ were obtained, an unweighted least squares equation of the form

$$\phi_L = am^{1/2} + bm + cm^{3/2} + dm^3 \qquad \text{(III-61)}$$

was determined for the whole concentration studied.

To find $\bar{L}_1$ and $\bar{L}_2$ as a function of $m^{1/2}$ a change of concentration variables must be made in equations III-24 and III-27. Since m is the concentration expressed as moles of solute per 1000 grams of solvent, n_1 and n_2 then become

$$n_1 = \frac{1000}{M_1}, \qquad \text{(III-62)}$$

where M_1 is the molecular weight of the solvent, and

$$n_2 = (m^{1/2})^2. \qquad \text{(III-63)}$$

Therefore, equations III-24 and III-27 become

$$\bar{L}_2 = \frac{m^{1/2}}{2}\left(\frac{\partial \phi_L}{\partial m^{1/2}}\right) + \phi_L, \qquad \text{(III-64)}$$

and

$$\bar{L}_1 = -\frac{m^{3/2}\,M_1}{2000}\left(\frac{\partial \phi_L}{\partial m^{1/2}}\right), \qquad \text{(III-65)}$$

respectively.

It is also possible to determine ϕ_L from heat of solution measurements. If a series of samples of pure solute, n_2', n_2'', ..., is successively dissolved into n_1 moles of solvent, the corresponding heats, q_1, q_2, ..., will be the heats of solution at concentrations m_1, m_2, ...

The integral heat of solution will be

$$\Delta H_S = \frac{\sum_i q_i}{\sum_i n_i}. \qquad \text{(III-66)}$$

An empirical equation determined by the least squares method may be obtained for ΔH_S as a function of $m^{1/2}$. If the integral heat of solution at infinite dilution is known, the equation III-42 may be used to find ϕ_L as a function of $m^{1/2}$.

However, caution must be exercised when equation III-42 is used to determine ϕ_L values. First, $L_2^\bullet$ is found by extrapolating values of ΔH_S to infinite dilution. Such extrapolations could lead to serious errors in $L_2^\bullet$ unless, of course, there are reliable ΔH_S values sufficiently close to infinite dilution. Second, as $m^{1/2}$ approaches zero, ΔH_S approaches $L_2^\bullet$ and ϕ_L becomes very small compared to either ΔH_S or $L_2^\bullet$. In essence then, ϕ_L is the difference between two relatively large numbers and would be liable to large errors if ΔH_S and $L_2^\bullet$ are not accurately known.

An alternate method can be used to compare ϕ_L values obtained from existing heat of solution data to those determined from heats of dilution. In view of equation III-42 it can be seen that the difference between any two heats of solution gives the difference in the corresponding ϕ_L values, that is,

$$\Delta H_S^* - \Delta H_S' = \phi_L^* - \phi_L'. \qquad \text{(III-67)}$$

A series of such differences can then be obtained for the complete concentration range of ΔH_S, hence,

$$\Delta H_S^* - H_S'' = \phi_L^* - \phi_L'', \quad (III-68)$$

$$\Delta H_S^* - H_S''' = \phi_L^* - \phi_L''', \quad (III-69)$$

and so on.

Since the difference between two heats of solution values can be found from existing data, all that needs to be known is the value for ϕ_L^* in order to determine ϕ_L', ϕ_L'', ϕ_L''', etc. The value for ϕ_L^* is obtained from the heat dilution data for that particular salt. Comparisons between ϕ_L values for a number of rare-earth chlorides are given in the Appendix.

6. Theoretical predictions of partial molal heat contents

The behavior of electrolytic solutions based on the assumption of complete dissociation of the solute and the effects of interionic attraction were first considered by van Laar (47). Later Sutherland (48) and Bjerrum (49,50) adopted this viewpoint in their investigations. Hertz (51) and Ghosh (52, 53, 54) attempted to treat the effects of interionic attraction mathematically, but their efforts proved to be inadequate. The problem was analyzed by Milner (55) who showed the correct concentration dependence for the activity coefficient; however, his treatment was involved and not entirely satisfactory.

Debye and Hückel (1) were the first to successfully predict the limiting law for activity coefficients of extremely dilute electrolytic solutions quantitatively. The basic assumptions of their theory can be summarized as follows:

1. Strong electrolytes are completely dissociated into ions in solution.
2. Deviations from ideality are due entirely to coulombic interactions among the ions.
3. The ions are rigid spheres, having a mean distance of closest approach.
4. The solvent is a continuous medium of uniform dielectric constant.
5. An ion, on the average, is surrounded by an excess of oppositely charged ions, which constitutes its ionic atmosphere. This atmosphere is spherically symmetrical in the absence of external fields.
6. The electrostatic potential at a point in a solution can be calculated from Poisson's equation and the Maxwell-Boltzmann distribution law.
7. The principle of linear superposition of fields and the linearized Poisson-Boltzmann equation are valid.

Using these assumptions Debye and Hückel formulated a mathematical expression for the mean ionic rational activity coefficient for extremely dilute solutions, which is given by

$$\log f_{\pm} = \frac{-\frac{1}{2.303\nu}\sum_{i=1}^{p} \nu_j z_j^2 \left(\frac{\pi N \epsilon^6}{1000(DkT)^3}\right)^{1/2} \sqrt{\Gamma}}{1 + a^{o}\left(\frac{4\pi\epsilon^2 N}{1000DkT}\right)^{1/2} \sqrt{\Gamma}},$$

$$= \frac{-\mathcal{S}_{(f)}\sqrt{\Gamma}}{1 + A\sqrt{\Gamma}}, \qquad \text{(III-70)}$$

where $f_{\pm}$ is the mean rational activity coefficient; ν is the total number of ions, of which ν_i are of the i kind with charge z_i; N is Avogadro's number; ϵ is the electronic charge; k is Boltzmann's constant; D is the dielectric constant of the medium; T is the absolute temperature; a^o is the mean distance of closest approach and Γ is the ional concentration. The ional concentration is defined as

$$\Gamma = \sum_{i=1}^{p} c_i z_i^2, \qquad \text{(III-71)}$$

where c_i is the concentration of an ion in moles per liter of solution. Considering the ions as point charges and approaching infinite dilution equation III-70 becomes

$$\log f_{\pm} = -\mathcal{S}_{(f)}\sqrt{\Gamma}. \qquad \text{(III-72)}$$

The relative molal heat content of the solute is related to the activity coefficient, i.e.,

$$\bar{L}_2 = \nu RT^2\left(\frac{\partial \ln f_\pm}{\partial T}\right)_p, \qquad \text{(III-73)}$$

where R is the gas constant. Differentiating equation III-72 with respect to temperature and substituting the result into equation III-73 the limiting law for $\bar{L}_2$ becomes

$$\bar{L}_2 = \mathcal{S}_{(H)}\sqrt{\Gamma} \qquad \text{(III-74)}$$

where $\mathcal{S}_{(H)} = -2.303\,\nu RT^2\,\mathcal{S}_{(f)}\,\frac{3}{2}\left(\frac{1}{T} + \frac{\partial \ln D}{\partial T} + \frac{\alpha}{3}\right)$. The term α is the coefficient of thermal expansion of the solution and is equal to $-\partial \ln\ /\partial T$.

It is convenient to replace the ional concentration by molality. From equation III-71

$$\Gamma = \sum_{i=1}^{p} c_i z_i^2 = c\sum_{i=1}^{p} \nu_i z_i^2. \qquad \text{(III-75)}$$

For very high dilutions c may be replaced by d_0m, where d_o is the density of pure solvent. Hence,

$$\Gamma = d_0 m\sum_{i=1}^{p} \nu_i z_i^2. \qquad \text{(III-76)}$$

Equation III-74 then becomes

$$\bar{L}_2 = \sqrt{d_0}\,S_{(H)}\sqrt{m}, \qquad \text{(III-77)}$$

where $S_{(H)} = \left(\sum_{i=1}^{p} \nu_i z_i^2\right)^{1/2} \mathcal{S}_{(H)}$. It follows from equations III-77 and III-64 that

$$\phi_L = \frac{2}{3}\sqrt{d_0}\, S_{(H)}\sqrt{m}. \qquad \text{(III-78)}$$

A more detailed treatment of the thermodynamic consequences of the Debye-Hückel limiting law is discussed by Harned and Owen (56). Using the values listed in their book, the slope of ϕ_L for 3-1 valence type solutes was calculated to be 6925 for aqueous solutions at infinite dilution.

Since the publication of the Debye-Hückel theory several attempts have been made to extend its validity to solutions of higher concentration. One of the first modifications was performed by Müller (57) and Gronwall _et al_. (58). It consisted of accepting higher terms of the Poisson-Boltzmann distribution function for symmetrical electrolytes. Later La Mer _et al_. (59) obtained an expression for unsymmetrical electrolytes by the same method. Fowler and Guggenheim (60) have pointed out that these extensions are not mathematically self-consistant as shown by the different results obtained from the Debye and Güntelberg (61) charging processes. According to Onsager (62) the Poisson-Boltzmann equation cannot be expected to hold at higher concentrations because the ionic potentials are no longer additive, that is, the principle of linear superposition of fields is no longer valid.

Bjerrum (63) has proposed a theory of ion pair formation and Fuoss and Kraus (64) have extended it to triple ions and quadrapole formation which avoids the difficulties of solving the Poisson-Boltzmann equation. The potential energy function is replaced by a simple Coulomb law. In this way Bjerrum shows that for a distance $r = q = \epsilon^2 |z_i z_j| / 2DkT$, the probability that an i-ion is at a distance r from a j-ion possesses a minimum if the ions are of opposite charge. At distances of r less than q two ions are assumed to be associated. This treatment has been highly successful in interpretating experimental results as a function of the dielectric constant.

Hückel (65) considered ion-solvent interactions in terms of salting-out effects caused by the displacement of ions around a centrally located ion by solvent molecules. He relates this to the change in the dielectric constant of the solution. Essentially his treatment leads to a term, linear in the concentration, which is added to the Debye-Hückel activity coefficient equation. However, this treatment is considered only an empirical extension of the theory. Later Scatchard (66) gave a more comprehensive theory for activity coefficients considering, among other factors, the salting-out effect. The theory gives good agreement with experiment for 1-1 valence type electrolytes, but has not been used extensively because of its mathematical complexity.

Ion-solvent interactions were also taken into account by Stokes and Robinson (67, 68). They suggest that the mean rational ionic activity coefficient of the hydrated ions is predicted by the Debye-Hückel theory. By considering ionic solvation they obtain an expression for the activity coefficient which contains two parameters, namely, the ionic size parameter and the solvation number. Glueckauf (69) has modified this treatment by replacing mole-fraction statistics with volume-fraction statistics. Although this treatment is able to predict the activity coefficients to high concentrations, the appearance of the two adjustable parameters tends to make the treatment another semi-empirical extension of the Debye-Hückel theory.

Bagchi and Dutta (70, 71, 72) proposed a modified distribution function of the Fermi-Dirac type in place of the Boltzmann distribution function used by Debye and Hückel. However, the activity coefficients give only qualitative agreement with experiment. Eigen and Wicke (73, 74, 75, 76), considering the numbers of available ion sites required by a hydrated ion in a unit volume, modified the Boltzmann distribution function and derived a relation for the activity coefficient. Lange and Möhring (77) have derived an expression for the relative apparent heat content from this theory. Even though their treatments agreed with experiment better than the Debye-Hückel theory, the quantitative interpretation of the parameters involved in the derivation is uncertain.

Adapting his cluster theory of imperfect gases (78) to electrolytic solutions Mayer (79) developed a theory which predicted osmotic pressures and activity coefficients. Poirier (80), using Mayer's rather complex expressions, derived relations from which thermodynamic quantities could more easily be obtained. Quantitative agreement with experiment extends as far as or, in some cases, slightly further than the Debye-Hückel treatment.

The above summary presents some of the attempts to obtain a clearer notion of solution chemistry. It seems, however, that the Debye-Hückel theory still remains the best theoretical treatment conceived thus far. Critical examinations of its basic assumptions are given by Kramers (81), Fowler (82), Onsager (62), Kirkwood (83), Fowler and Guggenheim (60) and Kirkwood and Poirier (84). These examinations have served to prove the validity of the limiting law. More comprehensive surveys of theoretical accounts to clarify solution behavior are given by Harned and Owen (56) and Robinson and Stokes (68).

IV. EXPERIMENTAL

A. Apparatus

An adiabatic calorimeter similar to the one developed by Gucker <u>et al</u>. (45) was used to measure the heats of dilution of the rare-earth chloride solutions. The calorimeter employed in this work was originally constructed by Naumann (85) with some modifications by Eberts (86). Additional changes of the apparatus were made throughout the course of this research whenever such changes indicated an increase in the performance of the calorimeter.

A schematic diagram of the calorimeter is given in Figure 1. Figures 2 and 3 show schematically the electrical circuits accompanying the calorimeter. References to figures will be designated by (i-X), where i refers to the figure and X to the alphabetically labeled parts.

1. Water bath

A 22 gallon water bath served as an adiabatic jacket for the calorimeter. The bath consisted of an inner copper tank and an outer galvanized iron casing with a plywood base. Two boards supported the inner tank above the casing base so that a three inch air space was left between the tank and the casing walls. The space was filled with exploded mica which was enclosed by a copper lid joined at the top

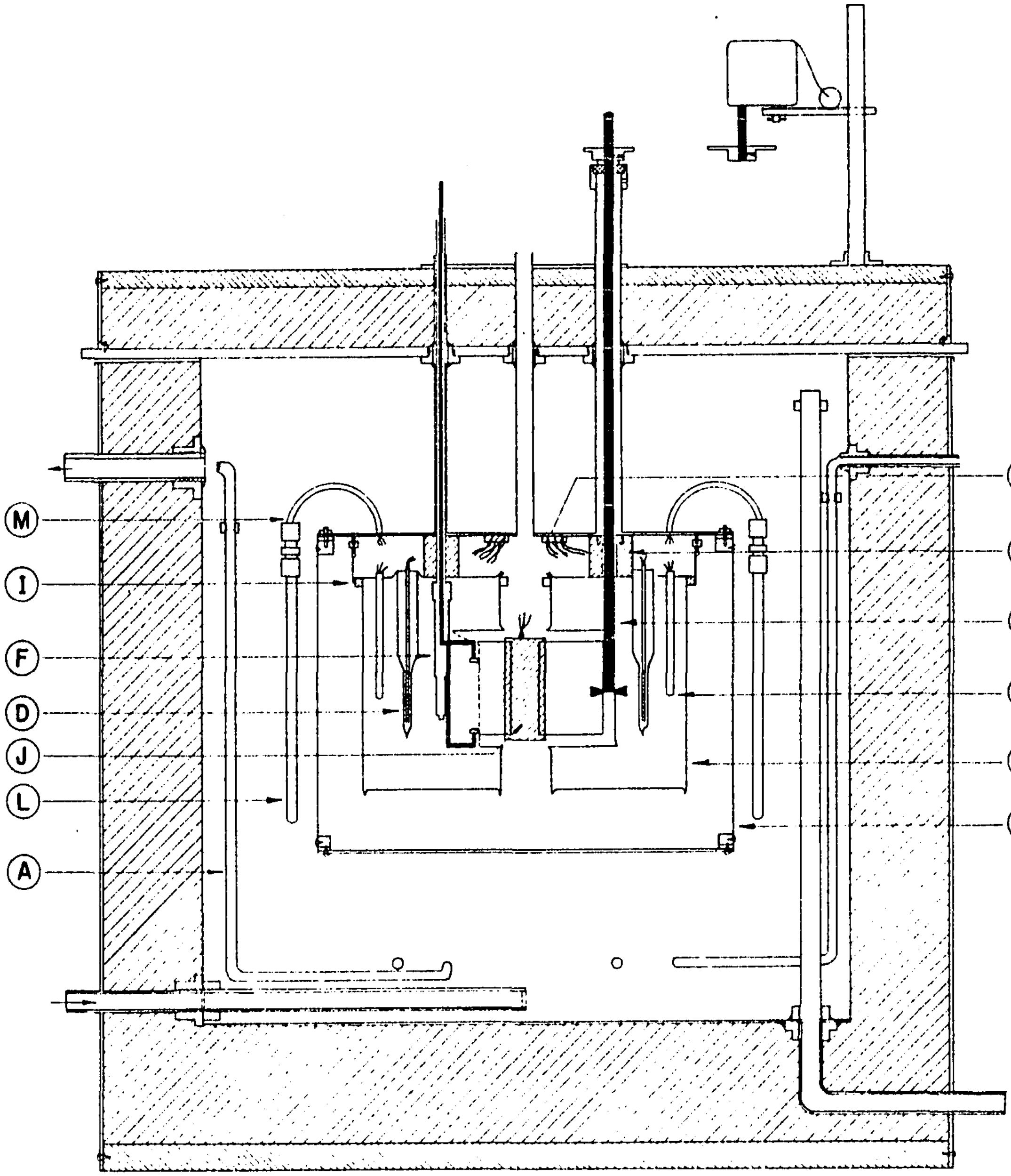


Figure 1. Adiabatically jacketed differential calorimeter

edges of the tank and casing walls.

The water bath lid was suspended 54 inches above the floor by an angle iron frame. The lid consisted of a 1/4 inch aluminum plate and a 1/2 inch plywood top. A galvanized iron casing connected the plate with the plywood top and enclosed 1 3/4 inches of hair felt insulation which separated the two. The bath and its circulating pump was mounted on a movable angle iron platform which could be rolled under the lid and raised or lowered by a hydraulic bumper jack also mounted on the platform.

The water in the bath was stirred by a centrifuge pump driven by a 1/4 horsepower motor. Water was removed from the bath through a pipe three inches below the top of the tank and was returned through a pipe at the bottom. The bath was also provided with an overflow pipe one inch from the top.

A cooling coil of 1/4 inch copper tubing (1-A) was fastened to two outlets three inches from the top and on opposite sides of the bath. The coil consisted of 1 1/2 turns at the bottom of the bath and the two lengths of tubing from the bottom to the outlets.

2. Submarine jacket

The submarine jacket (1-B) was constructed of 16 B and S gauge monel sheet. Its horizontal cross section had straight, parallel sides terminating in semicircular ends.

Brass flanges were soldered to the top and bottom of the inside walls. A 1/4 inch chromium plated copper piece was fastened permanently to the bottom flange. Studs were threaded into the top flange so that it could be fastened to the jacket lid. A 1/4 inch soft rubber gasket fitted between the jacket and lid.

The 1/4 inch chromium plated copper jacket lid was suspended five inches below the aluminum bath lid by eight brass tubes. These tubes were soldered to the top of the jacket lid and to brass collars which were threaded into the aluminum bath lid. The tubes acted as water tight passages for the various rods and shielded cables entering the calorimeter.

3. Calorimeter containers

Two cylindrical calorimeter containers (1-C), four inches in diameter and six inches long, were constructed from 15 mil tantalum. A thermal well of 15 mil tantalum, 2 1/4 inches deep with an opening of 3 3/8 inches by 3/8 inches, was welded into the side of each container. Boat shaped tantalum pieces were welded to the ends of the wells. A 15 mil tantalum disk was welded to each container to serve as the bottom. The tops of the containers had a 1/4 inch, 45 degree flange which matched a similar flange on the container lids.

Both container lids, also constructed of 15 mil tantalum, contained a heater well (1-D) and three 1/4 inch holes for a stirrer (1-E), sample holder rod (1-F) and control thermals (1-G). Four lucite spacers (1-H), three centimeters long, were mounted to the underside of the submarine jacket lid by machine screws. Each lid was fastened to two of these spacers also by machine screws. General Electric's Gyptal Enamel was then painted over the screw heads and applied to places where the lucite spacers made contact with the submarine jacket and container lids. The purpose of the enamel was to make certain that all such places were water and air tight.

Assembling the apparatus the two containers were raised to their lids by a small jack until the lid and container flanges fitted snugly together. Strips of Scotch electrical tape were wrapped tightly over the flanges and several drops of molten paraffin were applied to points where the tape overlapped. Again, this procedure was followed to insure an air tight seal throughout the determination. Each container was held in place by a lucite ring (1-I) suspended from the submarine jacket lid by three non-magnetic stainless steel hooks. The hooks were hung from the bottom of ball-bearing swivels which were soldered to large brass nuts. The brass nuts were threaded onto studs projecting downward from the jacket lid.

In the past 30 pound test nylon fish line had been used to support the lucite rings; however, during the course of a determination the line tended to stretch causing a slight separation between the container and its lid. At times this separation caused the tape to become undone thereby allowing solution to evaporate into the submarine jacket. The substitution of the hooks for the nylon fish line produced no noticeable difference in the performance of the calorimeter.

4. Sample holders

The sample holders were constructed entirely out of stainless steel. Each sample holder consisted of two thin walled tubes, two centimeters in diameter and four centimeters long, held together by a cross arm silver soldered to the tubes. The ends of the tubes were threaded to accommodate screw-on caps which held disks made from either 0.5 mil thick platinum or Dow Chemical Company's Saran Wrap. Vapor tight seals were obtained by applying a thin coating of silicon grease to the rims of the tubes and placing Teflon gaskets behind the disks. A hold was drilled in the cross arm so that the sample holder could fit snugly on the sample holder rod; a set screw held the sample holder firmly to the rod. The sample holders were opened by punching holes into the disks with a breaker rod having crown shaped tips.

Bakelite tubes extending out of the calorimeter supported the sample holder rods. Passing through the inside of the tubes were solid polyethylene rods which were fused to the ends of the breaker rods in order to reduce thermal conduction.

5. Calorimeter stirrers

Each stainless steel stirrer was held in place by ball bearings: one at the top of the brass tube extending above the water bath lid and the other in the lucite spacer beneath the jacket lid. It was very important to have the ball bearings fit tightly in the lucite spacers. If the bearings wobbled or if their outside race slipped while the stirrers rotated, then irregular amounts of heat were generated making it impossible for a thermal steady state equilibrium of the system to occur.

A 150 rpm synchronous motor drove a sprocket and chain mechanism which was geared to rotate the stirrers at a speed of 282 rpm. The propellers and chain drive were arranged so that liquid in the two containers were stirred in opposite directions.

The stirrers were constructed as identical as possible so that the same amount of heat due to stirring was produced in each container. The trickel heaters compensated for any differences in the mechanical heat produced by the stirring. Maintenance of a constant thermal heat between the two containers is discussed in the section on experimental procedure.

6. Calorimeter heaters and circuits

Each heater well held two heaters (1-D, 2-A, 2-A'). The first was the main calorimeter heater which consisted of a 50 ohm winding of 38 B and S gauge manganin wire. The second heater, the auxiliary trickle heater, consisted of a 1.5 ohm winding of 30 B and S gauge constantan wire. Both heaters were wound around a thin mica strip and set into the heater wells. The air space around the heaters was filled with naphthalene.

Two 30 B and S gauge copper lead wires were soldered to each end of a main calorimeter heater and one lead wire, also of 30 B and S gauge copper, was soldered to each end of an auxiliary heater. The leads were connected to a six terminal lucite junction strip (1-K) which was fastened to the underside of the submarine jacket lid; the terminals consisted of brass machine screws and nuts. A similar junction strip accommodated the leads from the other pair of heaters.

Terminal lugs, soldered to the leads of a six lead shielded cable, were connected by means of brass nuts to each of the terminals of the junction strips. The cables passed from the calorimeter and its various leads were

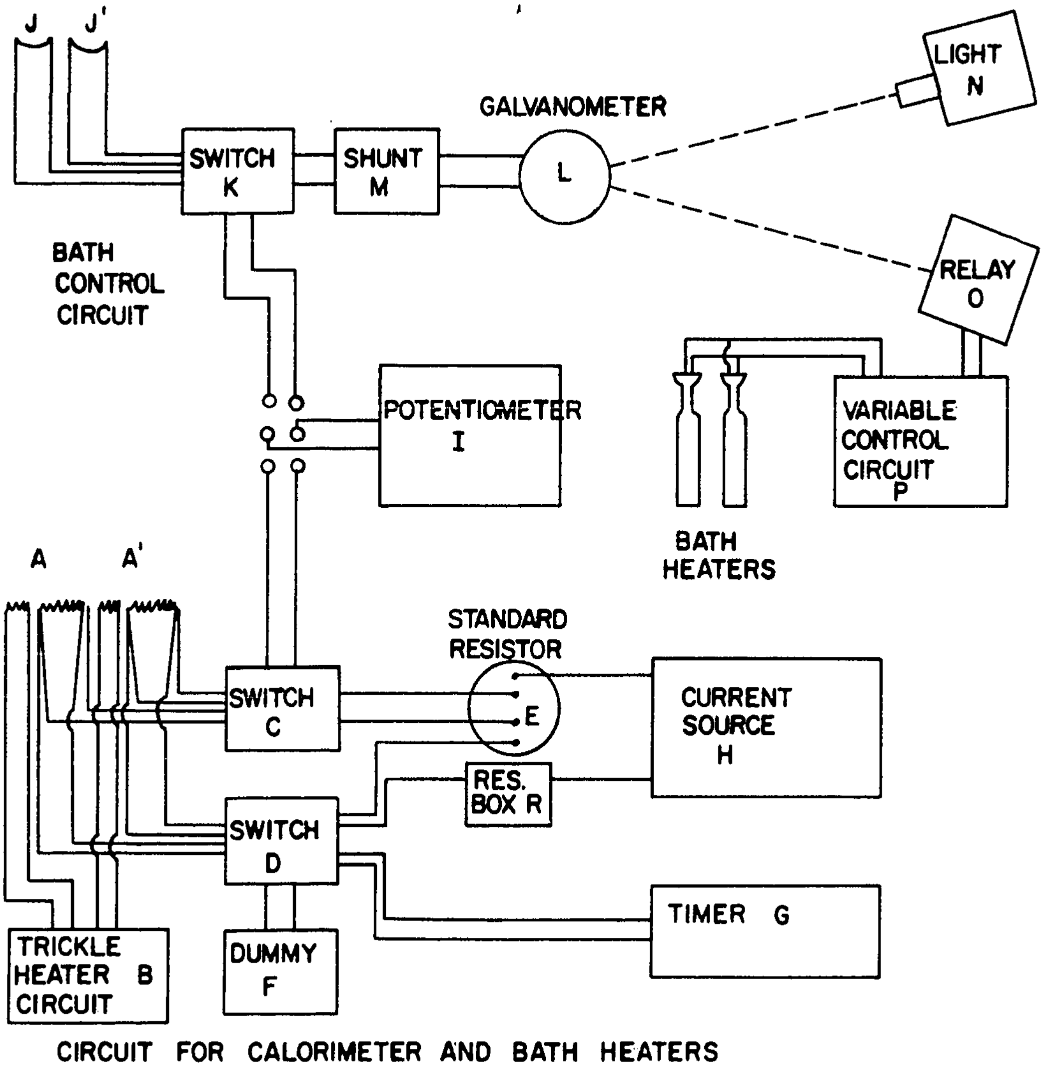
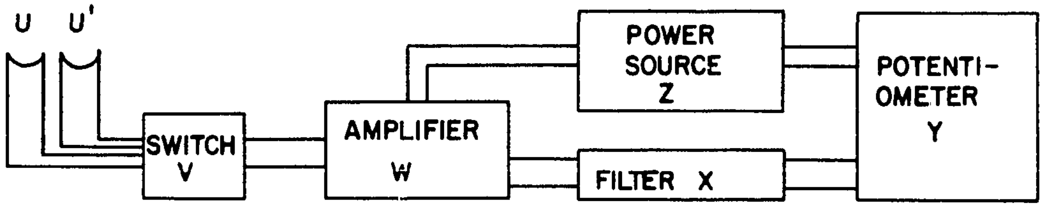


Figure 2. Schematic diagram of calorimeter circuit

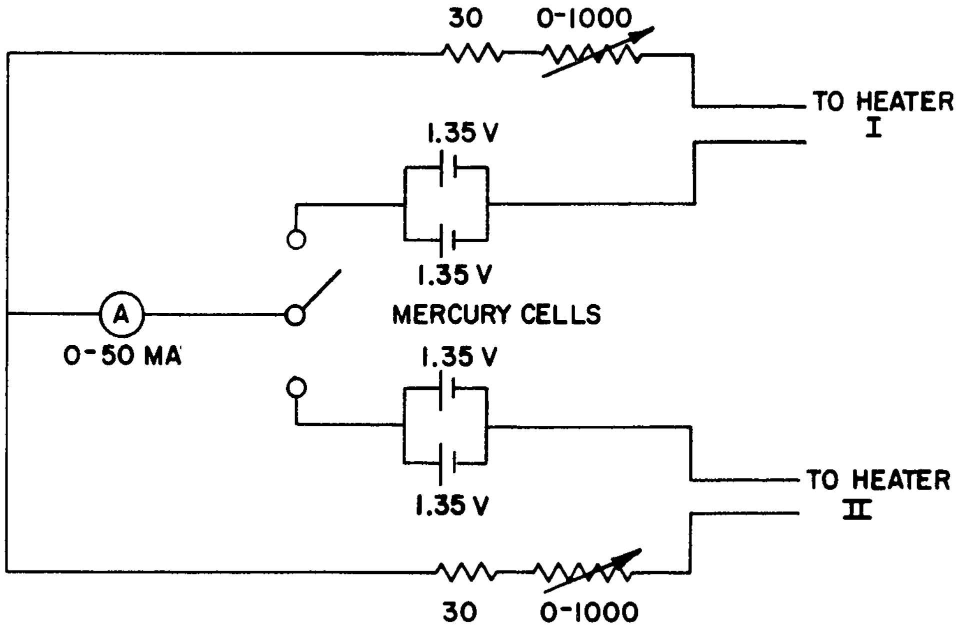
connected to rotary switches. One lead from each end of the main heater was soldered to the terminals of a 3 pole-11 position ceramic rotary switch (2-C). Likewise, the other leads from the main heater were soldered to the terminals of another 3 pole-11 position ceramic rotary switch (2-D). Switch (2-C) was wired so that the potential drop across either heater, across the two heaters in series, across the standard resistor (2-E), or across the dummy heater (2-F) could be measured. Switch (2-D) was wired so that the current could be passed through either heater, through the two heaters in series, or through the dummy heater. When switch (2-D) was closed to let current pass through the heaters, an electronic timer (2-G) began to record time.

The current source for the main heaters (2-H) was a two volt Willard, low discharge, storage battery. The current could be varied by changing the resistance of a resistance decade box (2-R) in series with the battery. A source of extremely constant current for the auxiliary trickle heaters was supplied by 1.35 volt mercury batteries connected in parallel. The auxiliary heaters were used to compensate for any thermal head that might exist between the two calorimeter containers. Figure 3 shows schematically the trickle heater circuit.

The potential drop was measured by a Leeds and Northrup K-2 type potentiometer. The standard resistor and the



CIRCUIT FOR MAIN THERMEL



CURRENT SOURCE FOR TRICKLE HEATERS

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

standard cell used with the potentiometer had been recently calibrated by the National Bureau of Standards. The electronic timer was calibrated to within 0.01 seconds against the National Bureau of Standards station WWV.

7. Thermopile and circuit

The temperature difference between the calorimeter containers was detected by a 60 junction thermopile consisting of two 30 junction sections. The thermopile was constructed from 60 pieces of 24 B and S gauge constantan wire 11 centimeters long and 60 pieces of 32 B and S gauge copper wire 11.3 centimerers long. In each section the copper wires were wrapped tightly around the ends of the constantan wires which were mounted on thin mica sheets. When all the connections had been made, the ends of the wires were dipped into a flux of rosin dissolved in ethyl alcohol, then into molten solder. The solder was supplied by the Liston-Becker Instrument Company for use in the input circuits of their D. C. breaker amplifier. Lead wires of 30 B and S gauge copper were attached to each end of the two sections.

A thin sheet of mica was placed between the two 30 junction sections. Each end of the thermopile was enclosed in a thin copper shield; a lucite collar held the two shields together. The thermopile junctions were insulated from the copper walls by a thin sheet of mica and the remaining air space was filled with naphthalene.

The lead wires were connected to pure copper machine screws and nuts fastened to two lucite junction strips held to the underside of the submarine jacket. Pure copper lugs, soldered to the leads of a four-lead shielded cable, were attached to the copper screws; the leads at the other end were soldered to a Leeds and Northrup 31-3-0-3, 12 position silver contact rotary selector switch (3-V). A two-lead shielded cable connected the selector switch with a slightly modified model 14 Liston-Becker breaker type D. C. amplifier (3-W). The switch was wired so that the potential of either thermopile section separately, in series or in opposition could be fed into the D. C. amplifier with either direct or reversed polarities. In addition, the selector switch was equipped to place resistances of 0, 10 or 20 ohms into the input circuit. The switch was mounted in a steel casing to which the braided shieldings of the incoming and outgoing cables were grounded. The case was placed in a Dewar flask and surrounded with blown mica insulation.

The output of the amplifier was fed into a filter circuit (3-X) which attenuated the signal slightly and reduced its noise level. The signal was then recorded by a Brown recording potentiometer (3-Y) with a 0 to 60 millivolt range. A type IE-5101 Stabiline voltage regulator (3-Z) supplied the power for the amplifier and potentiometer.

8. Adiabatic controls

When a system is thermally insulated so that no heat passes to or from the surroundings, adiabatic conditions exist. Any temperature change that results in the system would lead to a flow of heat unless the surroundings reflect a similar change. Therefore, to maintain adiabatic conditions for the calorimeter the temperature of the containers and bath must be the same at all times. This was accomplished by having controls heat or cool the bath whenever the containers heated or cooled.

Two 10 junction copper-constantan thermals (2-J, 2-J') were used to detect temperature differences between the bath and containers. They were constructed of 36 B and S gauge copper wire and 30 B and S gauge constantan wire. The junctions in the water bath were spaced at two centimeter intervals and placed in a copper tube (1-L). The junctions in the containers were bundled in two groups of five two centimeters apart and placed in a glass tube (1-G); both tubes were filled with nephthalene. The copper tubes were connected to semicircular sections of copper tubing (1-M) which were soldered to the submarine jacket; the glass tubes were held to the container lids by paraffin.

The lead wires were connected to pure copper machine screws and nuts fastened to the same lucite junction strips which held the thermopile connections. A four-lead shielded cable was also connected to the copper screws and passed from the calorimeter to a Leeds and Northrup 31-3-0-3 selector switch (2-K). By means of this switch either thermal or both in series could be connected to the bath control circuit. The potential drop across either thermal or both in series could be measured by the potentiometer (2-I) by turning the switch to the appropriate setting.

For bath control, switch (2-K) connected a Leeds and Northrup, type HS, reflecting galvanometer (2-L) through an Aryton shunt (2-M) with the thermals in series. A Warner model 62L light source (2-N) was focused to reflect light from the galvanometer to a Warner model 62R photoelectric receiver and relay (2-O) three meters away.

When the light fell on the photoelectric receiver current, regulated by a powerstat (2-P), flowed through the bath heaters until the bath heated enough to cause the galvanometer to deflect the light away from the receiver. Cooling water which flowed through the cooling coils (1-A) at a constant rate cooled the bath until the galvanometer again reflected the light on the receiver. The powerstat and cooling water were regulated so that equal periods of heating and cooling of 30 to 40 seconds were obtained. In this way the bath was controlled to ±0.003° C. of the containers. The temperature of the bath was measured by a platinum resistance thermometer calibrated by the National Bureau of Standards. The resistance of the thermometer was measured by a Leeds and Northrup Mueller Temperature Bridge.

B. Preparation of Solutions

The rare-earth chloride solutions used in this research were prepared from the pure oxides furnished by the rare-earth separation group of the Ames Laboratory of the Atomic Energy Commission. Table 1 gives a summary of the spectrographic analysis of the rare-earth oxides. The percentages listed in the table are the lowest limits that the spectrographic method can accurately ascertain. Therefore, the amounts of impurities contained in the oxides may be much less than the values reported.

The oxides were added with heating to C. P. hydrochloric acid until the acid had completely reacted; enough oxide was added so that a slight excess remained. The solution was allowed to cool and the excess oxide was filtered off. Usually a colloidal suspension of partially reacted and unreacted oxide was present in the solution after filtration. To dissolve most of this colloid small amounts of acid were added to the solution. Since the dissolution of the colloid was very slow the solution was gently heated and allowed to digest for several hours.

An aqueous solution of rare-earth chloride contains

Table 1. Spectrographic analysis of rare-earth oxides

Oxide	Analysis (per cent)
Sm_2O_3	Nd: less than 0.02 Eu: less than 0.01 Gd: less than 0.02 Ca: less than 0.05
Gd_2O_3	Y: less than 0.05 Sm: less than 0.05 Eu: less than 0.01 Tb: less than 0.02 Ca: less than 0.05 Fe: less than 0.01
Dy_2O_3	Y: less than 0.007 Tb: less than 0.01 Ho: less than 0.05 Er: less than 0.01 Yb: less than 0.005 Ca: less than 0.05
Ho_2O_3	Y: less than 0.01 Tm: less than 0.01 Er: less than 0.007 Dy: less than 0.04
Tm_2O_3	Er: less than 0.004 Yb: less than 0.02 Lu: less than 0.003 Th: not detected

hydrolysis products of the tri-valent rare-earth ion; the major hydrolysis reaction is considered to be:

$$R^{+++} + H_2O \rightleftarrows R(OH)^{++} + H^{+}.$$

Thus such a solution will be acidic and will have a definite pH depending upon the concentration and the particular rare-earth ion.

In order to assure that all the colloidal material had reacted giving an equivalent amount of rare-earth and chloride ions in solution, a titration with hydrochloric acid was made. A 25 milliliter portion of the bulk solution was titrated with 0.1 N hydrochloric acid. The course of the titration was followed by a Beckman Model G pH meter. A plot of pH versus milliliters of acid gave a strong acid-weak base titration curve. From a differential plot of (Δ pH/Δ milliliters) versus average milliliters of acid added, the equivalence pH value was determined. The bulk solution was adjusted to this pH and heated for several hours to dissolve any colloid that might have remained after the first digestion period. If the pH of the bulk solution had changed another titration was performed and the bulk solution again adjusted to the equivalence pH determined by the second titration. Usually the equivalence pH of the two titrations agreed to 0.1 pH units. When the bulk solution showed no change in pH after digesting with acid, it was stored in a volumetric flask to be used as the stock solution for subsequent dilutions. Table 2 contains pH data of solutions used in this research.

The concentration of the stock solution was determined by two analyses: an oxalate analysis to determine the rare-earth ion concentration, and a chloride analysis to determine

Table 2. pH data of solutions

				Dilution experiment	
Salt.	Sol. no.	m	pH of solution	pH of water	pH of final solution
$SmCl_3$	1	0.01976	5.13	5.77	5.63
	2	0.03988	4.99	5.77	5.58
	3	0.06665	4.94	5.77	5.48
	4	0.1297	4.69	5.77	5.39
	5	0.2606	4.42	5.77	5.31
	stock	0.3151	4.40		
$GdCl_3$	1	0.02054	5.10	5.77	5.61
	2	0.04118	4.83	5.77	5.52
	3	0.06744	4.77	5.77	5.42
	4	0.1227	4.58	5.77	5.37
	5	0.2406	4.33	5.77	5.30
	stock	0.3591	4.28		
$DyCl_3$	1	0.02804	5.08	5.80	5.64
	2	0.04183	4.99	5.82	5.62
	3	0.06971	4.81	5.95	5.70
	4	0.1673	4.54	5.70	5.58
	5	0.2324	4.41	5.73	5.61
	stock	0.3526	4.26		
$HoCl_3$	1	0.01747	5.16	5.82	5.68
	2	0.03445	5.11	5.82	5.62
	3	0.06712	4.98	5.82	5.49
	4	0.1283	4.76	5.82	5.45
	5	0.2524	4.49	5.82	5.34
	stock	0.3544	4.31		
$TmCl_3$	1	0.02055	4.98	5.77	5.51
	2	0.04215	4.90	5.77	5.44
	3	0.08266	4.78	5.77	5.38
	4	0.1618	4.56	5.77	5.31
	5	0.2989	4.38	5.77	5.26
	stock	0.4306	4.30		

the chloride ion concentration. For the rare-earth analysis, weighed amounts of solution were precipated with a slight excess of recrystallized oxalic acid in weighed crucibles. After evaporation to dryness the crucibles were fired at 900° C. in a muffle furnace. From the amounts of oxide after ignition and the weights of the solutions the molality was calculated. Precision of better than one part per thousand was obtained for all analyses.

The chloride ion concentration was determined by a standard gravimetric method. The molality determined by the analyses was approximately 0.1 per cent lower than that obtained by the oxalate analyses. Since the error in such chloride analyses is about 0.1 per cent, it was assumed that the molality determined by the oxalate analyses was correct and that an equivalent amount of rare-earth and chloride ions was present in the stock solution.

Known weights of stock solution were diluted with weighed amounts of conductivity water to obtain a series of solutions ranging from approximately 0.02 to 0.5 molal. The conductivity water, prepared by the distillation of ordinary distilled water from an alkaline potassium permanganate solution, had a specific conductance of less than 1.0×10^{-6} mhos per centimeter and a pH of 5.7 to 6.2.

All weights were corrected to weight in vacuo. The density of the solutions used in these corrections were determined by a pycnometric method or from the data obtained by Saeger (16).

C. Experimental Procedure

In all the experiments performed with the adiabatic calorimeter the following procedure was employed. Each pair of sample holders was filled with 20 grams of the appropriate solution, 10 grams in each holder, and the containers were filled with 880 grams of water. After the apparatus was assembled the containers were brought to $25.00 \pm 0.02^\circ$ C. by heating (or cooling) the bath by an amount predetermined by experience. Once the containers were brought to the desired temperature adiabatic conditions were maintained. Heat was then supplied to one of the containers to reduce the temperature difference between the containers to the microdegree range. When enough heat was supplied so that the pen of the recording potentiometer was able to record on the chart at an amplifier gain of 19 the microdegree range was attained. Current was passed through one of the trickle heaters so that any constant drift of the potentiometer pen was nearly eliminated.

Constant potentiometer pen drifts could be attributed to several causes. First, even though the stirrers were rotated at the exact same speed, the stirrer blades may have been constructed so that they produced different amounts of heat while the calorimeter liquid was stirred. Second, the bearings holding the stirrer shafts may have produced different amounts of heat while the stirrers rotated. Third, the rates of evaporation of the calorimeter liquid in the two containers may have been slightly different. Evaporation was reduced to a minimum by the use of tape, paraffin and enamel at points where evaporation might occur. Some evaporation did occur around the stirrer shafts and sample holder rods; however, this was very slight. As long as the heat effects produced by any of these causes were constant throughout an experiment, the trickle heaters could be used to eliminate the pen drift.

On several occasions shifts were noted in the pen tracings. The recorder pen would trace a straight line for several minutes, then it would be displaced a noticeable distance and begin to trace a straight line parallel to the original line. This would indicate that one of the containers had gained or lost a small amount of heat. If several shifts were noted prior to any experimental determinations, the apparatus was dismantled so that the cause could be found.

The shifts were attributed to fluctuations of the room and bath temperatures, breaks in one of the many air tight and water tight seals or to poor thermopile lead connections at the lucite junction strips. To guard against possible shifts the room temperature was held to ± 0.1° C. and the heating and cooling periods of the bath were kept as equal as possible during the course of an experiment. All seals were inspected before and after an experiment to make certain none were broken; the thermopile contacts were cleaned regularly to assure good electrical connections. Whenever such shifts did occur during an experiment, the data for that particular run was discarded and was not used in any subsequent calculations.

1. <u>Calibration experiments</u>

For the calibration experiments each pair of sample holders was filled with 20 grams of water or solution and the containers with 880 grams of water. After the calorimeter had attained equilibrium a known amount of heat was passed through one of the container heaters and the distance the pen deflected was measured. Periods of 15 to 30 minutes were allowed for the pen to record at a chart speed of half an inch per minute before and after the heatings. Lines were drawn through these fore and after tracings, and the distance in millimeters between the lines was measured perpendicular to the fore tracing at a point where heat was first introduced and perpendicular to the after tracing at a point where equilibrium was again attained. The two measurements were then averaged.

The amount of heat produced by a heater was calculated by the relation,

$$q_e = \frac{1}{4.1480} \frac{R_h}{R_s^2} E_s^2 t, \qquad \text{(IV-1)}$$

where q_e is the heat liberated in defined calories (1 calorie - 4.1480 absolute joules); R_h is the heater resistance; R_s is the resistance of the standard resistor, which has a value of 10.0087 ohms; E_s is the potential drop across the standard resistor; and t is the time in seconds that current flowed through the heater. The sensitivity of the calorimeter was determined by dividing the average pen displacement into the amount of heat liberated.

The heater resistance was determined by passing current through the heater and measuring the potential drop across it and the standard resistor. Current was allowed to flow through a dummy heater for at least 30 minutes before any measurements were undertaken. In this way any fluctuations of current through the calorimeter heaters were held to a minimum.

A summary of the electrical calibration values of the calorimeter is given in Table 3. The calibration series is given in the first column. Results from series A_I were applied to the heats of opening of the platinum disks and to

Table 3. Summary of electrical calibrations

Series	Number of determinations	Average sensitivity[a]	$\bar{\sigma}$[a]
A_I	33	3.37	0.02
A_{II}	25	3.27	0.03
A_{III}	26	3.44	0.03
A_{IV}	30	3.07	0.03

[a] The sensitivity and the standard error are given in cal/mm x 10^4.

the dysprosium chloride data; results from A_{II} were applied to the heats of opening of the Saran disks and to the samarium chloride, gadolinium chloride and the first five determinations of the thulium chloride data; results from series A_{III} were applied to the remainder of the thulium chloride data; and results from series A_{IV} were applied to the holmium chloride data. The various series of calibrations were necessary because the sensitivity changed when tubes in the amplifier and recorder circuits were replaced or when the lead wires of the thermopile were lengthened.

The number of determinations made by heating in each container is given in column two. The average values of the sensitivity were found for each container; however, no significant difference was noted between the two values.

Therefore, the average sensitivity, listed in column three, was used for the system.

The standard deviation of the mean or the standard error, $\bar{\sigma}$, is defined as

$$\bar{\sigma} = \left[\frac{\sum_{i=1}^{n} (\bar{X} - X_i)^2}{n(n - 1)} \right]^{1/2} , \qquad \text{(IV-2)}$$

where $\bar{X}$ is the average value; X_i is the value of determination i; and n is the number of determinations. Values of $\bar{\sigma}$ are listed in column four.

2. Heats of opening experiments

The heat produced opening the sample holders, q_O, was determined by punching holes into the disks held by the screw-on caps of the sample holders and measuring the displacement of the potentiometer pen. The displacement, in millimeters, was multiplied by the sensitivity to give the heat liberated in calories. Each sample holder tube was filled with ten grams of water when the measurements were made.

A summary of the heats of opening is given in Table 4. Series P refers to the heats of opening of platinum disks and series S to the heats of opening of Saran disks. The average values with their standard errors are given in

Table 4. Summary of heats of opening

Series	Number of determinations	Average $q_0 \times 10^3$ [a]	$\bar{\sigma} \times 10^3$ [a]
P	25	16.7	0.6
S	15	4.8	0.3

[a] The average values and the standard errors are expressed in defined calories.

columns three and four, respectively.

The error involved in the heats of opening were ascribed to the manual operation of the sample breaker rod, the inability to puncture the disks exactly the same in all experiments and the uncertainty in the sensitivity value.

3. Dilution experiments

Ten milliliters of solution were transferred to each sample holder tube. The exact amount of solution was determined by weighing the sample holders empty and after each ten milliliter addition to a tenth of a milligram. To detect any leaks the sample holders were reweighed eight to ten hours after the first weighing. Usually the sample holders with the platinum disks lost 0.2 milligrams and the sample holders with the Saran disks lost 0.7 milligrams. Several experiments were carried out where sample holders filled with solution were submerged in water for periods of a few hours to two days. In all cases the sample holders did not deviate by more than one milligram from their original weight. When a noticeable difference in weight did occur, that sample was not used for any heat of dilution determination.

If no leaks were detected, water was weighed into each calorimeter container to give a total liquid content of 900 grams. The water was weighed to the nearest milligram. The apparatus was then assembled, brought to 25° C. and adjusted to the microdegree range. About five hours after the apparatus had been assembled all the temperature fluctuations had subsided and the calorimeter was in thermal equilibrium.

When the recorder pen had traced a straight line for approximately 25 minutes a sample was opened in one of the containers. Enough heat was supplied to the other container to balance the heat of dilution and bring the pen to nearly the same position on the chart it had occupied before the dilution process. The pen was allowed to record for 30 minutes after equilibrium was restored.

The time necessary for the re-establishment of equilibrium after a dilution depended on the concentration of the sample and the amount of current passed through the heater. Periods of 20 minutes for the most dilute samples and 45 minutes for the most concentrated samples were observed before all heating effects within the calorimeter had been dissipated.

The heat supplied to the containers was calculated by equation IV-1; the distances between the fore and after tracings were measured similar to those of the calibration experiments. The heat of dilution was determined by

$$q_i - q_0 = q_e \pm q_d, \qquad \text{(IV-3)}$$

where q_i is the total observed heat; q_0 is the heat of opening; q_e is the electrical heat; and q_d depends on the relative position of the after tracing to the fore tracing.

A current of 15 milliamperes was passed through the heaters when dilute samples were opened. For the more concentrated samples 25 milliamperes were used.

4. Treatment of data

A series of five solutions ranging from 0.02 to 0.25 molal were prepared from the corresponding rare-earth chloride stock solution. Several samples of a particular solution in a series were diluted. Values of q_1 and q_2 were determined from IV-3 and related to $\Delta H_{1,2}$, $\Delta H_{1,3}$ and $\Delta H_{3,2}$ by equations III-48, III-49 and III-50. It was possible, then, to obtain several values of $\bar{P}_i$ for each solution of the series.

Chords of $\bar{P}_i$ having $(m_{2,i})^{1/2}$ and $(m_{3,i})^{1/2}$ as their end points were plotted against $m^{1/2}$. The $\bar{P}_i$ chords for each solution were averaged, and an empirical least squares equation passing through the midpoints of the chords was determined. Since there was more scatter among the $\overline{P}_i$ values at the lower end of the concentration range, weighting factors were introduced into the least squares determinations. The weight factor for each $\overline{P}_i$ (ave.) value was inversely proportional to the square of its standard error. Thus more weight was given to those $\overline{P}_i$ values which had the least amount of scatter, and therefore, the most certain average value.

The $\overline{P}_i$ equation was integrated to give ϕ_L as a function of $m^{1/2}$ for the dilute concentration range from which values of $\phi_{L(m_2)}$ and $\phi_{L(m_3)}$ were obtained. Values of $\phi_{L(m_1)}$ were then determined from equations III-45 and III-46. A second least squares determination was applied to the unweighted $\phi_{L(m_1)}$, $\phi_{L(m_2)}$ and $\phi_{L(m_3)}$ values to obtain an equation as a function of $m^{1/2}$ for the entire concentration range studied. Equations of $\overline{L}_2$ and $\overline{L}_1$ were found by substituting ϕ_L into equations III-64 and III-65.

The treatment of data by the least squares method is described by Worthing and Geffner (87), Beers (88) and Topping (89).

D. Heats of Dilution

Heats of dilution of several aqueous solutions of lanthanum chloride, samarium chloride, gadolinium chloride, dysprosium chloride, holmium chloride and thulium chloride were measured. The experimental data and the thermodynamic quantities derived from these measurements are presented in Tables 5 through 20 and in Figures 4 through 13. Since all the data except that for lanthanum chloride are represented similarly, a general explanation of the tables and figures will be given here to avoid needless repetition.

Tables 6, 9, 12, 15 and 18 contain experimental data associated with the heats of dilution. Solutions numbered in the order they were prepared and their molalities are given in the first column; the order in which they were diluted is given by the subscript in column two. The calorimeter container in which the dilution took place, represented by the Roman numeral, and the order each tube of the sample holder was opened is listed in column three. The electrical heat as given by equation IV-1 and the heat determined by the pen displacement is contained in columns four and five. In column six the heats of dilution, determined from equation IV-3, is given. The number of moles of solute present in the calorimeter containers after each dilution process is listed in column seven. The heats of dilution per mole, determined from equations III-48 and III-49, are

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given in columns eight and nine. Values for $\bar{P}_i$, determined from equation III-52, are listed in column ten. Averages and their standard errors of $\Delta H_{1,2}$, $\Delta H_{1,3}$ and $\bar{P}_i$ are also given.

Tables 7, 10, 13, 16 and 19 contain the short chord data and the relative apparent molal heat contents. The concentrations of the samples before dilution are given in column two; the concentrations after dilution are given in column three; and the averages of the values listed in column three are given in column four. The average $\bar{P}_i$ values are listed in column five. Values of ϕ_L for concentrations of m_2 and m_3 are given in column six. The average values of the heats of dilution per mole are given in column seven. Values of ϕ_L for concentrations m_1, determined by equations III-45 and III-46, are listed in column eight, while the averages of these values are listed in column nine. While it is realized that the last figures of $\Delta H_{1,2}$, $\Delta H_{1,3}$, $\bar{P}_i$ and ϕ_L values are not significant, they were used in applying the least squares treatment to the data.

Tables 8, 11, 14, 17 and 20 contain the smoothed values of ϕ_L, $\bar{L}_1$ and $\bar{L}_2$. These data were obtained from the equations which were a function of $m^{1/2}$ for the entire concentration range studied.

The short chord data are plotted in Figures 4, 6, 8, 10 and 12. Several weighted least squares treatments were applied to the $\bar{P}_i$ data; except for those of dysprosium chloride, only the equations which best fit the data are given in the following sections.

The concentration dependence of ϕ_L is shown in Figures 5, 7, 9, 11 and 13. An IBM 650 computer was used to obtain a number of unweighted least squares equations of ϕ_L versus $m^{1/2}$. A four parameter equation in the form of equation III-61 was chosen because it fit the experimental data better than equations with less parameters. Equations with more parameters did not improve the fit greatly, and they only added to the labor needed to obtain the ϕ_L values. Equations III-64 and III-65 were used to find $\bar{L}_2$ and $\bar{L}_1$ as a function of $m^{1/2}$.

All thermal quantities are expressed in defined calories or defined calories per mole, whichever is appropriate. One defined calorie equals 4.1480 absolute joules.

1. Lanthanum chloride

The heats of dilution of several lanthanum chloride solutions were determined at various times during the course of this research to check the performance of the calorimeter. The results obtained were compared with the data of Nathan et al. (90) and Spedding et al. (21). Values for ϕ_L at several concentrations are given in Table 5.

Table 5. Relative apparent molal heat contents of lanthanum chloride solutions at 25° C.

$m^{\frac{1}{2}}$	ϕ_L		
	Nathan *et al.*	Spedding *et al.*	This research
0.03153	141	204	204
0.04626	269	290	290
0.2481	1026	1037	1030
0.3641	1152	1274	1288

2. Samarium chloride

The data for samarium chloride are listed in Tables 6, 7 and 8 and are plotted in Figures 4 and 5.

Several weighted least squares determinations were made using the $\bar{P}_1$ data, and the best fit was a straight line given by

$$\bar{P}_1 = 6779 - 29331\, x_1, \tag{IV-4}$$

which was integrated to give

$$\phi_L = 6779\, m^{1/2} - 14666\, m \tag{IV-5}$$

for the concentration range of $m < 0.006$.

Table 6. Heats of dilution of samarium chloride solutions at 25° C.

Sol. no. m	Run	Sample	q_ex10^3	q_dx10^3	q_1-q_0x10^3 q_2-q_0x10^3	n_2'x10^3 $(n_2'+n_2'')$x10^3	$-\Delta H_{1,2}$	$-\Delta H_{1,3}$	$\bar{P}_1$
1 0.019764	C_2	II-in	144.5	-12.5	127.2	0.19663	646.9	597.2	8230
		II-out	84.8	+27.7	107.7	0.39336			
		I-out	149.5	-23.8	120.9	0.19676	614.5	575.8	6410
		I-in	142.4	-32.0	105.6	0.39337			
	C_4	I-in	104.2	+18.2	117.6	0.19650	598.5	551.0	7870
		I-out	116.5	-12.8	98.9	0.39294			
	C_{11}	I-out	133.6	-11.4	117.4	0.19632	598.0	567.8	5010
		I-in	116.0	- 5.7	105.5	0.39257			
	C_{14}	I-out	127.8	- 9.6	113.4	0.19652	577.0	554.4	3750
		I-in	109.9	- 0.7	104.4	0.39284			
		II-in	133.4	-10.1	118.5	0.19681	602.1	577.7	4050
		II-out	109.5	+ 3.8	108.5	0.39294			
	C_{16}	I-out	124.2	+ 2.1	121.5	0.19648	618.4	581.9	6040
		I-in	108.9	+ 3.2	107.3	0.39318			
1' 0.039878	C_{18}	I-in	112.1	+50.6	157.9	0.19797	798.6[a]	755.1[a]	7130
		I-out	116.6	+29.3	141.1	0.39596			
		II-in	164.2	+ 0.8	151.7	0.19787	809.6[a]	775.8[a]	5540
		II-out	159.7	- 8.0	146.9	0.39584			
						Average	607.9	572.1	6003
						Standard error	8.2	6.1	527

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[a] The average and standard error do not include these values

Table 6. (Continued)

Sol. no. m	Run	Sample	$q_e x10^3$	$q_d x10^3$	$q_1-q_0 x10^3$ $q_2-q_0 x10^3$	$n_2' x10^3$ $(n_2'+n_2'') x10^3$	$-\Delta H_{1,2}$	$-\Delta H_{1,3}$	$\bar{P}_i$
2	C_1	II-out	295.1	+19.3	309.6	0.39613	781.6	734.5	5490
0.039878		II-in	260.1	+17.6	272.9	0.79305			
		I-in	292.7	+10.6	298.5	0.39650	752.8	687.1	7660
		I-out	266.1	-15.0	246.3	0.79294			
	C_8	II-in	294.0	+16.7	305.9	0.39653	771.4	718.7	6160
		II-out	256.1	+12.2	263.5	0.79221			
		I-in	310.4	- 3.3	302.3	0.39626	762.9	719.2	5090
		I-out	271.3	+ 1.5	268.0	0.79294			
	C_{13}	I-in	300.2	+ 1.1	296.5	0.39658	747.6	702.7	5240
		I-out	262.8	+ 2.8	260.8	0.79303			
	C_{17}	I-in	298.0	+ 9.0	302.2	0.39623	762.7	706.5	6540
		I-out	255.1	+ 8.1	258.4	0.79353			
		II-in	306.6	- 5.9	295.9	0.39684	745.6	688.3	6690
		II-out	263.8	- 9.2	249.8	0.79287			
						Average	760.6	708.1	6124
						Standard error	5.0	5.8	349

Table 6. (Continued)

Sol. no. m	Run	Sample	$q_e x10^3$	$q_d x10^3$	$q_1-q_0 x10^3$ $q_2-q_0 x10^3$	$n_2' x10^3$ $(n_2'+n_2'')x10^3$	$-\Delta H_{1,2}$	$-\Delta H_{1,3}$	$\bar{P}_1$
3	C_3	I-in	592.8	+ 3.1	591.1	0.66289	891.7	822.5	6240
0.066653		I-out	530.7	-26.2	499.7	1.32625			
	C_7	II-out	593.2	- 6.7	581.7	0.66340	876.8	816.6	5440
		II-in	521.0	-15.7	500.5	1.32521			
		I-in	588.6	- 7.0	576.8	0.66052	873.3	816.3	5140
		I-out	496.9	+10.8	502.9	1.32271			
	C_{12}	II-in	600.0	-13.3	581.9	0.66284	877.9	807.7	6340
		II-out	513.6	-20.3	488.5	1.32530			
	C_{16}	II-out	592.3	- 4.8	582.7	0.66250	879.5	817.3	5610
		II-in	502.3	+ 2.9	500.4	1.32525			
	C_{19}	I-in	583.6	- 7.4	571.4	0.66135	864.0	801.8	5610
		I-out	491.3	+ 3.4	489.9	1.32359			
						Average	877.2	813.7	5730
					Standard error		3.7	3.1	191

Table 6. (Continued)

Sol. no. m	Run	Sample	$q_e \times 10^3$	$q_d \times 10^3$	$q_1 - q_0 \times 10^3$ $q_2 - q_0 \times 10^3$	$n_2' \times 10^3$ $(n_2' + n_2'') \times 10^3$	$-\Delta H_{1,2}$	$-\Delta H_{1,3}$	$\bar{P}_1$
4 0.12965	C_5	I-in	1326.1	+ 0.3	1321.6	1.2876	1026.4	946.9	5150
		I-out	1104.4	+14.9	1114.5	2.5728			
		II-in	1323.0	+34.2	1352.4	1.2880	1050.0	962.7	5650
		II-out	1098.0	+32.8	1126.0	2.5745			
	C_{10}	II-in	1333.1	+16.4	1344.7	1.2860	1045.6	959.8	5550
		II-out	1119.7	+ 9.0	1123.9	2.5721			
		I-in	1297.0	+48.7	1340.9	1.2856	1043.0	956.7	5590
		I-out	1141.5	-18.7	1118.0	2.5703			
	C_{15}	I-in	1323.4	+12.8	1331.4	1.2860	1035.3	951.3	5430
		I-out	1119.1	+ 2.5	1116.8	2.5734			
						Average	1040.1	955.5	5474
					Standard error		4.2	2.9	89

Table 6. (Continued)

Sol. no. m	Run	Sample	$q_e x10^3$	$q_d x10^3$	$q_1-q_0 x10^3$ $q_2-q_0 x10^3$	$n_2' x10^3$ $(n_2'+n_2'')x10^3$	$-\Delta H_{1,2}$	$-\Delta H_{1,3}$	$\bar{P}_1$
5 0.26057	C_6	I-out	3152.2	+41.9	3189.3	2.5778	1237.2	1136.3	4620
		I-in	2671.1	+ 0.1	2666.4	5.1533			
		II-out	3239.7	-29.3	3205.6	2.5773	1243.8	1140.1	4740
		II-in	2694.9	-17.2	2672.9	5.1562			
	C_9	I-in	3151.4	+56.8	3203.4	2.5734	1244.8	1135.7	4990
		I-out	2681.8	-35.1	2641.9	5.1468			
		II-in	3219.1	+ 8.3	3222.6	2.5815	1248.3	1139.2	4980
		II-out	2731.1	-66.7	2659.6	5.1634			
	C_{15}	II-in	3232.4	- 5.4	3222.2	2.5765	1250.6	1141.2	5000
		II-out	2651.4	+ 3.7	2659.9	5.1544			
						Average	1244.9	1138.5	4866
					Standard error		2.3	1.1	78

Table 7. Short chord data and relative apparent molal heat contents of samarium chloride solutions at 25° C.

Sol. no.	$m_1^{\frac{1}{2}}$	$m_k^{\frac{1}{2}}x10^2$	$x_i x10^2$	$\bar{P}_i$	$\phi_{L(m_k)}$	$-\Delta H_{1,k}$	$\phi_{L(m_1)}$	$\bar{\phi}_L$
1	0.14059	1.4855	1.7862	6003	97.5	609.9	707.4	707.5
		2.0889			135.2	572.3	707.5	
2	0.19969	2.1096	2.5384	6124	136.5	760.6	897.1	896.7
		2.9671			188.2	708.1	896.3	
3	0.25817	2.7271	3.2813	5730	174.0	877.2	1051.2	1051.7
		3.8355			238.4	813.7	1052.1	
4	0.36007	3.8015	4.5736	5474	236.5	1040.1	1276.6	1276.3
		5.3457			320.5	955.5	1276.0	
5	0.51046	5.3822	6.4758	4866	322.4	1244.9	1567.3	1567.5
		7.5694			429.1	1138.5	1567.6	

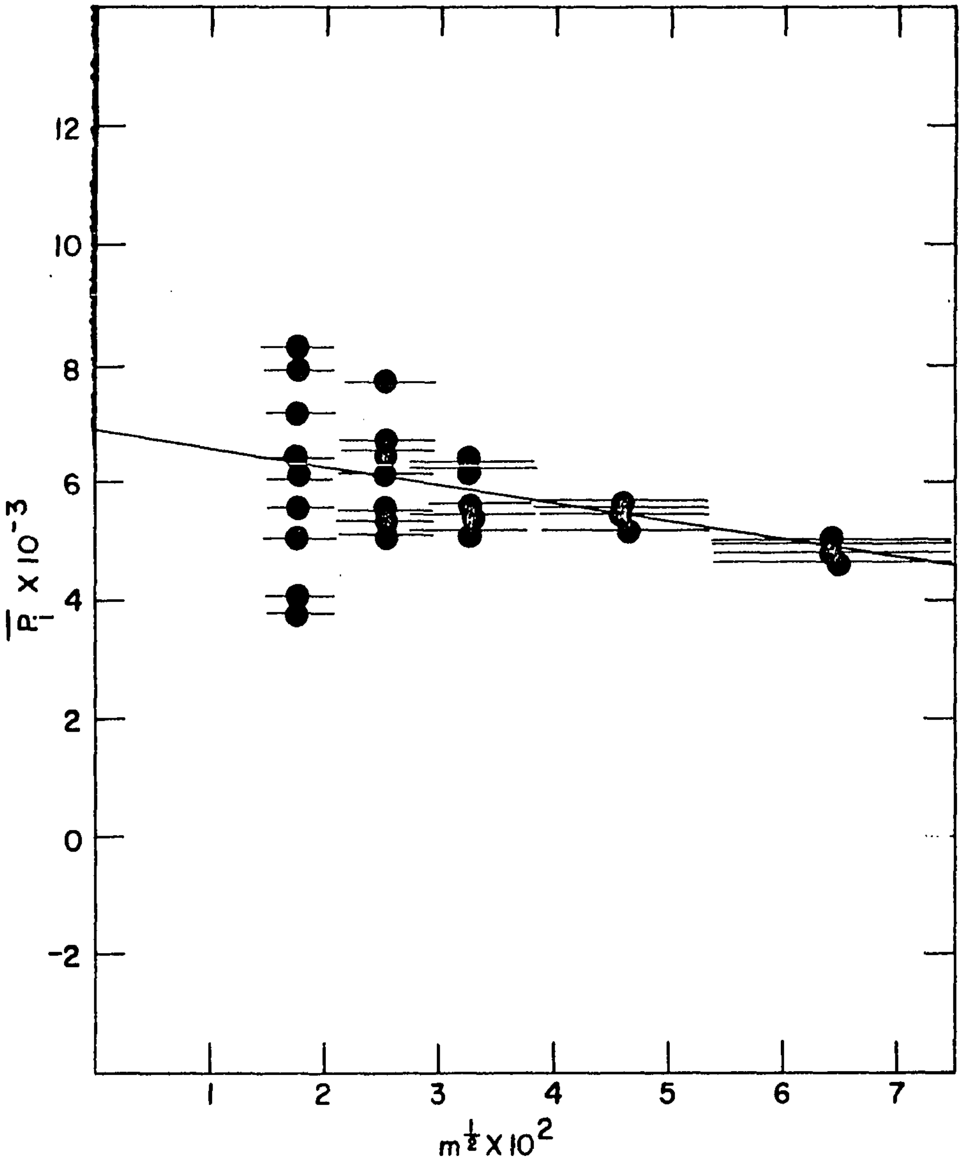

Figure 4. Short chords of samarium chloride solutions at 25° C.

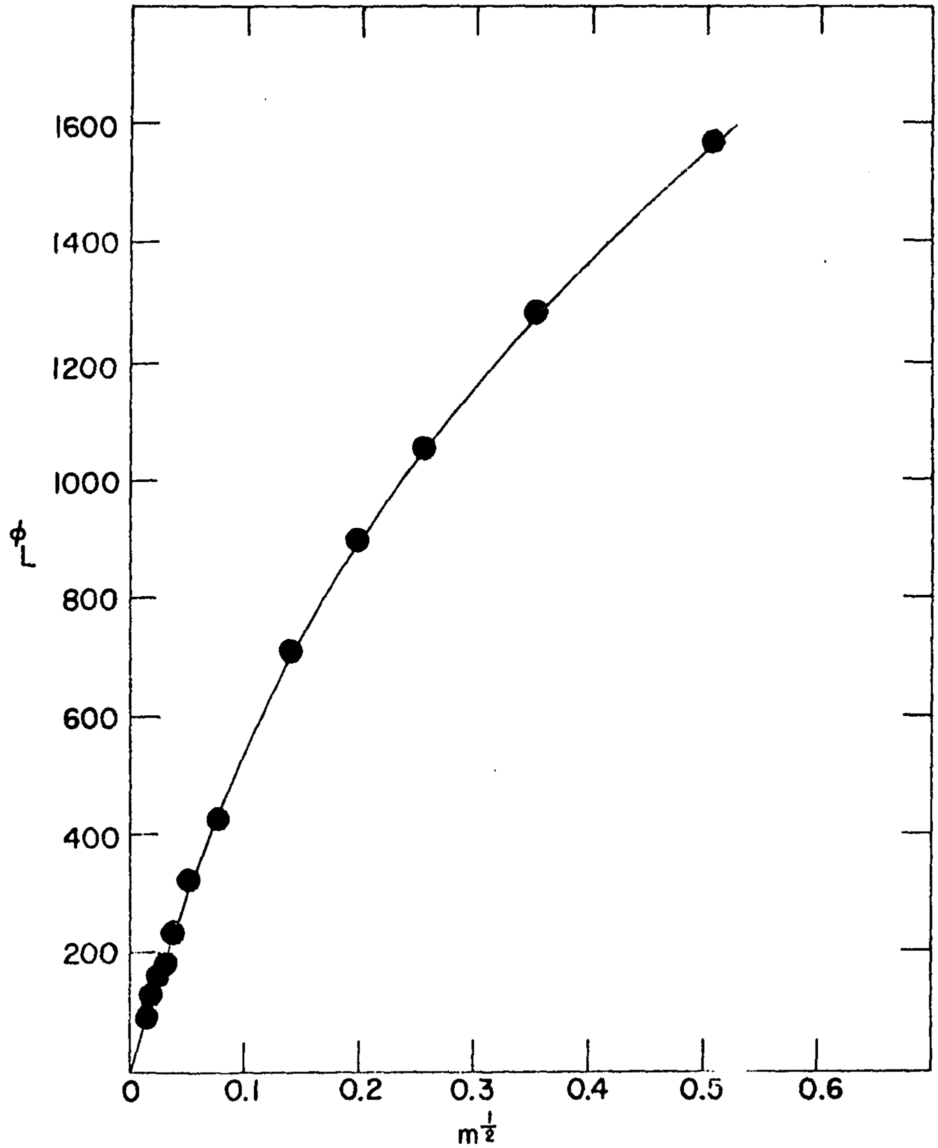

Figure 5. Relative apparent molal heat contents of samarium chloride solutions at 25° C.

Table 8. Thermodynamic properties of samarium chloride solutions at 25° C.

$m^{\frac{1}{2}}$	ϕ_L	$\bar{L}_2$	$-\bar{L}_1 x 10^3$
0.0100	66	99	0.061
0.0200	130	191	0.446
0.0500	303	437	6.05
0.0700	405	577	15.2
0.1000	543	757	38.7
0.2000	896	1187	210.0
0.3000	1150	1492	553.0
0.4000	1362	1761	1150.0
0.5000	1548	1970	1902.0

Using the data listed in Table 7 an unweighted least squares determination resulted in

$$\phi_L = 6788\ m^{1/2} - 15926\ m + 25037\ m^{3/2} - 15902\ m^2 \qquad \text{(IV-6)}$$

for the whole concentration range studied. Equations for $\bar{L}_1$ and $\bar{L}_2$ are:

$$\bar{L}_1 = -61.146\ m^{3/2} + 286.92\ m^2 - 676.61\ m^{5/2} + 572.98\ m^3 \qquad \text{(IV-7)}$$

and

$$\bar{L}_2 = 10182\ m^{1/2} - 31852\ m + 62593\ m^{3/2} - 47706\ m^2. \qquad \text{(IV-8)}$$

3. Gadolinium chloride

The data for gadolinium chloride are listed in Tables 9, 10 and 11 and are plotted in Figures 6 and 7.

A linear equation for the concentration dependence of $\bar{P}_i$ was found to be:

$$\bar{P}_i = 7178 - 32211\ x_i, \tag{IV-9}$$

which was integrated to give

$$\phi_L = 7178\ m^{1/2} - 16106\ m \tag{IV-10}$$

for the concentration range of $m < 0.006$.

From the data listed in Table 10, the equation of ϕ_L valid for the entire concentration range is:

$$\phi_L = 7234\ m^{1/2} - 19171\ m + 34487\ m^{3/2} - 24139\ m^2. \tag{IV-11}$$

Equations for $\bar{L}_1$ and $\bar{L}_2$ are:

$$\bar{L}_1 = -65.164\ m^{3/2} + 345.38\ m^2 - 931.99\ m^{5/2} + 869.78\ m^3 \tag{IV-12}$$

and

$$\bar{L}_2 = 10851\ m^{1/2} - 38342\ m + 86218\ m^{3/2} - 72417\ m^2. \tag{IV-13}$$

Table 9. Heats of dilution of gadolinium chloride solutions at 25° C.

Sol. no. m	Run	Sample	$q_e \times 10^3$	$q_d \times 10^3$	$q_1 - q_0 \times 10^3$ $q_2 - q_0 \times 10^3$	$n_2' \times 10^3$ $(n_2' + n_2'') \times 10^3$	$-\Delta H_{1,2}$	$-\Delta H_{1,3}$	$\bar{P}_1$
1 0.020539	D_2	II-in	148.6	- 2.7	141.1	0.20436	690.5	626.9	10330
		II-out	128.1	- 8.2	115.1	0.40870			
		I-in	149.2	-15.9	128.5	0.20434	630.2	606.0	3940
		I-out	126.5	- 2.8	118.9	0.40824			
	D_6	I-in	177.5	-53.0	119.7	0.20434	585.8	571.7	2290
		I-out	124.7	- 6.0	113.9	0.40861			
		II-out	157.1	-34.7	117.6	0.20561	572.0	553.3	3050
		II-in	114.9	- 1.0	109.1	0.40973			
	D_{11}	I-in	107.2	+23.5	125.9	0.20427	616.3	566.4	8110
		I-out	123.2	-12.9	105.5	0.40854			
		II-in	122.3	+17.4	134.9	0.20457	659.4	608.2	8320
		II-out	110.2	+ 8.4	113.8	0.40889			
	D_{13}	I-out	123.3	+10.3	128.8	0.20425	630.6	578.2	8500
		I-in	115.3	- 2.9	107.6	0.40885			
	D_{17}	I-out	121.6	+12.2	129.0	0.20458	630.6	585.3	7370
		I-in	111.2	+ 3.9	110.3	0.40882			
		II-in	137.1	- 6.2	126.1	0.20449	616.7	584.7	5200
		II-out	123.7	- 6.0	112.9	0.40879			
						Average	625.8	586.7	6346
					Standard error		11.8	7.7	935

Table 9. (Continued)

Sol. no. m	Run	Sample	$q_e \mathrm{x} 10^3$	$q_d \mathrm{x} 10^3$	$q_1 - q_0 \mathrm{x} 10^3$ $q_2 - q_0 \mathrm{x} 10^3$	$n_2' \mathrm{x} 10^3$ $(n_2' + n_2'') \mathrm{x} 10^3$	$-\Delta H_{1,2}$	$-\Delta H_{1,3}$	$\bar{P}_i$
2 0.041178	D_1	I-in	297.0	+20.1	312.3	0.40938	762.8	701.5	7030
		I-out	254.8	+12.3	262.3	0.81914			
		II-in	305.4	+32.4	333.0	0.40969	812.8	759.0	6170
		II-out	338.2	-44.5	288.9	0.81935			
	D_4	I-out	306.6	+ 8.0	309.8	0.40851	758.4	710.4	5510
		I-in	256.1	+19.9	271.2	0.81785			
		II-in	307.0	+16.3	318.5	0.40971	777.3	724.1	6110
		II-out	264.2	+15.0	274.4	0.81881			
	D_9	I-in	307.4	+19.9	322.5	0.40899	788.5	725.8	7180
		I-out	255.9	+21.1	272.2	0.81932			
		II-out	313.0	+12.8	321.0	0.40926	784.3	730.6	6160
		II-in	299.2	-17.4	277.0	0.81856			
	D_{15}	I-out	313.6	+13.7	322.5	0.40981	787.0	725.4	7060
		I-in	252.6	+24.5	272.3	0.81997			
		II-in	322.8	+ 2.9	320.9	0.40929	784.3	723.2	7010
		II-out	274.8	+ 1.0	271.0	0.81847			
						Average	781.9	725.0	6529
						Standard error	5.9	5.9	218

Table 9. (Continued)

Sol. no. m	Run	Sample	q_ex10^3	q_dx10^3	q_1-q_0x10^3 q_2-q_0x10^3	n_2'x10^3 $(n_2'+n_2'')$x10^3	$-\Delta H_{1,2}$	$-\Delta H_{1,3}$	$\bar{P}_1$
3 0.067441	D_3	I-out	573.6	+22.1	590.9	0.67016	881.7	819.1	5620
		I-in	521.4	-10.1	506.5	1.33974			
		II-out	552.8	+46.5	597.5	0.66906	893.0	836.1	5110
		II-in	520.0	+ 7.6	522.8	1.33987			
	D_7	I-in	570.4	+29.8	595.4	0.66999	888.7	824.7	5740
		I-out	529.9	-14.9	510.2	1.34061			
		II-out	558.7	+36.0	589.9	0.67018	880.2	819.9	5410
		II-in	537.0	-23.1	509.1	1.34042			
	D_{14}	I-out	567.9	+19.3	582.4	0.66940	870.0	813.9	5030
		I-in	519.1	- 6.3	508.0	1.33978			
		II-in	656.7	-34.2	617.7	0.66930	922.4	844.8	6960
		II-out	521.9	- 3.7	513.4	1.33895			
	D_{19}	I-in	606.9	+ 9.1	611.2	0.67028	911.9	834.9	6920
		I-out	529.2	-17.2	507.2	1.33959			
						Average	892.6	827.6	5827
						Standard error	7.0	5.9	303

Table 9. (Continued)

Sol. no. m	Run	Sample	$q_e x10^3$	$q_d x10^3$	$q_1-q_0 x10^3$ $q_2-q_0 x10^3$	$n' x10^3$ $(n_2'+n_2'')x10^3$	$-\Delta H_{1,2}$	$-\Delta H_{1,3}$	$\bar{P}_1$
4 0.12680	D_5	II-in	1330.5	+22.8	1348.5	1.2585	1071.5	982.8	5810
		II-out	1122.9	+ 6.5	1124.6	2.5164			
		I-in	1281.6	+76.6	1353.4	1.2604	1073.8	981.3	6050
		I-out	1190.5	-66.3	1119.4	2.5199			
	D_{12}	II-out	1305.6	+41.6	1342.4	1.2583	1070.7	985.7	5550
		II-in	1146.6	- 2.5	1139.3	2.5178			
		I-in	1302.8	+40.9	1338.9	1.2576	1064.6	976.8	5740
		I-out	1129.3	- 4.6	1119.9	2.5173			
	D_{18}	I-in	1319.5	+17.7	1332.4	1.2587	1058.6	975.8	5420
		I-out	1125.8	+ 2.6	1123.6	2.5170			
		II-out	1346.7	+10.9	1352.8	1.2600	1073.7	987.3	5650
		II-in	1158.3	-17.8	1135.7	2.5206			
						Average	1068.8	981.6	5703
					Standard error		2.4	1.9	134

Table 9. (Continued)

Sol. no. m	Run	Sample	$q_e x10^3$	$q_d x10^3$	$q_1-q_0 x10^3$ $q_2-q_0 x10^3$	$n_2' x10^3$ $(n_2'+n_2'') x10^3$	$-\Delta H_{1,2}$	$-\Delta H_{1,3}$	$\bar{P}_i$
5	D_8	I-in	3295.7	+39.5	3330.4	2.5417	1308.8	1193.9	5280
0.25691		I-out	2764.6	-17.7	2742.1	5.0864			
	D_{10}	I-in	3282.0	+22.2	3299.4	2.5394	1299.3	1186.4	5190
		I-out	2756.9	-17.1	2735.0	5.0861			
		II-in	3269.7	+39.1	3304.0	2.5401	1300.5	1188.7	5150
		II-out	2758.7	-18.8	2735.1	5.0806			
	D_{16}	I-in	3274.1	+31.1	3300.4	2.5436	1297.5	1189.2	4980
		I-out	2753.0	+ 5.5	2753.7	5.0909			
		II-out	3307.8	- 1.3	3301.7	2.5416	1299.1	1191.7	4940
		II-in	2773.5	-13.0	2755.7	5.0832			
						Average	1301.0	1190.0	5108
						Standard error	2.0	1.3	46

Table 10. Short chord data and relative apparent molal heat contents of gadolinium chloride solutions at 25° C.

Sol. no.	$m_i^{\frac{1}{2}}$	$m_k^{\frac{1}{2}}\times10^2$	$x_i\times10^2$	$\bar{P}_i$	$\phi_{L(m_k)}$	$-\Delta H_{i,k}$	$\phi_{L(m_i)}$	$\bar{\phi}_L$
1	0.14331	1.5154	1.8230	6346	105.0	625.8	730.8	731.6
		2.1305			145.6	586.7	732.3	
2	0.20292	2.1436	2.5795	6529	146.5	781.9	928.4	927.6
		3.0154			201.8	725.0	926.8	
3	0.25969	2.7427	3.2999	5827	184.8	892.6	1077.4	1079.0
		3.8571			252.9	827.6	1080.5	
4	0.35609	3.7604	4.5247	5703	247.1	1068.8	1315.9	1315.5
		5.2889			334.5	981.6	1315.1	
5	0.50687	5.3446	6.4317	5108	337.6	1301.0	1638.6	1638.6
		7.5188			448.6	1190.0	1638.6	

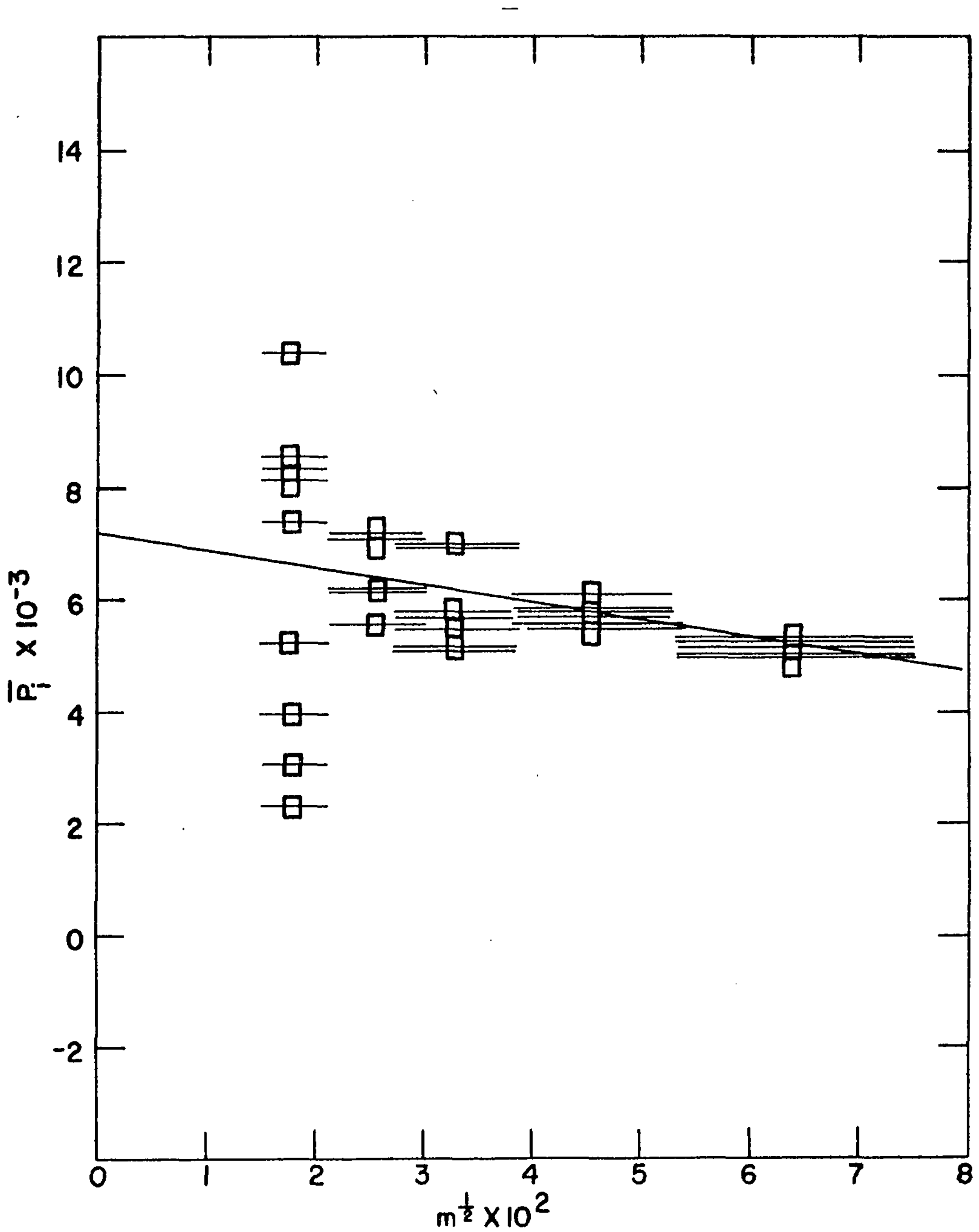

Figure 6. Short chords of gadolinium chloride solutions at 25° C.

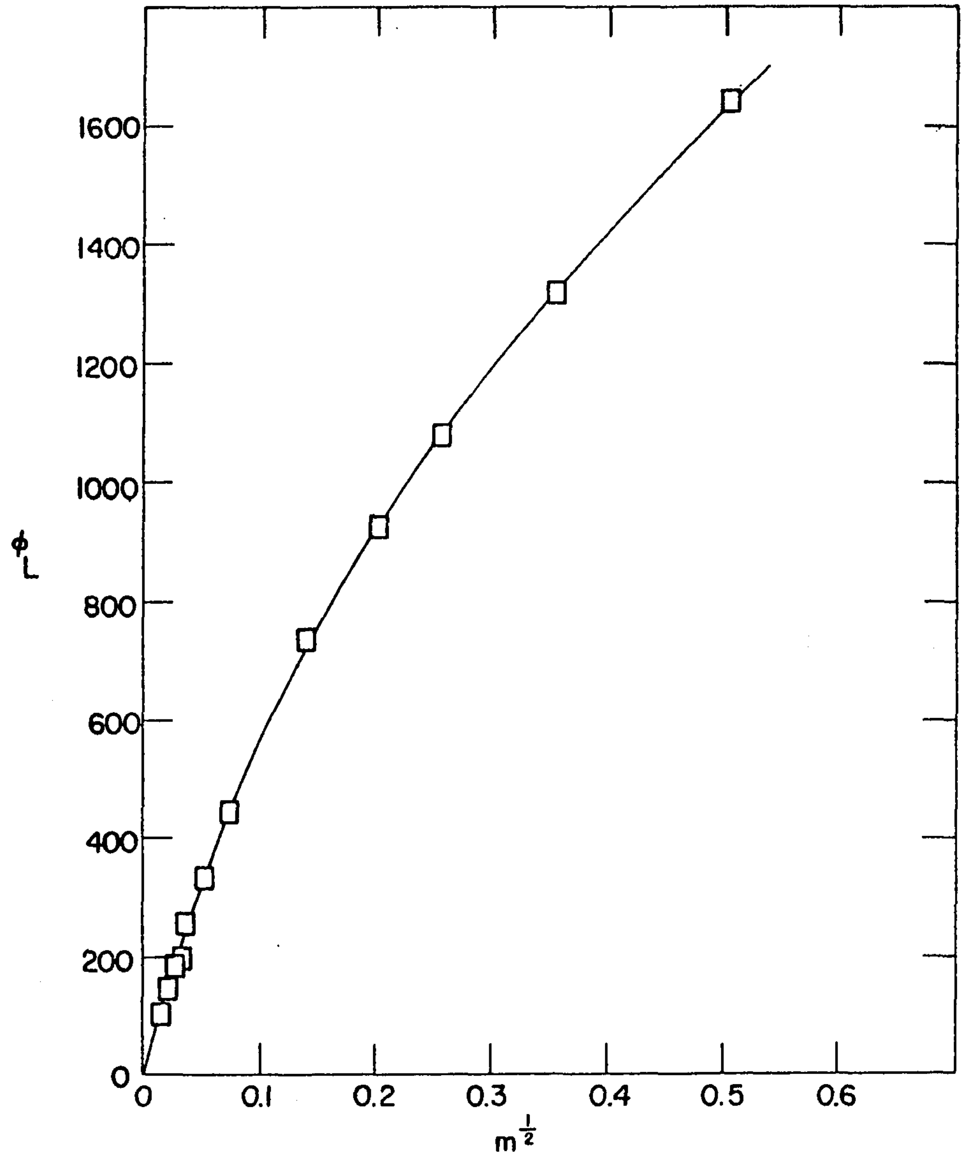

Figure 7. Relative apparent molal heat contents of gadolinium chloride solutions at 25° C.

Table 11. Thermodynamic properties of gadolinium chloride solutions at 25° C.

$m^{\frac{1}{2}}$	ϕ_L	$\bar{L}_2$	$-\bar{L}_1 \mathrm{x} 10^3$
0.0100	71	106	0.062
0.0200	137	202	0.469
0.0500	318	457	6.26
0.0700	424	600	15.5
0.1000	564	781	39.1
0.2000	917	1210	211.0
0.3000	1180	1546	592.0
0.4000	1415	1870	1310.0
0.5000	1626	2091	2094.0

4. Dysprosium chloride

The data for dysprosium chloride are listed in Tables 12, 13 and 14 and are plotted in Figures 8 and 9.

Several weighted least squares determinations were performed on the $\bar{P}_1$ data, one of which was an equation in the form of equation III-59. It is given by

$$\bar{P}_1 = 6883 - 51706\, x_1 + 3.4487 \times 10^5 \left(x_1^2 + \frac{\delta_1^2}{12}\right). \qquad \text{(IV-14)}$$

Two straight line equations were also determined. The first is given by

$$\bar{P}_i = 6198 - 1.9558 \times 10^5\ x_i. \qquad \text{(IV-15)}$$

The second, using the theoretical limiting slope of ϕ_L, is given by

$$\bar{P}_i = 6925 - 32544\ x_i. \qquad \text{(IV-16)}$$

Of the two straight lines, equation IV-16 fit the experimental data better; however, the fit was not as good as that obtained from equation IV-14. Consequently the ϕ_L equation for the dilute concentration range was determined by integrating equation IV-14. The resulting equation for $m < 0.006$ is:

$$\phi_L = 6883\ m^{1/2} - 25853\ m + 1.1496 \times 10^5\ m^{3/2}. \qquad \text{(IV-17)}$$

Using the data listed in Table 13, the ϕ_L equation valid for the entire concentration range is:

$$\phi_L = 6654\ m^{1/2} - 15816\ m + 30889\ m^{3/2} - 26415\ m^2. \qquad \text{(IV-18)}$$

The equations for $\bar{L}_1$ and $\bar{L}_2$ are:

$$\bar{L}_1 = -59.939\ m^{3/2} + 284.94\ m^2 - 834.74\ m^{5/2} + 951.88\ m^3 \qquad \text{(IV-19)}$$

and

$$\bar{L}_2 = 9981\ m^{1/2} - 31632\ m + 77223\ m^{3/2} - 79245\ m^2. \qquad \text{(IV-20)}$$

Table 12. Heats of dilution of dysprosium chloride solutions at 25° C.

Sol. no. m	Run	Sample	$q_e \times 10^3$	$q_d \times 10^3$	$q_1-q_0 \times 10^3$ $q_2-q_0 \times 10^3$	$n_2' \times 10^3$ $(n_2'+n_2'') \times 10^3$	$-\Delta H_{1,2}$	$-\Delta H_{1,3}$	$\bar{P}_1$
1 0.028037	B_1	I-in	202.8	+11.9	198.0	0.27915	709.3	655.1	7690
		I-out	170.3	+13.8	167.4	0.55774			
		II-out	202.6	+21.6	207.5	0.27877	744.3	689.4	7640
		II-in	182.2	+11.2	176.7	0.55729			
	B_6	I-in	206.9	+ 3.9	194.1	0.27917	695.2	637.3	8060
		I-out	172.9	+ 5.2	161.4	0.55784			
	B_3	II-in	206.0	+ 1.4	190.7	0.27909	684.5	667.4	2380
		II-out	172.5	+25.7	181.5	0.55769			
		I-in	182.6	+17.7	183.6	0.27881	658.5	616.5	5840
		I-out	176.8	+ 0.2	160.3	0.55783			
	B_{10}	II-in	206.6	+10.8	200.7	0.27885	719.7	674.1	6340
		II-out	175.4	+16.6	175.3	0.55774			
		I-in	207.3	+ 0.0	190.6	0.27887	683.5	638.9	6190
		I-out	177.0	+ 5.8	166.1	0.55832			
						Average	699.3	654.1	6306
						Standard error	10.6	9.4	729

Table 12. (Continued)

Sol. no m	Run	Sample	$q_e x10^3$	$q_d x10^3$	$q_1-q_0 x10^3$ $q_2-q_0 x10^3$	$n_2' x10^3$ $(n_2'+n_2'')x10^3$	$-\Delta H_{1,2}$	$-\Delta H_{1,3}$	$\bar{P}_1$
2	B_2	I-in	333.3	+11.3	327.9	0.41577	788.7	724.4	7330
0.041828		I-out	311.0	-20.0	274.3	0.83127			
		II-out	312.7	+42.3	338.3	0.41584	813.5	746.6	7620
		II-in	304.9	- 5.5	282.7	0.83177			
	B_3	I-in	314.3	+10.0	307.6	0.41602	739.4	716.5	2610
		I-out	313.2	- 7.9	288.6	0.83207			
		II-out	384.0	-33.0	334.3	0.41580	804.0	749.1	6250
		II-in	304.6	+ 1.0	288.9	0.83195			
	B_7	II-out	314.5	+26.9	324.7	0.41628	780.0	734.2	5210
		II-in	294.6	+ 8.5	286.4	0.83231			
		I-out	312.0	+23.1	318.4	0.41607	765.3	711.8	6090
		I-in	293.1	- 2.3	274.1	0.83237			
						Average	781.8	730.4	5851
						Standard error	11.0	6.3	739

Table 12. (Continued)

Sol. no. m	Run	Sample	$q_e x10^3$	$q_d x10^3$	$q_1-q_0 x10^3$ $q_2-q_0 x10^3$	$n_2' x10^3$ $(n_2'+n_2'')x10^3$	$-\Delta H_{1,2}$	$-\Delta H_{1,3}$	$\bar{P}_i$
3 0.069710	B_9	II-in	634.0	+13.1	630.4	0.69184	911.2	852.4	5190
		II-out	513.8	+52.3	549.4	1.38403			
		I-in	644.0	- 2.2	625.1	0.69259	902.6	843.5	5220
		I-out	617.9	-58.0	543.2	1.38504			
	B_{11}	I-out	633.2	+ 8.3	624.8	0.69332	901.2	848.2	4690
		I-in	659.0	- 1.5	550.8	1.38603			
		II-in	586.0	+61.3	630.6	0.69280	910.2	861.7	4280
		II-out	563.4	+17.0	563.7	1.38594			
	B_{16}	I-out	737.2	-59.8	660.7	0.69322	953.1	877.0	6710
		I-in	656.5	-84.1	555.7	1.38707			
	B_{17}	I-in	631.4	+30.3	645.0	0.69321	930.4	862.6	5980
		I-out	578.7	-11.3	550.7	1.38615			
		II-out	593.0	+71.3	647.6	0.69296	934.5	872.4	5480
		II-in	544.8	+33.5	561.6	1.38607			
						Average	920.5	859.7	5364
						Standard error	7.2	4.7	302

Table 12. (Continued)

Sol. no. m	Run	Sample	$q_e \times 10^3$	$q_d \times 10^3$	$q_1 - q_0 \times 10^3$ $q_2 - q_0 \times 10^3$	$n_2' \times 10^3$ $(n_2' + n_2'') \times 10^3$	$-\Delta H_{1,2}$	$-\Delta H_{1,3}$	$\bar{P}_1$
4 0.16731	B_{12}	II-out	1942.9	+ 0.3	1926.5	1.6600	1160.5	1077.2	4740
		II-in	1650.9	+ 16.3	1650.5	3.3208			
		I-in	1890.6	+ 56.1	1930.0	1.6610	1162.0	1068.4	5320
		I-out	1636.0	+ 1.2	1620.5	3.3233			
	B_{14}	I-in	1940.0	+ 15.0	1938.3	1.6567	1170.0	1074.1	5460
		I-out	1638.9	+ 2.9	1625.1	3.3176			
		II-out	1936.5	+ 23.1	1942.9	1.6579	1171.9	1079.8	5240
		II-in	1651.9	+ 4.9	1640.1	3.3183			
						Average	1166.1	1074.9	5190
					Standard error		2.9	2.5	156
5 0.23241	B_{13}	I-out	2973.7	- 28.8	2928.2	2.3040	1270.9	1174.8	4650
		I-in	2462.7	+ 39.9	2485.9	4.6085			
		II-out	2938.1	+ 46.5	2967.9	2.3039	1288.2	1184.0	5040
		II-in	2478.3	+ 24.8	2486.4	4.6067			
	B_{15}	II-in	3072.5	- 77.5	2978.0	2.301.8	1293.7	1186.9	5170
		II-out	2586.6	- 86.1	2483.8	4.6017			
		I-in	2858.1	+114.1	2955.5	2.3025	1283.6	1176.9	5160
		I-out	2457.0	+ 24.9	2465.2	4.6058			
						Average	1284.1	1180.7	5005
					Standard error		4.9	2.8	126

Table 13. Short chord data and relative apparent molal heat contents of dysprosium chloride solutions at 25° C.

Sol. no.	$m_1^{\frac{1}{2}}$	$m_k^{\frac{1}{2}}x10^2$	x_1x10^2	$\bar{P}_1$	$\phi_{L(m_k)}$	$-\Delta H_{1,k}$	$\phi_{L(m_1)}$	$\bar{\phi}_L$
1	0.16744	1.7700	2.1291	6306	114.3	699.3	813.6	812.4
		2.4882			157.1	654.1	811.2	
2	0.20452	2.1610	2.6001	5851	137.8	781.8	919.6	919.3
		3.0392			188.5	730.4	918.9	
3	0.26403	2.7892	3.3560	5364	174.4	920.5	1094.9	1095.9
		3.9228			237.1	859.7	1096.8	
4	0.40904	4.3171	5.1953	5190	258.1	1166.1	1424.2	1423.8
		6.0736			348.4	1074.9	1423.3	
5	0.48209	5.0876	6.1212	5005	298.4	1284.1	1582.5	1582.8
		7.1549			402.3	1180.7	1583.0	

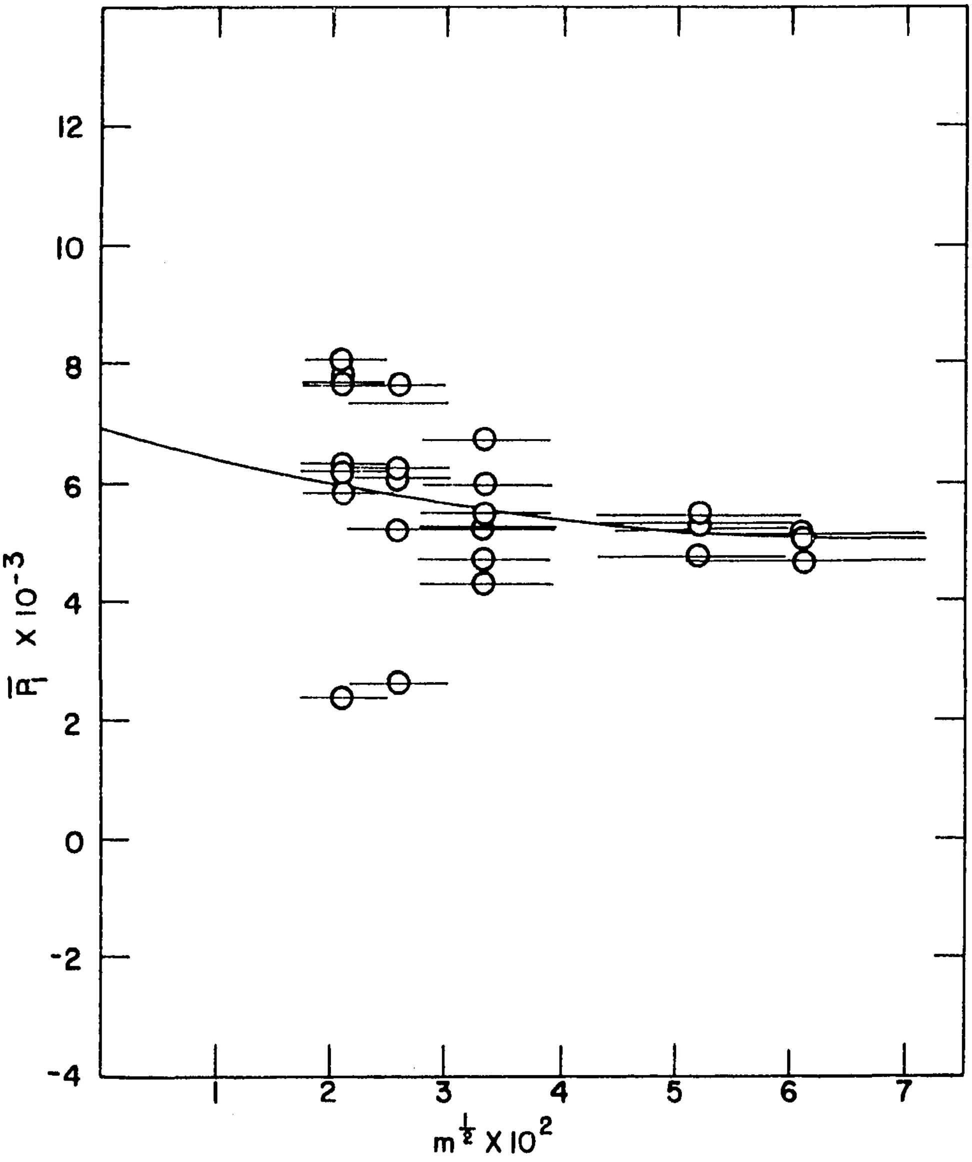

Figure 8. Short chords of dysprosium chloride solutions at 25° C.

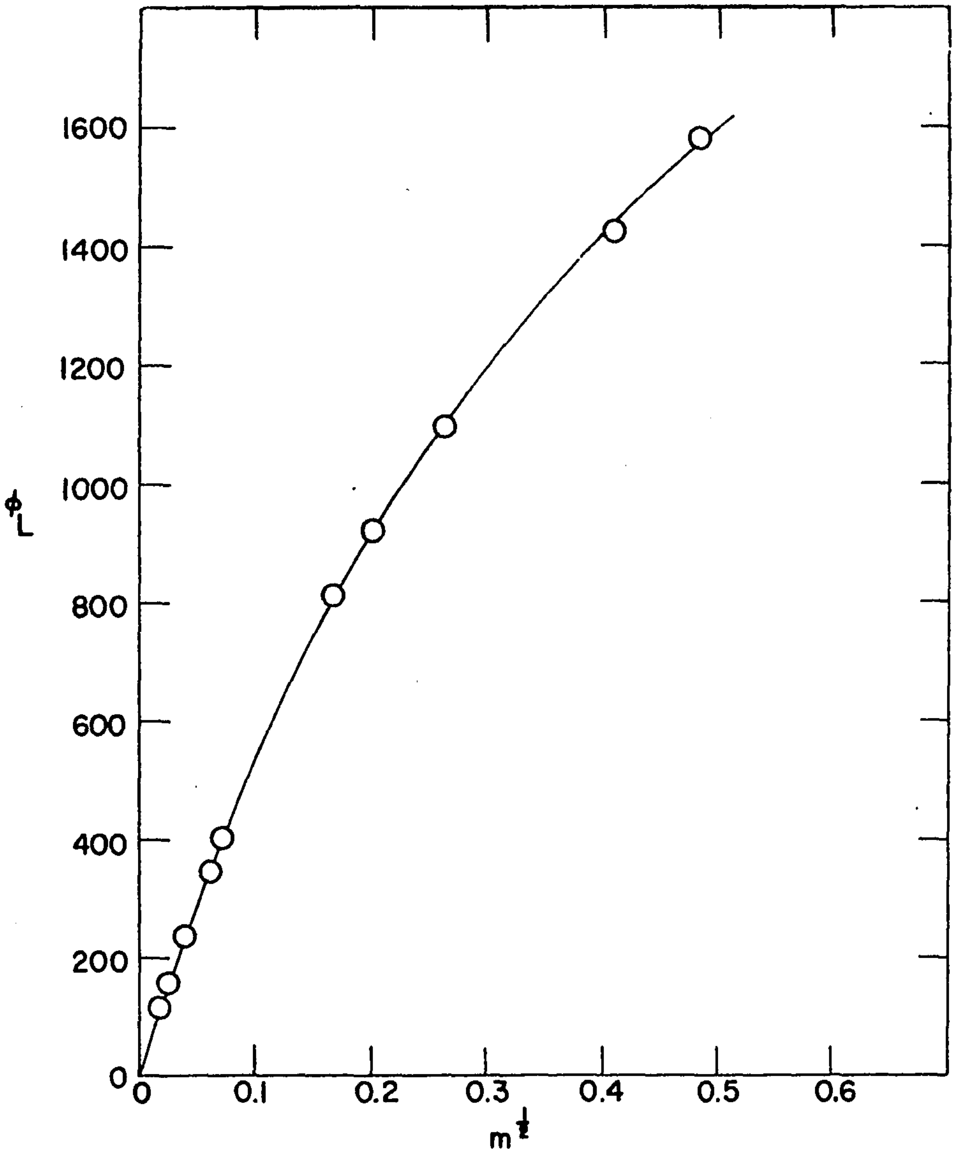

Figure 9. Relative apparent molal heat contents of dysprosium chloride solutions at 25° C.

Table 14. Thermodynamic properties of dysprosium chloride solutions at 25° C.

$m^{\frac{1}{2}}$	ϕ_L	$\bar{L}_2$	$-\bar{L}_1 x 10^3$
0.0100	65	97	0.057
0.0200	127	188	0.437
0.0500	297	429	5.96
0.0700	398	568	15.0
0.1000	536	751	38.9
0.2000	903	1222	230.0
0.3000	1193	1591	645.0
0.4000	1432	1845	1190.0
0.5000	1583	1783	896.0

5. Holmium chloride

The data for holmium chloride are listed in Tables 15, 16 and 17 and are plotted in Figures 10 and 11.

The best fit for the $\bar{P}_1$ data was a straight line given by

$$\bar{P}_1 = 6806 - 22629\ x_1, \tag{IV-21}$$

which was integrated to give

$$\phi_L = 6806\ m^{1/2} - 11315\ m \tag{IV-22}$$

for the concentration range of $m < 0.006$.

Table 15. Heats of dilution of holmium chloride solutions at 25° C.

Sol. no. m	Run	Sample	$q_e x10^3$	$q_d x10^3$	$q_1-q_0 x10^3$ $q_2-q_0 x10^3$	$n_2' x10^3$ $(n_2'+n_2'')x10^3$	$-\Delta H_{1,2}$	$-\Delta H_{1,3}$	$\bar{P}_i$
1	F_6	I-in	92.8	+21.2	109.2	0.17468	625.1	565.8	10440
0.017553		I-out	85.0	+ 8.1	88.3	0.34904			
		II-in	143.3	-32.1	106.4	0.17455	609.6	568.4	7240
		II-out	114.2	-17.3	92.1	0.34921			
	F_{12}	II-in	92.2	+12.1	103.6	0.17466	593.7	576.8	2970
		II-out	82.5	+20.1	97.8	0.34915			
		I-in	101.2	- 3.5	92.9	0.17478	531.7	515.0	2930
		I-out	92.8	- 0.9	87.1	0.34949			
	F_{16}	II-out	85.0	+26.7	106.9	0.17479	611.5	577.0	6070
		II-in	85.5	+14.0	94.7	0.34937			
		I-out	101.9	- 2.0	95.1	0.17453	544.9	510.3	6080
		I-in	89.6	- 1.7	83.1	0.34918			
	F_{18}	II-in	101.2	+10.4	106.8	0.17472	611.3	555.6	9790
		II-out	94.7	- 2.5	87.4	0.34951			
		I-in	102.1	+ 1.4	98.7	0.17450	565.6	545.1	3600
		I-out	94.7	+ 1.7	91.6	0.34908			
	F_{19}	II-in	106.3	+ 8.6	110.1	0.17462	630.5	574.4	9850
		II-out	102.5	- 7.2	90.5	0.34923			
						Average	591.5	554.3	6552
						Standard error	11.9	8.6	1001

Table 15. (Continued)

Sol. no. m	Run	Sample	$q_e x10^3$	$q_d x10^3$	$q_1-q_0 x10^3$ $q_2-q_0 x10^3$	$n_2' x10^3$ $(n_2'+n_2'') x10^3$	$-\Delta H_{1,2}$	$-\Delta H_{1,3}$	$\bar{P}_1$
2 0.03445	F_7	I-in	241.3	+ 0.0	236.5	0.34281	689.9	654.4	4460
		I-out	210.4	+ 6.4	212.0	0.68531			
		II-in	240.7	+ 3.0	238.9	0.34273	697.1	657.0	5030
		II-out	188.5	+27.6	211.3	0.68519			
	F_{10}	I-out	230.8	+30.2	256.2	0.34224	748.5	694.3	6800
		I-in	210.4	+13.8	219.4	0.68497			
		II-in	251.1	+10.8	257.1	0.34209	751.6	702.3	6180
		II-out	284.4	-55.7	223.7	0.68461			
	F_{15}	II-in	270.6	- 4.3	261.5	0.34238	763.7	707.4	7070
		II-out	290.5	-62.9	222.8	0.68458			
		I-out	231.7	+24.4	251.3	0.34219	734.4	684.8	6220
		I-in	220.9	+ 1.5	217.6	0.68465			
						Average	730.9	683.4	5960
						Standard error	12.4	9.4	415

Table 15. (Continued)

Sol. no. m	Run	Sample	$q_e x10^3$	$q_d x10^3$	$q_1-q_0 x10^3$ $q_2-q_0 x10^3$	$n_2' x10^3$ $(n_2'+n_2'') x10^3$	$-\Delta H_{1,2}$	$-\Delta H_{1,3}$	$\bar{P}_i$
3 0.067120	F_3	I-out	550.4	+41.5	587.1	0.66754	879.5	821.7	5190
		I-in	515.8	- 1.0	510.0	1.33524			
		II-in	560.8	+38.1	594.1	0.66742	890.1	826.4	5730
		II-out	534.4	-20.7	508.9	1.33465			
	F_5	I-in	560.8	+49.0	605.0	0.66779	906.0	827.5	7050
		I-out	513.0	- 8.0	500.2	1.33566			
		II-in	661.7	-54.6	602.3	0.66755	902.3	838.4	5740
		II-out	596.0	-74.3	516.9	1.33499			
	F_{17}	II-in	647.5	-38.8	603.9	0.66687	905.6	841.7	5740
		II-out	547.7	-23.5	519.4	1.33462			
		I-in	593.1	- 0.8	587.5	0.66700	880.8	813.9	6010
		I-out	465.0	+38.4	498.6	1.33443			
						Average	894.1	828.3	5910
						Standard error	5.0	4.2	175

Table 15. (Continued)

Sol. no. m	Run	Sample	$q_e x10^3$	$q_d x10^3$	$q_1-q_0 x10^3$ $q_2-q_0 x10^3$	$n_2' x10^3$ $(n_2'+n_2'')x10^3$	$-\Delta H_{1,2}$	$-\Delta H_{1,3}$	$\bar{P}_1$
4 0.12827	F_9	I-in	1348.0	+ 24.0	1367.2	1.2745	1072.7	982.1	5890
		I-out	1146.9	- 5.5	1136.6	2.5494			
		II-in	1433.7	- 51.7	1377.2	1.2740	1080.6	993.0	5700
		II-out	1263.4	-105.1	1153.5	2.5485			
	F_{13}	II-in	1366.5	+ 4.1	1365.8	1.2740	1072.8	980.5	6000
		II-out	1180.0	- 43.5	1131.7	2.5471			
		I-in	1329.0	+ 43.9	1368.1	1.2735	1074.5	985.4	5800
		I-out	1176.8	- 30.5	1141.5	2.5468			
						Average	1075.2	985.3	5847
						Standard error	1.9	2.8	77
5 0.25237	F_{11}	I-in	3219.8	+ 60.2	3275.2	2.4973	1311.5	1192.0	5550
		I-out	2683.6	- 1.1	2677.7	4.9941			
		II-out	3253.8	- 8.4	3240.6	2.4982	1297.2	1188.1	5060
		II-in	2770.1	- 68.5	2696.8	4.9972			
	F_{14}	II-in	3231.8	+ 23.8	3250.8	2.4974	1301.7	1188.4	5260
		II-out	2720.3	- 28.4	2687.1	4.9967			
		I-in	3281.9	- 33.5	3243.6	2.5010	1296.9	1181.5	5350
		I-out	2682.6	- 14.0	2663.8	5.0000			
						Average	1301.8	1187.5	5305
						Standard error	3.4	2.2	104

Table 16. Short chord data and relative apparent molal heat contents of holmium chloride solutions at 25° C.

Sol. no.	$m_1^{\frac{1}{2}}$	$m_k^{\frac{1}{2}}x10^2$	x_ix10^2	$\bar{P}_i$	$\phi_{L(m_k)}$	$-\Delta H_{1,k}$	$\phi_{L(m_1)}$	$\bar{\phi}_L$
1	0.13249	1.4001 1.9690	1.6846	6552	93.1 129.6	591.5 554.3	684.6 683.9	684.3
2	0.18559	1.9606 2.7576	2.3591	5960	129.1 179.1	730.9 683.4	860.0 862.5	861.3
3	0.25908	2.7374 3.8501	3.2938	5910	177.8 245.2	894.1 828.3	1071.9 1073.5	1072.7
4	0.35815	3.7825 5.3201	4.5513	5847	241.2 330.1	1075.2 985.3	1316.4 1315.4	1315.9
5	0.50237	5.2994 7.4533	6.3764	5305	328.9 444.4	1301.8 1187.5	1630.7 1631.9	1631.3

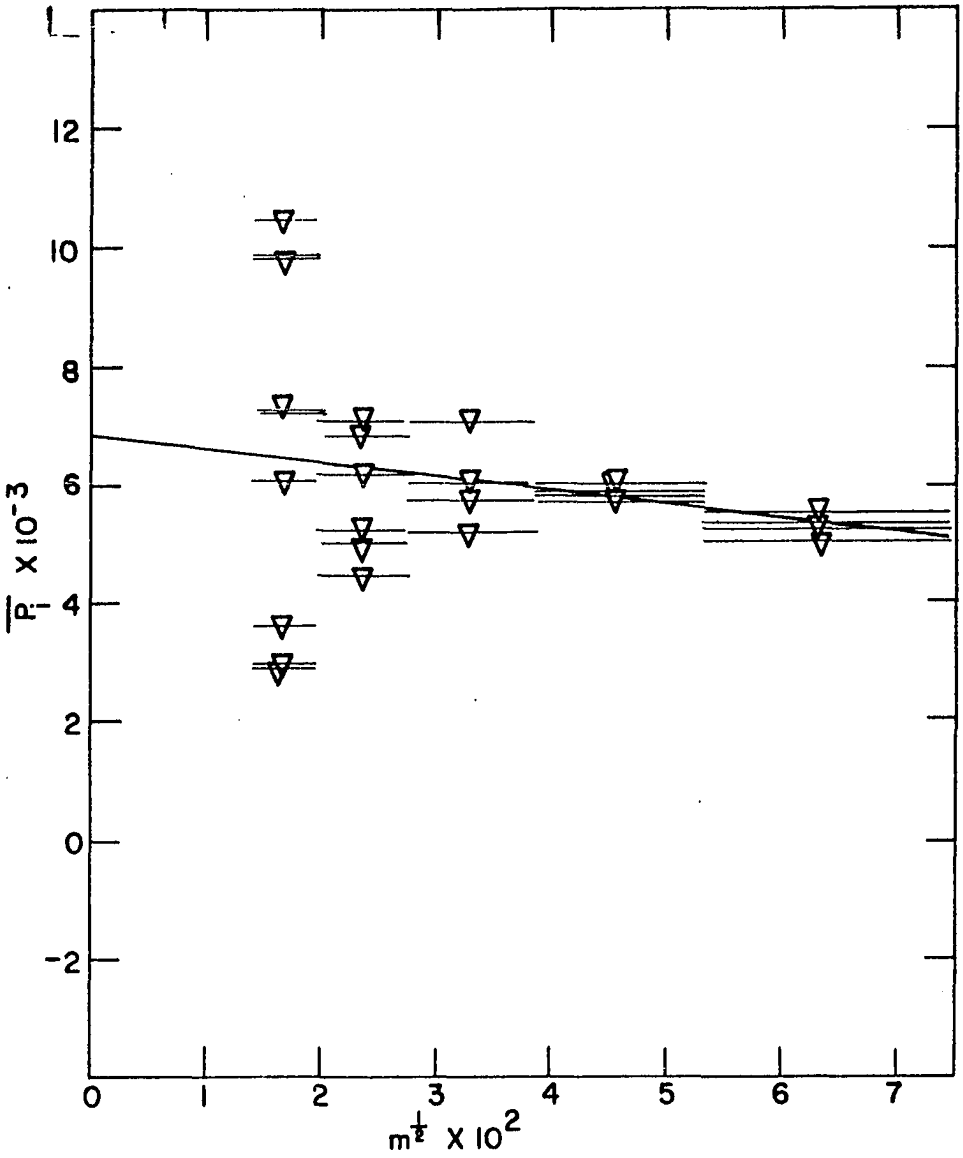

Figure 10. Short chords of holmium chloride solutions at 25° C.

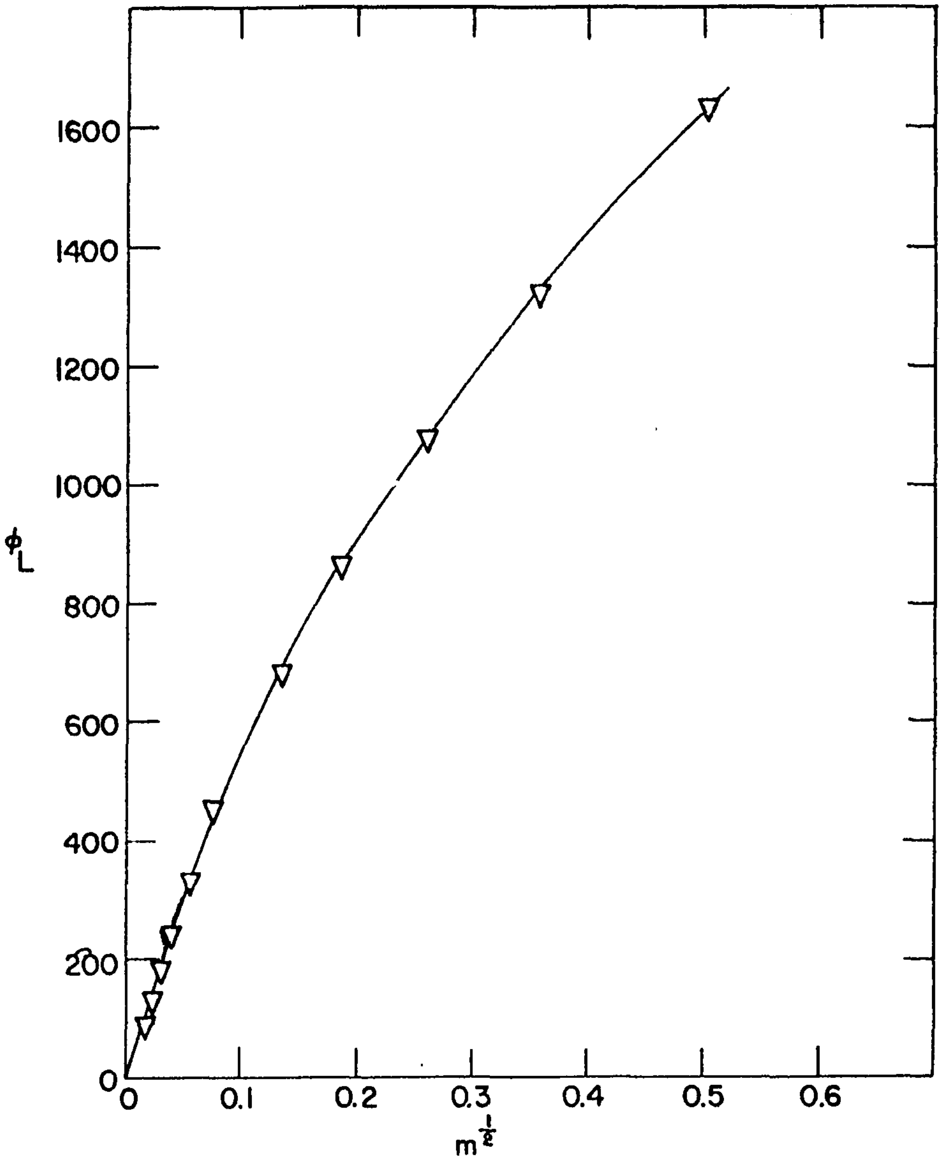

Figure 11. Relative apparent molal heat contents of holmium chloride solutions at 25° C.

Table 17. Thermodynamic properties of holmium chloride solutions at 25° C.

$m^{\frac{1}{2}}$	ϕ_L	$\bar{L}_2$	$-\bar{L}_1 \times 10^3$
0.0100	68	101	0.060
0.0200	132	195	0.454
0.0500	310	448	6.23
0.0700	415	592	15.6
0.1000	557	778	39.8
0.2000	917	1210	211.0
0.3000	1171	1510	549.0
0.4000	1390	1836	1283.0
0.5000	1631	2294	2988.0

From the data listed in Table 16, the ϕ_L equation valid for the entire concentration range is:

$$\phi_L = 6907\ m^{1/2} - 15222\ m + 19588\ m^{3/2} - 7447\ m^2. \qquad \text{(IV-23)}$$

The equations for $\bar{L}_1$ and $\bar{L}_2$ are:

$$\bar{L}_1 = -62.227\ m^{3/2} + 274.24\ m^2 - 529.35\ m^{5/2} + 268.33\ m^3 \qquad \text{(IV-24)}$$

and

$$\bar{L}_2 = 10361 m^{1/2} - 30444\ m + 48970\ m^{3/2} - 22341\ m^2. \qquad \text{(IV-25)}$$

6. <u>Thulium chloride</u>

The data for thulium chloride are listed in Tables 18, 19 and 20 and are plotted in Figures 12 and 13.

The best fit for the $\bar{P}_1$ data was a straight line given by

$$\bar{P}_1 = 6672 - 27992\ x_1, \qquad \text{(IV-26)}$$

which was integrated to give

$$\phi_L = 6672\ m^{1/2} - 13996\ m \qquad \text{(IV-27)}$$

for the concentration range of $m < 0.006$.

From the data listed in Table 19, the ϕ_L equation valid for the entire concentration range was found to be:

$$\phi_L = 6670\ m^{1/2} - 14951\ m - 22708\ m^{3/2} - 13465\ m^2. \qquad \text{(IV-28)}$$

The equations for $\bar{L}_1$ and $\bar{L}_2$ are:

$$\bar{L}_1 = -60.083\ m^{3/2} + 269.36\ m^2 - 613.66\ m^{5/2} + 485.17\ m^3 \qquad \text{(IV-29)}$$

and

$$\bar{L}_2 = 10005\ m^{1/2} - 29902\ m + 56770\ m^{3/2} - 40395\ m^2. \qquad \text{(IV-30)}$$

Table 18. Heats of dilution of thulium chloride solutions at 25° C.

Sol. no. m	Run	Sample	q_ex10^3	q_dx10^3	q_1-q_0x10^3 q_2-q_0x10^3	n_2'x10^3 (n_2'+n_2'')x10^3	-$\Delta H_{1,2}$	-$\Delta H_{1,3}$	$\bar{P}_1$
1	E_1	II-in	127.0	+20.1	142.3	0.20457	695.6	653.4	6850
0.020551		II-out	127.7	+ 2.1	125.0	0.40911			
		I-in	139.3	-25.6	108.9	0.20456	532.4	510.8	3510
		I-out	76.2	+28.6	100.0	0.40900			
	E_3	I-in	125.8	+ 3.3	124.3	0.20462	608.7	548.6	9750
		I-out	86.9	+17.9	100.0	0.40884			
	E_5	I-in	133.4	- 6.7	121.9	0.20468	595.6	570.1	4140
		I-in	94.8	+24.2	114.2	0.40905			
		II-in	160.2	-15.3	140.1	0.20451	685.0	627.8	9290
		II-out	105.1	+16.4	116.7	0.40904			
	E_8	II-in	116.6	+18.8	130.6	0.20430	639.3	600.8	6260
		II-out	108.5	+11.2	114.9	0.40862			
		I-in	127.5	+ 3.0	125.7	0.20409	615.9	581.7	5560
		I-out	104.3	+12.3	111.8	0.40826			
	E_{11}	I-in	129.0	+ 0.4	124.6	0.20443	609.5	578.9	4970
		I-out	115.4	+ 1.4	112.0	0.40868			
		II-in	132.9	+ 2.5	130.6	0.20466	661.6	603.4	9460
		II-out	115.2	+ 5.8	116.2	0.40904			
	E_{19}	I-out	76.7	+52.2	114.1	0.20427	558.6	531.2	4450
		I-in	84.6	+33.1	102.9	0.40852			
						Average	620.2	580.7	6424
					Standard error		16.4	13.7	739

Table 18. (Continued)

Sol. no. m	Run	Sample	$q_e \times 10^3$	$q_d \times 10^3$	$q_1 - q_0 \times 10^3$ $q_2 - q_0 \times 10^3$	$n_2' \times 10^3$ $(n_2' + n_2'') \times 10^3$	$-\Delta H_{1,2}$	$-\Delta H_{1,3}$	$\bar{P}_i$
2 0.042145	E_6	I-in	281.0	+46.2	322.4	0.41912	769.2	726.2	4880
		I-out	284.2	+ 6.6	286.0	0.83781			
		II-out	300.7	+26.9	322.6	0.41841	771.0	729.5	4710
		II-in	285.2	+ 8.4	288.8	0.83814			
	E_{10}	II-in	314.5	+23.0	332.7	0.41909	793.9	736.1	6560
		II-out	295.8	- 6.8	284.2	0.83810			
		I-out	301.8	+25.0	322.0	0.41947	768.6	725.3	4900
		I-in	270.7	+20.4	286.3	0.83863			
	E_{13}	II-in	306.0	+23.6	324.8	0.41964	774.0	715.7	6610
		II-out	273.8	+ 6.8	275.8	0.83923			
		I-in	305.6	+28.3	329.1	0.41884	785.7	731.7	6120
		I-in	293.7	- 4.6	284.3	0.83829			
	E_{15}	I-in	305.7	+19.7	320.6	0.41899	765.2	699.5	7460
		I-out	275.0	- 4.8	265.4	0.83778			
		II-in	376.2	-28.9	342.5	0.41879	817.8	769.9	5430
		II-out	378.3	-70.9	302.6	0.83792			
						Average	780.7	729.2	5834
						Standard error	6.3	7.1	355

Table 18. (Continued)

Sol. no. m	Run	Sample	$q_e x10^3$	$q_d x10^3$	$q_1-q_0 x10^3$ $q_2-q_0 x10^3$	$n_2' x10^3$ $(n_2'+n_2'') x10^3$	$-\Delta H_{1,2}$	$-\Delta H_{1,3}$	$\bar{P}_1$
3 0.084582	E_4	I-out	710.2	+76.4	781.8	0.83991	930.8	863.9	5360
		I-in	642.0	+32.0	669.2	1.67956			
		II-in	852.0	-39.6	807.6	0.83953	962.0	888.4	5890
		II-out	759.2	-69.0	685.4	1.68063			
	E_{12}	I-in	792.9	+ 5.4	793.5	0.84105	943.5	868.9	5970
		I-out	686.7	-13.9	668.0	1.68206			
		II-in	804.9	- 8.5	791.6	0.84074	941.2	870.9	5630
		II-out	715.8	-37.9	673.1	1.68176			
	E_{17}	II-in	785.8	+ 2.6	783.6	0.83972	933.2	870.3	5040
		II-out	660.3	+23.0	678.5	1.68001			
		I-in	799.6	-20.7	774.1	0.84162	919.8	852.3	5400
		I-out	661.5	+ 2.9	659.6	1.68220			
						Average	938.3	869.1	5548
					Standard error		6.0	4.9	143

Table 18. (Continued)

Sol. no. m	Run	Sample	q_ex10^3	q_dx10^3	q_1-q_0x10^3 q_2-q_0x10^3	n_2'x10^3 $(n_2'+n_2'')$x10^3	$-\Delta H_{1,2}$	$-\Delta H_{1,3}$	$\bar{P}_1$
4	E_7	II-in	1921.0	+ 15.5	1931.7	1.6797	1150.0	1051.5	5580
0.16938		II-out	1625.7	- 19.9	1601.0	3.3595			
		I-out	1905.8	+ 11.2	1912.2	1.6778	1139.7	1052.2	4960
		I-in	1613.8	+ 9.1	1618.1	3.3553			
	E_{18}	I-in	1911.9	+ 21.8	1928.9	1.6819	1147.3	1048.7	5580
		I-out	1543.7	+ 60.2	1599.2	3.3642			
		II-in	1902.5	+ 25.2	1922.9	1.6782	1145.8	1050.2	5420
		II-out	1637.4	- 29.4	1603.2	3.3576			
						Average	1145.7	1050.7	5385
					Standard error		2.2	0.8	147
5	E_9	II-in	4421.3	- 7.9	4408.6	3.2157	1371.0	1262.9	4420
0.32571		II-out	3712.4	+ 13.9	3721.5	6.4378			
		I-out	4412.3	+ 34.7	4442.2	3.2205	1379.4	1266.3	4630
		I-in	3750.4	- 36.5	3709.1	6.4370			
	E_{16}	II-in	4506.8	- 23.4	4478.6	3.2220	1390.0	1273.0	4780
		II-out	3801.0	- 73.0	3723.2	6.4422			
						Average	1380.1	1267.4	4607
					Standard error		5.4	2.9	105

Table 19. Short chord data and relative apparent molal heat contents of thulium chloride solutions at 25° C.

Sol. no.	$m_1^{\frac{1}{2}}$	$m_k^{\frac{1}{2}}\mathrm{x}10^2$	$x_i\mathrm{x}10^2$	$\bar{P}_i$	$\phi_{L(m_k)}$	$-\Delta H_{1,k}$	$\phi_{L(m_1)}$	$\bar{\phi}_L$
1	0.14336	1.5150 2.1304	1.8227	6424	97.9 135.7	620.2 580.7	718.1 716.4	717.3
2	0.20529	2.1689 3.0507	2.6098	5834	138.1 190.5	780.7 729.2	918.8 919.7	919.3
3	0.29083	3.0715 4.3244	3.6980	5548	191.7 262.3	938.3 869.1	1130.0 1131.4	1130.7
4	0.41156	4.3438 6.1093	5.2266	5385	263.4 355.4	1145.7 1050.7	1409.1 1406.1	1407.6
5	0.57071	6.0170 8.4625	7.2398	4607	350.8 464.4	1380.1 1267.4	1730.9 1731.8	1731.4

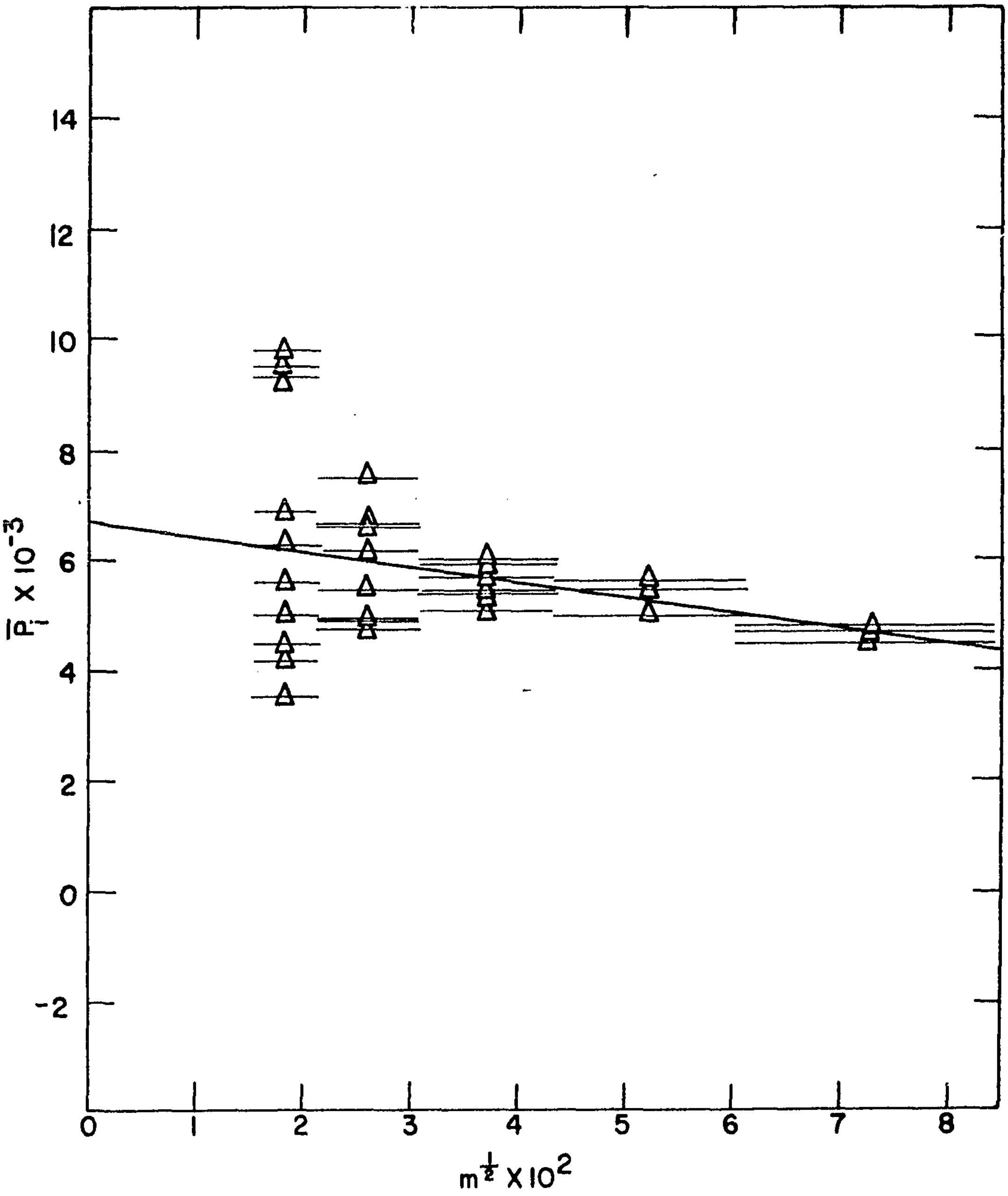

Figure 12. Short chords of thulium chloride solutions at 25° C.

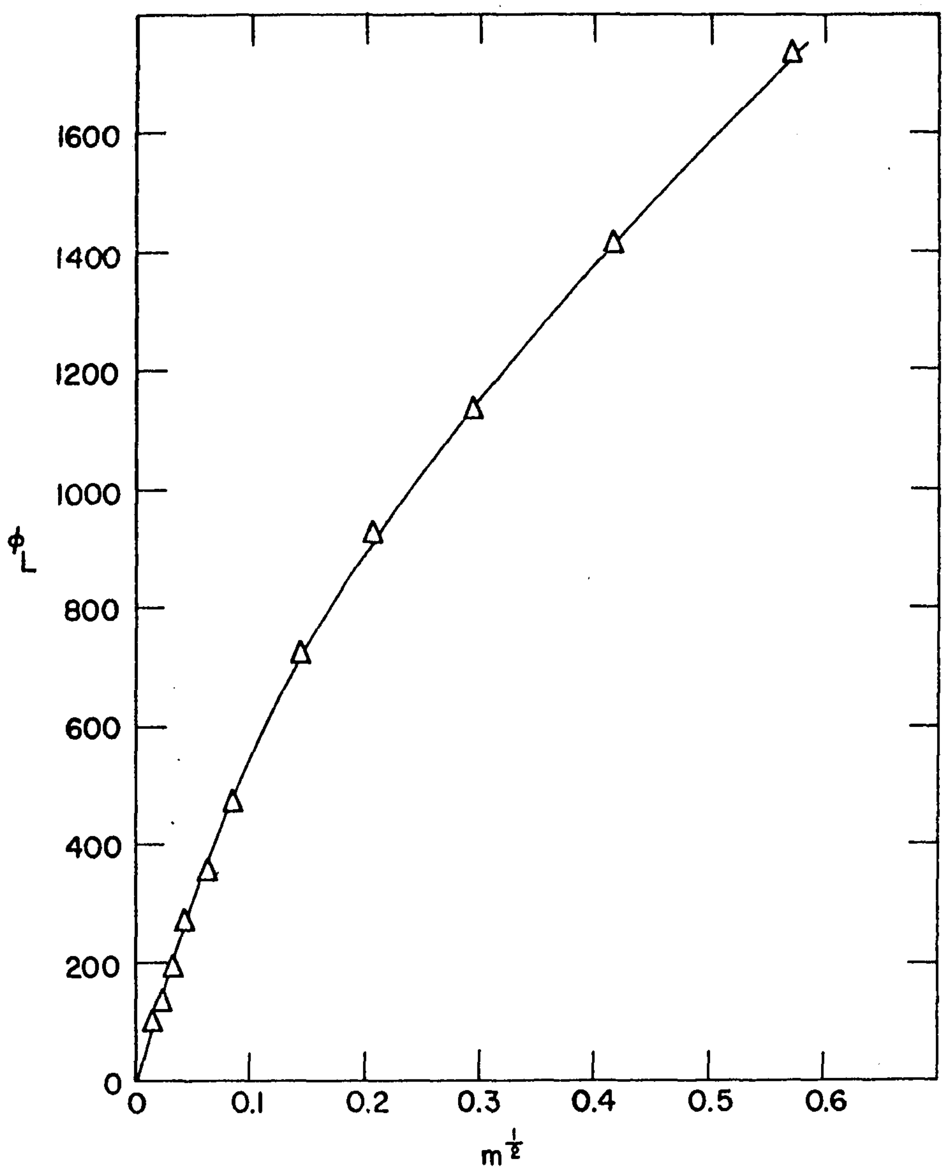

Figure 13. Relative apparent molal heat contents of thulium chloride solutions at 25° C.

Table 20. Thermodynamic properties of thulium chloride solutions at 25° C.

$m^{\frac{1}{2}}$	ϕ_L	$\bar{L}_2$	$-\bar{L}_1 x10^3$
0.0100	65	97	0.057
0.0200	128	189	0.440
0.0500	299	432	6.01
0.0700	401	572	15.1
0.1000	539	754	38.8
0.2000	896	1195	215.0
0.3000	1159	1516	578.0
0.4000	1384	1817	1246.0
0.5000	1594	2099	2271.0

E. Error Analysis

It is realized that a strict statistical analysis of the data is not entirely valid in view of the small number of experimental points involved. However, it is necessary to have some idea of the accuracy of the experimental quantities in order to judge the reliability of the experimental results. With this in mind an error analysis is carried out to obtain estimates of errors that can be assigned to the data. The method of propagation of errors and the estimation of the accuracy of least squares coefficients as described by Worthing and Geffner (87), Beers (88) and Topping (89) are used to estimate uncertainties in this work.

If a quantity U is a function of independent measurable quantities x_1, x_2, ..., x_n, then the error in the average value of U is estimated by

$$(e_{\overline{U}})^2 = \sum_{i=1}^{n} \left(\frac{\partial U}{\partial x_i}\right)^2 (e_{\overline{x}_i})^2, \qquad \text{(IV-31)}$$

where $e_{\overline{U}}$ is the error in $\overline{U}$, the average value of U; $\overline{x}_i$ is the average value of the measured quantity x_i; and $e_{\overline{x}_i}$ is the error in $\overline{x}_i$. In this work the standard error, defined by equation IV-2, was used as an estimate of the uncertainty in all measured and derived quantities.

The standard errors of $\Delta H_{1,2}$ and $\Delta H_{1,3}$ were derived using the following equations:

$$q_e = \frac{1}{4.148} \frac{R_h}{R_s^2} E_s^2 \, t, \qquad \text{(IV-1)}$$

$$q_e + q_0 \pm q_d = q_i, \qquad \text{(IV-3)}$$

$$-\frac{q_1 - q_0}{n'_2} = \Delta H_{1,2}, \qquad \text{(III-48)}$$

and

$$-\frac{q_1 + q_2 - 2q_0}{n_2' + n_2''} = \Delta H_{1,3}. \qquad \text{(III-49)}$$

Errors in E_s and t were estimated to be 1 x 10^{-5} volts and 1 x 10^{-2} seconds, respectively; errors in resistance values were estimated to be 1 x 10^{-3} ohms. In order to assign an error to q_d, the uncertainty in measuring the distance between the fore and after tracings had to be estimated. Judging from the changes in the slopes of the fore and after tracings, an error of 2.5 millimeters was assigned to the distance measurements. The error in q_0 can be found in Table 4. The errors in n_2' and n_2'' were estimated to be 5 x 10^{-7} moles.

The calculated errors of $\Delta H_{1,2}$ and $\Delta H_{1,3}$ agreed reasonably well with the values given in Tables 6, 9, 12, 15 and 18 indicating that no other sources of random errors of considerable magnitude were involved in the experimental procedure. When uncertainties of the apparent molal heat contents were determined, the errors of $\Delta H_{1,2}$ and $\Delta H_{1,3}$ listed in the tables were used.

Table 21 contains the standard errors of the least squares coefficients appearing in the $\overline{P}_i$ equations.

The uncertainty in ϕ_L was derived using the data in Table 21 and the following equations:

$$\phi_{L(m_k)} = S^o\, m_k^{1/2} + \frac{B}{2}\, m_k \qquad \text{(IV-32)}$$

Table 21. Standard errors of coefficients appearing in the $\overline{P}_i$ equations

Salt	Standard error		
	S^0	B	C
$SmCl_3$	120	2140	
$GdCl_3$	200	3190	
$DyCl_3$	250	3500	20000
$HoCl_3$	240	1530	
$TmCl_3$	220	3710	

and

$$\phi_{L(m_1)} = \phi_{L(m_k)} - \Delta H_{1,k}. \qquad \text{(IV-33)}$$

Table 22 summarizes the standard errors of ϕ_L using the gadolinium chloride data.

Table 22. Summary of error analysis

$m_1^{\frac{1}{2}}$	$m_k^{\frac{1}{2}}$	Standard error			
		$\phi_{L(m_k)}$	$\Delta H_{1,k}$	$\phi_{L(m_1)}$	$\overline{\phi}_L$
0.15	0.015	3	12	12	15
	0.020	5	8	9	
0.25	0.025	7	7	10	15
	0.040	10	6	12	
0.50	0.050	16	2	16	29
	0.075	24	1	24	

V. SUMMARY AND DISCUSSION

The heats of dilution of aqueous samarium chloride, gadolinium chloride, dysprosium chloride, holmium chloride and thulium chloride solutions were measured at 25° C. Measurements were made with an adiabatically jacketed differential calorimeter having a sensitivity of 3×10^{-4} calories per millimeter pen displacement of a recording potentiometer. Samples of concentrations ranging from 0.02 to 0.25 molal were diluted and their corresponding heats of dilution were determined to a few thousandths of a calorie.

From the heats of dilution it was possible to calculate the following thermodynamic properties: $\bar{P}_1$, the slope of ϕ_L versus $m^{1/2}$ in the dilute concentration region; ϕ_L, the relative apparent molal heat content; $\bar{L}_1$, the relative molal heat content of the solvent; and $\bar{L}_2$, the relative molal heat content of the solute.

The short chord method of treating the heat of dilution data in the very dilute concentration region resulted in equations for the concentration dependence of $\bar{P}_1$. All the equations were linear with the exception of the $\bar{P}_1$ equation of dysprosium chloride. It also could have been represented by a straight line within experimental error; however, it would not have fit the data as well as the parabolic equation that was used.

The $\bar{P}_1$ data were extrapolated to infinite dilution, and the values agreed with the Debye-Hückel limiting law within experimental error. This fact, however, should not be surprising since the activity coefficients for these salts also obeyed the limiting law. Unfortunately it was not possible to calculate values of ϕ_L at concentrations other than infinite dilution. The lack of data for the temperature and concentration dependence of the dielectric constant and the coefficient of thermal expansion prevented any such calculation.

If estimates for the dependence of the dielectric constant and expansion coefficient are made, it appears that the limiting law, and even the extended law, is valid only for a small concentration range near infinite dilution. However, when the extended law is used, two more parameters must be estimated: the distance of closest approach and its dependence on the temperature. Nevertheless, ionic association of the rare-earth ions probably occurs at lower concentrations than lower valence type ions resulting in marked deviations from theoretical predictions.

Empirical equations were obtained for the thermodynamic properties as a function of $m^{1/2}$ from infinite dilution to approximately 0.25 molal. For samarium chloride solutions:

$$\phi_L = 6788\ m^{1/2} - 15926\ m + 25037\ m^{3/2} - 15902\ m^2 \qquad \text{(IV-6)}$$

$$\bar{L}_1 = -61.146\ m^{3/2} + 286.92\ m^2 - 676.61\ m^{5/2} + 572.98\ m^3 \qquad \text{(IV-7)}$$

$$\bar{L}_2 = 10182\ m^{1/2} - 31852\ m + 62593\ m^{3/2} - 47706\ m^2. \qquad \text{(IV-8)}$$

For gadolinium chloride solutions:

$$\phi_L = 7234\ m^{1/2} - 19171\ m + 34487\ m^{3/2} - 24139\ m^2 \qquad \text{(IV-11)}$$

$$\bar{L}_1 = -65.164\ m^{3/2} + 345.38\ m^2 - 931.99\ m^{5/2} + 869.78\ m^3 \qquad \text{(IV-12)}$$

$$\bar{L}_2 = 10851\ m^{1/2} - 38342\ m + 86218\ m^{3/2} - 72417\ m^2. \qquad \text{(IV-13)}$$

For dysprosium chloride solutions:

$$\phi_L = 6654\ m^{1/2} - 15816\ m + 30889\ m^{3/2} - 26415\ m^2 \qquad \text{(IV-18)}$$

$$\bar{L}_1 = -59.939\ m^{3/2} + 284.94\ m^2 - 834.74\ m^{5/2} + 951.88\ m^3 \qquad \text{(IV-19)}$$

$$\bar{L}_2 = 9981\ m^{1/2} - 31632\ m + 77223\ m^{3/2} - 79245\ m^2. \qquad \text{(IV-20)}$$

For holmium chloride solutions:

$$\phi_L = 6907\ m^{1/2} - 15222\ m + 19588\ m^{3/2} - 7447\ m^2 \qquad \text{(IV-23)}$$

$$\bar{L}_1 = -62.227\ m^{3/2} + 274.24\ m^2 - 529.35\ m^{5/2} + 268.33\ m^3 \qquad \text{(IV-24)}$$

$$\bar{L}_2 = 10361\ m^{1/2} - 30444\ m + 48970\ m^{3/2} - 22341\ m^2. \qquad \text{(IV-25)}$$

For thulium chloride solutions:

$$\phi_L = 6670\ m^{1/2} - 14951\ m + 22708\ m^{3/2} - 13465\ m^2 \qquad \text{(IV-28)}$$

$$\bar{L}_1 = -60.083\ m^{3/2} + 269.36\ m^2 - 613.66\ m^{5/2} + 485.17\ m^3 \qquad \text{(IV-29)}$$

$$\bar{L}_2 = 10005\ m^{1/2} - 29902\ m + 56770\ m^{3/2} - 40395\ m^2. \qquad \text{(IV-30)}$$

The concentration dependence of ϕ_L above 0.004 molal is shown in Figure 14. Below 0.004 molal the curves begin to converge within experimental error.

Combining the data from this research with those of Naumann (85), Eberts (86) and Saeger (16), plots of the relative apparent molal heat contents and apparent molal volumes were made. When the two were compared, a striking resemblance was noted. Starting from lanthanum both curves drop to neodymium; from neodymium the curves gradually increase to a maximum near terbium, and then decrease to their lowest values at ytterbium.

The trends of ϕ_L and ϕ_V indicate a close association between the two properties. Effects which alter the volume properties, such as hydrolysis and ionic association, would also be reflected in the thermal properties. As indicated by Saeger, the coordination numbers of the rare-earth ions appear to change toward the middle of the series, which is manifested in the shape of the curve just described. If a change in coordination number does occur, then it surely should be evident in the ϕ_L data. The ϕ_L value of thulium chloride lies above the curve. It would be interesting to see if the value of ϕ_V for this salt also has a correspondingly high value.

The relative apparent molal heat contents from this work was compared to those derived from heat of solution

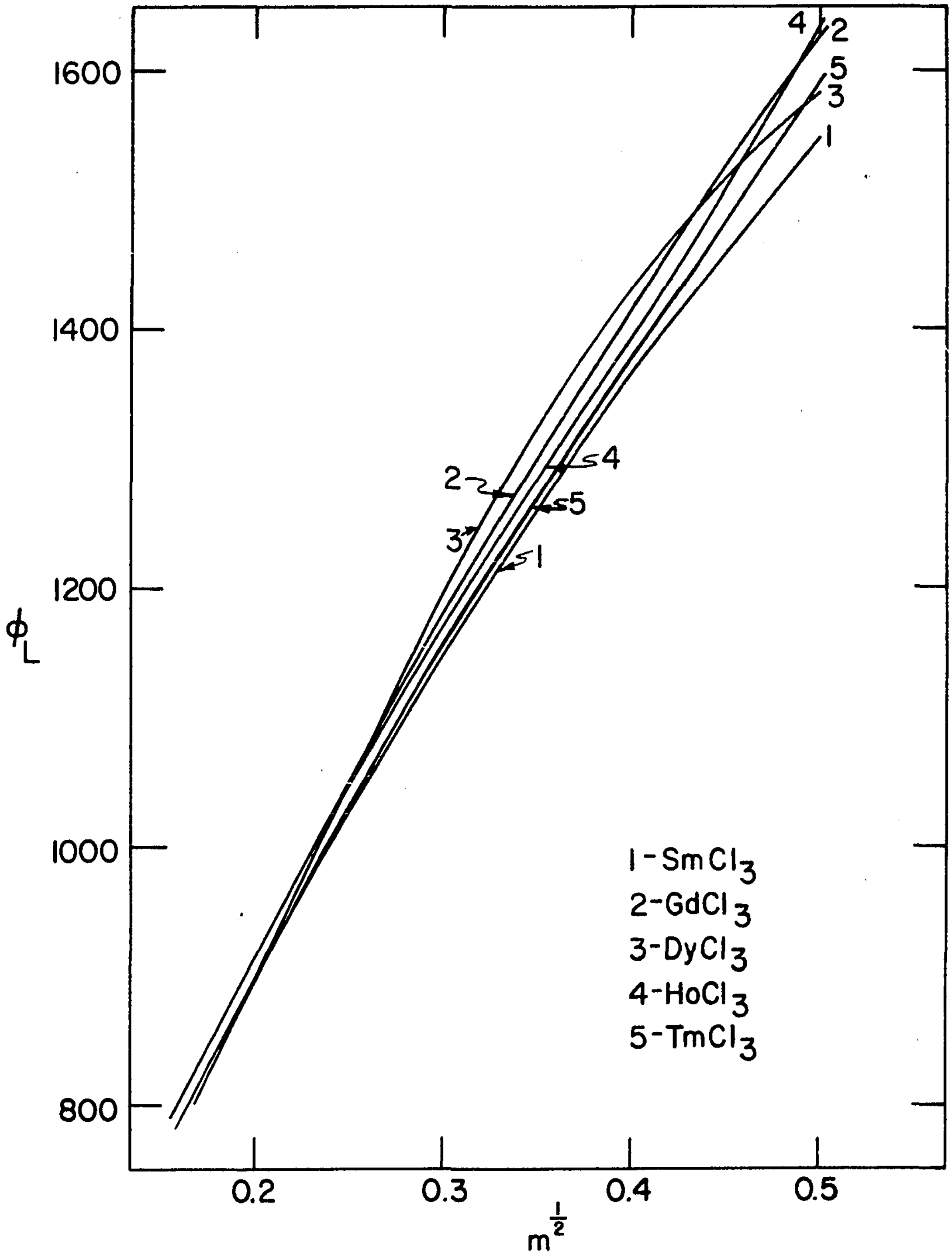

Figure 14. Relative apparent molal heat contents of some rare-earth chloride solutions at 25° C.

measurements. In Figures 15, 16 and 17 it can be seen that the ϕ_L values determined from heat of solution measurements are usually higher than those of this research.

An explanation of the anomalous results, assuming that the heat of dilution values are correct, is that the heats of solution are too low. If this were true, then the corresponding ϕ_L values would be too high. There are several ways in which the low heats of solution could have been obtained.

First, the heats of solution of the anhydrous rare-earth chlorides were measured in an isothermally jacketed calorimeter (19, 20, 21). If the salts were not completely anhydrous, the measured heats of solution would be low. Second, in the preparation of anhydrous rare-earth chlorides the formation of the oxychloride is possible unless the utmost care is taken. Traces of oxychloride present in the salt would naturally lead to low heat of solution results. Third, the low results can be explained by postulating two solution reactions. The first reaction would involve the partial dissolution of the salt leaving a Werner type complex; the second, a slow reaction, would be the complete hydration of the rare-earth and chloride ions. The isothermally jacketed calorimeter was designed so that it could measure reactions involving large amounts of heat in a short period of time. If the slow reaction did occur, the heat evolved by the reaction would not have been detected.

In the case of lanthanum chloride the first two reasons do not appear to be the cause of the anomalous results. Montgomery (91) has also measured the heat of solution of anhydrous lanthanum chloride and has obtained good agreement with Spedding and Flynn (19).

In support of the third reason are the results obtained for the heats of solution of the hydrated neodymium and dysprosium chlorides. The ϕ_L values of both salts are in very good agreement with the existing heat of dilution data. Since water molecules of the hydrated salt already are in the coordination sphere of the rare-earth ions, the resulting dissolution should not give rise to the slow type reaction.

In order to determine the existence of such a slow reaction the heats of solution could be measured in the adiabatically jacketed calorimeter. The present sample holders would have to be modified so that anhydrous salts could be used. The advantage of using this calorimeter is that small amounts of heat liberated over long periods of time can accurately be measured.

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VIII. APPENDIX:

COMPARISON OF RELATIVE APPARENT MOLAL HEAT CONTENTS

The heats of solution of anhydrous lanthanum, samarium and gadolinium chlorides have been determined by Spedding and Flynn (19); the heats of solution of anhydrous holmium and thulium chlorides have been determined by Bisbee (20); and the heats of solution of dysprosium chloride hexahydrate have been determined during the course of this research.

The apparatus used for the determination of the heats of solution of dysprosium chloride hexahydrate has been described previously (19, 21). Table 23 contains the heat of solution data. The data are listed in groups, each group being a series of determinations. The sample size and the final concentrations are listed in columns two and three. The temperature rise, energy equivalent of the calorimeter and the corrected heat in defined calories of the determinations are listed in columns four, five and six, respectively. The integral heats of solution are given in column seven.

An unweighted least squares determination was performed on the data, and the resulting concentration dependence of the integral heats of solution was found to be:

$$- \Delta H_S = 10067 - 6925\, m^{1/2} + 11228\, m. \qquad \text{(VIII-1)}$$

The coefficient of $m^{1/2}$ was chosen to be the Debye-Hückel

Table 23. Heats of solution of dysprosium chloride hexahydrate in water at 25° C.

Run	n	$m^{\frac{1}{2}}$	ΔT	W	q_1^{25}	$-\Delta H_S$
1	0.01873	0.1116	0.1070	1645.4	176.1	9397
2	0.02378	0.1265	0.1369	1625.4	222.5	9358
	0.01997	0.1715	0.1116	1623.4	181.1	9227
3	0.02592	0.1439	0.1724	1403.8	241.7	9324
	0.01665	0.1844	0.1068	1402.4	149.7	9193
	0.02302	0.2288	0.1452	1400.4	203.1	9063
4	0.02163	0.1328	0.1471	1377.7	202.4	9355
	0.02365	0.1920	0.1546	1375.6	212.3	9159
	0.02021	0.2308	0.1296	1373.9	177.8	9046

limiting slope. The uncertainty in ΔH_S increases from 15 calories per mole at the lowest concentration to 25 calories per mole at the highest concentration studied.

The concentration dependence of ϕ_L is shown in Figures 15, 16 and 17. The solid line represents the values determined from heats of dilution, and the dashed lines represent the values determined from the heats of solution. The method of comparison is described in the theory section.

Figure 15. Relative apparent molal heat contents of (A) lanthanum chloride and (B) samarium chloride solutions at 25° C.

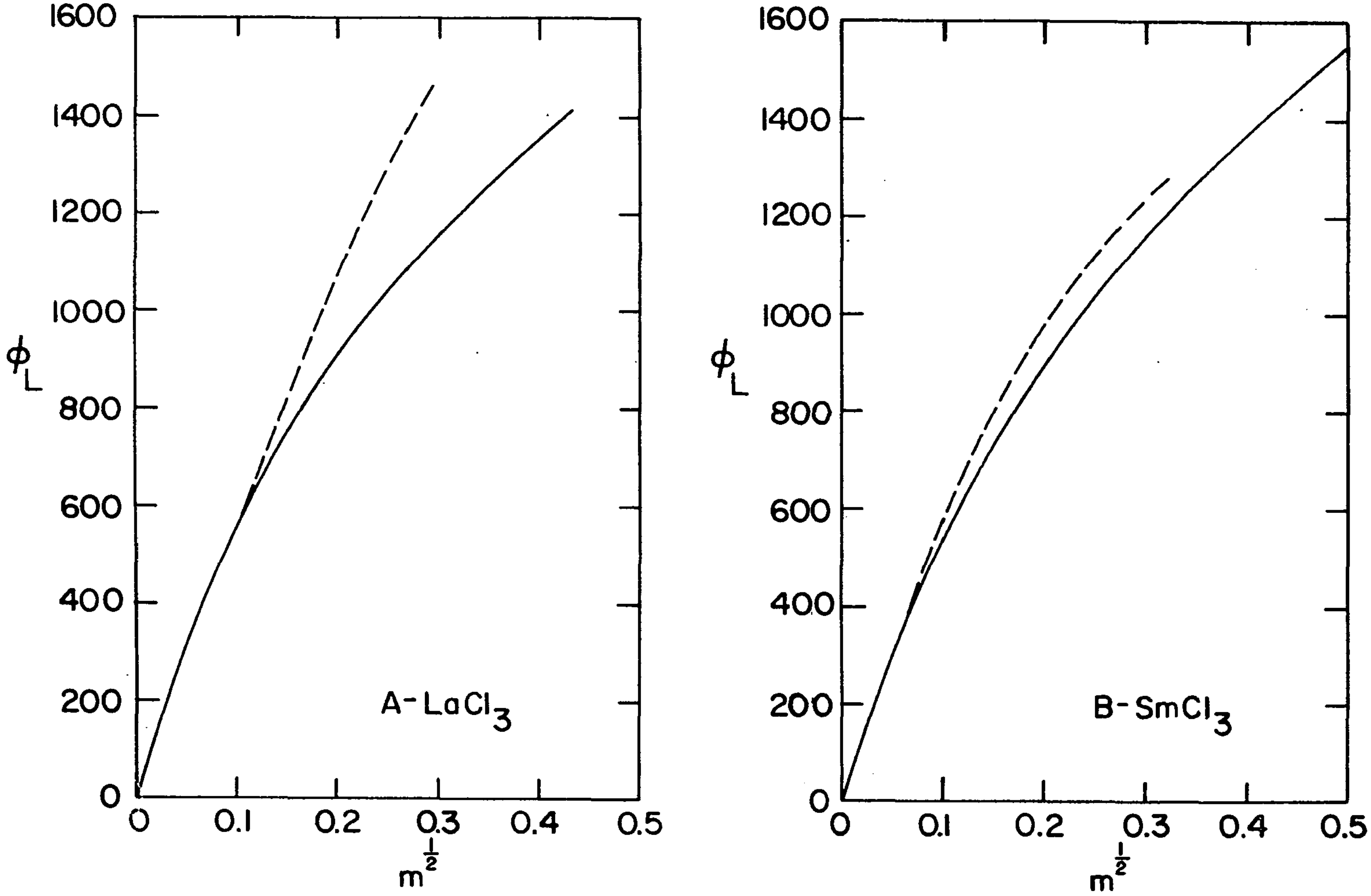

1600
1400
1200
1000
800
600
400
200
0
ϕ_L
0
0.1
0.2
0.3
0.4
0.5
$m^{\frac{1}{2}}$
A- $LaCl_3$
1600
1400
1200
1000
800
600
400
200
0
ϕ_L
0
0.1
0.2
0.3
0.4
0.5
$m^{\frac{1}{2}}$
B- $SmCl_3$

Figure 16. Relative apparent molal heat contents of (A) gadolinium chloride and (B) dysprosium chloride solutions at 25° C.

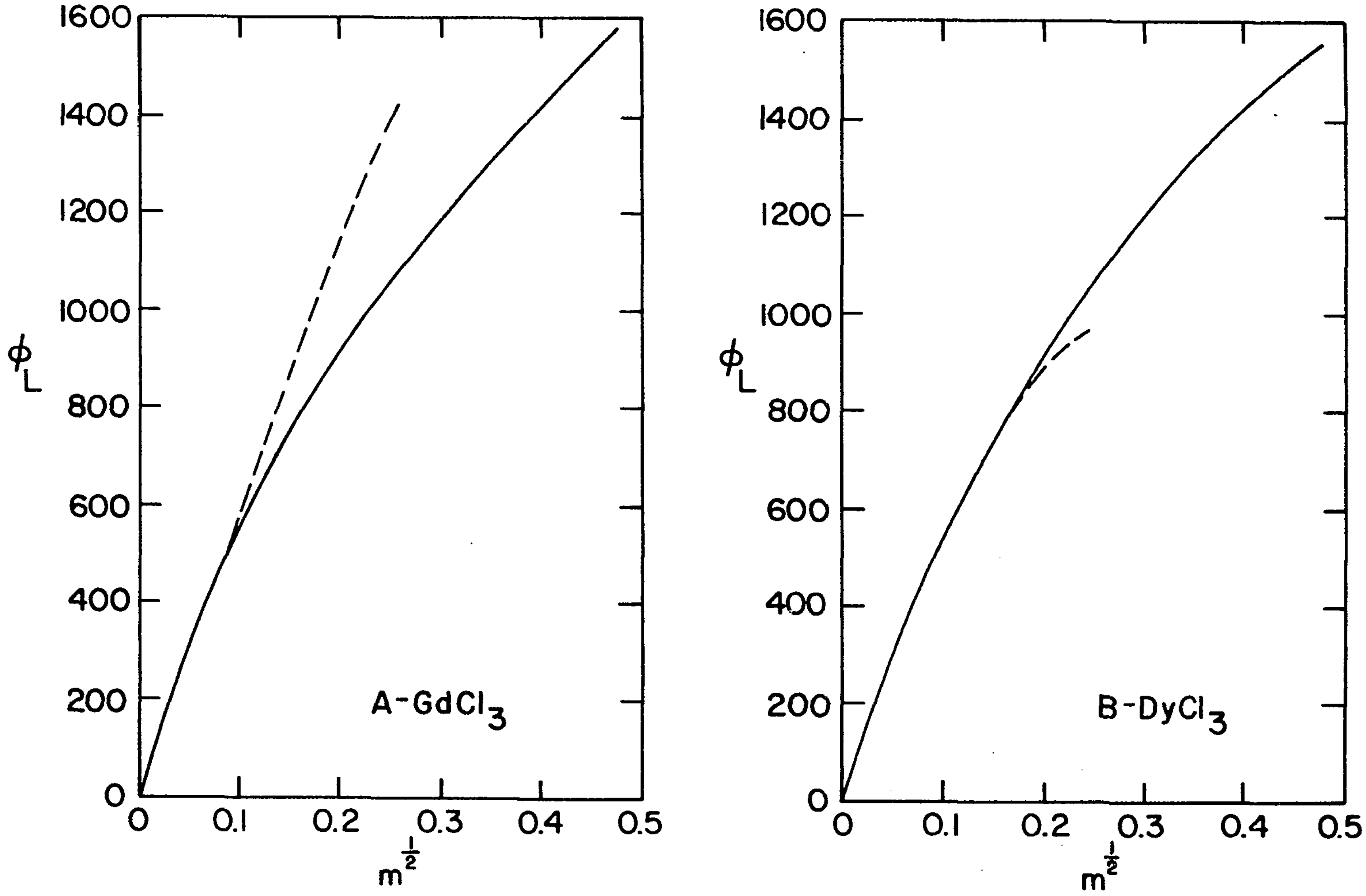
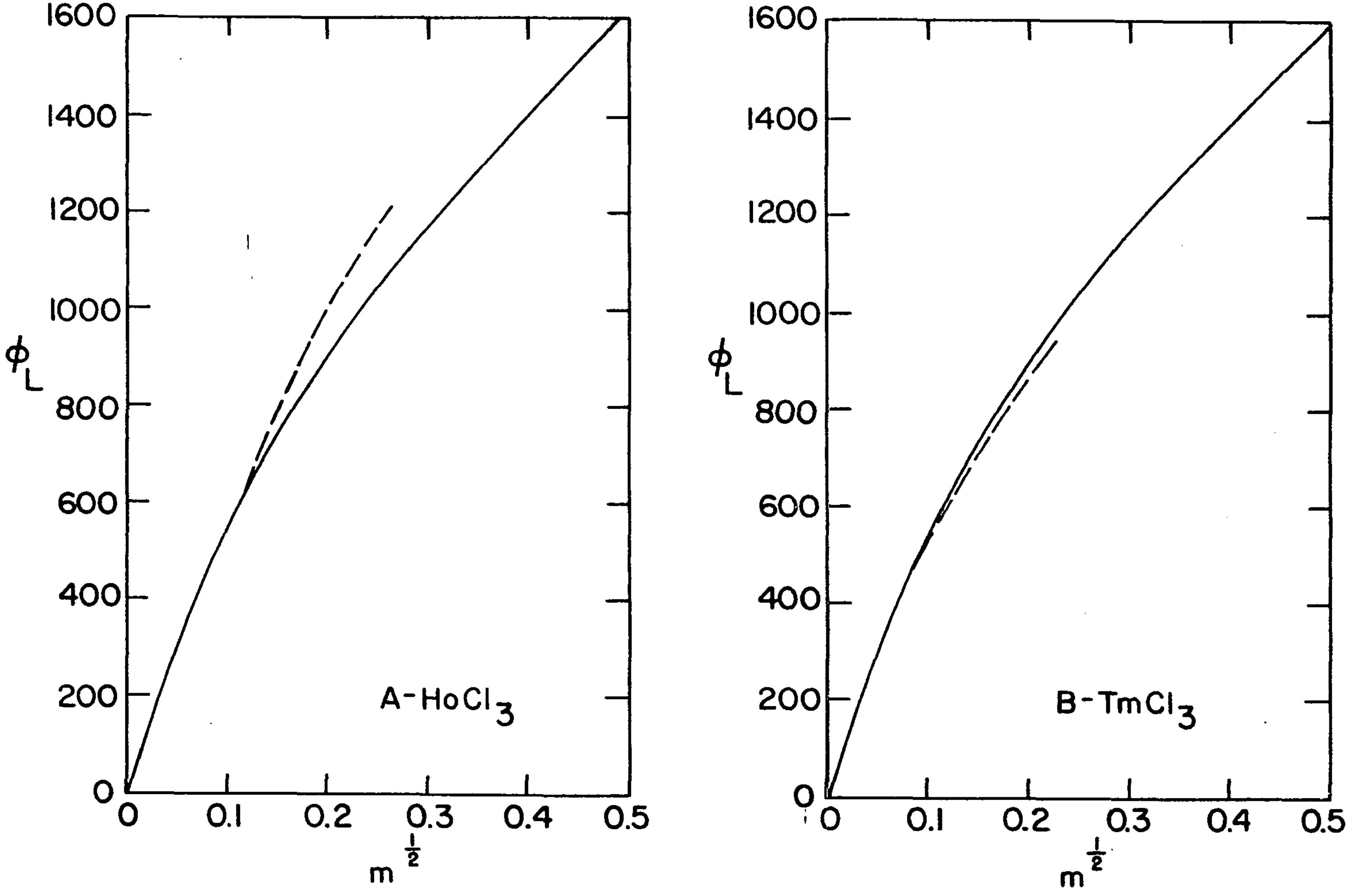

1600
1400
1200
1000
800
600
400
200
0
ϕ_L
0
0.1
0.2
0.3
0.4
0.5
$m^{\frac{1}{2}}$
A-$GdCl_3$
1600
1400
1200
1000
800
600
400
200
0
ϕ_L
0
0.1
0.2
0.3
0.4
0.5
$m^{\frac{1}{2}}$
B-$DyCl_3$

Figure 17. Relative apparent molal heat contents of (A) holmium chloride and (B) thulium chloride solutions at 25° C.


1600
1400
1200
1000
800
600
400
200
0
ϕ_L
0
0.1
0.2
0.3
0.4
0.5
$m^{\frac{1}{2}}$
A-HoCl$_3$
B-TmCl$_3$