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# Partial molal heat capacities of some aqueous rare earth chlorides, nitrates and perchlorates from tenth molal to saturation at 25°C

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PARTIAL MOLAR HEAT CAPACITIES OF SOME

AQUEOUS RARE EARTH CHLORIDES, NITRATES AND PERCHLORATES

FROM TENTH MOLAL TO SATURATION AT 25°C

by

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# ABSTRACT

The specific heat capacities of aqueous $PrCl_3$, $SmCl_3$, $EuCl_3$, $GdCl_3$, $TbCl_3$, $HoCl_3$, $TmCl_3$, $LuCl_3$, $La(NO_3)_3$, $Nd(NO_3)_3$, $Gd(NO_3)_3$, $Er(NO_3)_3$, $Lu(NO_3)_3$, $La(ClO_4)_3$, $Nd(ClO_4)_3$, $Gd(ClO_4)_3$ and $Lu(ClO_4)_3$ were measured from 0.1 molal to saturation at $25^\circ C$ in an adiabatic single can solution calorimeter. Apparent molar heat capacities, $\phi_{cp}$'s, were calculated from the specific heat capacities. Empirical polynomial equations, determined by a least squares method on an IBM 360 computor, were used to express $\phi_{cp}$ versus square root of molality. Partial molar heat capacities of solvent, $\overline{C}_{p1}$, and solute, $\overline{C}_{p2}$, as well as $\phi_{cp}$ were calculated from the polynomial equations at rounded values of square root of molality.

The data of this work show that in the $\phi_{cp}$'s at moderate concentration the rare earth chlorides form two series, one for the heavy rare earths and one for the light with Sm, Eu and Gd intermediate. The perchlorates show similar behavior. The phenomenon is explained by assuming different first sphere coordination numbers for the light and heavy series. The heavier smaller rare earths can accommodate fewer tightly bound waters in the inner hydration sphere and consequently have more positive $\phi_{cp}$'s.

The $\overline{C}_{p1}$ data of the concentrated heavy rare earth nitrates and chlorides are evidence for inner hydration sphere complexation of cation by anion. This property shows an

upturn as concentration increases which would be observed if such ionic interaction were present. $Lu(NO_3)_3$ is the most extreme example. The $\overline{C}_{pl}$'s in solutions around 6 molal approach that of free water.

## I.  INTRODUCTION

A major problem of physical chemistry has been adequate
theoretical treatment of moderately and highly concentrated
aqueous electrolyte solutions.  One method of attack of
this problem is detailed study of the thermodynamic proper-
ties of such solutions.  Due to the lack of data in the
literature, a great deal of experimental work needs to be
done on the properties of such solutions before the develop-
ment of adequate theories is feasible.  It is therefore
desirable that good thermodynamic data on concentrated solu-
tions be collected.  Since the rare earths, Ce through Lu,
as well as La are chemically similar they are a good system
for such a study.  They all form trivalent cations in aqueous
solution which exhibit a rather regular decrease of ionic
radii with increase of atomic number.  The chemical similar-
ity of the rare earths arises from the fact that the only
electronic difference between the trivalent rare earth ions
is the degree of filling of the 4f subshell.  Since the 4f
subshell is well shielded by the completely filled 5s and 5p
subshells, all the trivalent rare earth ions appear very
similar in solution.

The rare earth ions, being small and highly charged,
hydrate very strongly in aqueous solution.  Since the reduc-
tion in the heat capacity of the tied down water is greater
than the heat capacity of the solute in dilute solution,

apparent molar heat capacities in such solutions are quite negative. Thus a study of the heat capacities of such solutions should yield information on hydration.

As the rare earth solutions become more concentrated it is known that most of them form complexes between anion and cation (1, 2). Since this affects the heat capacities, the thermodynamic properties should provide evidence of complexation. The rare earth chlorides, nitrates and perchlorates were chosen for this work to study the effects of varying degrees of ionic interaction in aqueous solution.

Because many of the rare earth salts are highly soluble in water, data on this system should help make possible new approaches in theory of concentrated aqueous electrolyte solutions. In the highly concentrated ranges, the amount of water surrounding the ions and complexes becomes very small and it is certain that this water has considerably different properties from pure solvent. It has been suggested (3) that extension of fused salt theory might be a better way of approaching theory of concentrated electrolyte solutions. This is indicated in the present work in that saturated $Lu(NO_3)_3$ has only eight waters per lutetium ion and must not be much different from a fused salt.

In this work, the specific heat capacities of aqueous $PrCl_3$, $SmCl_3$, $EuCl_3$, $GdCl_3$, $TbCl_3$, $HoCl_3$, $TmCl_3$, $LuCl_3$, $La(NO_3)_3$, $Nd(NO_3)_3$, $Gd(NO_3)_3$, $Er(NO_3)_3$, $Lu(NO_3)_3$, $La(ClO_4)_3$,

$Nd(ClO_4)_3$, $Gd(ClO_4)_3$ and $Lu(ClO_4)_3$ were measured at 0.1 intervals of square root of molality from 0.1 molal to saturation at 25°C. Saturation molality varies from approximately 3.6 molal for $TbCl_3$ to over 6.8 molal for $Lu(NO_3)_3$. This work and the work of Jones (4, 5) on the specific heat capacities of $LaCl_3$, $NdCl_3$, $DyCl_3$, $ErCl_3$ and $YbCl_3$ were done on a single can adiabatic solution calorimeter. $\phi_{cp}$'s, the apparent molar heat capacities, were calculated from the specific heat capacities while the partial molar heat capacities of solvent and solute were derived from derivatives of least squares fits of $\phi_{cp}$ data versus square root of molality.

The results of this work show that the heat capacity properties of dilute aqueous rare earth chlorides and perchlorates follow no simple monotonic behavior as the ionic radii do. Rather, the $\phi_{cp}$'s fall into two groups, one for the light rare earths and one for the heavy. A few elements in the center of the series are intermediate. This behavior is explained by assuming different first sphere hydration numbers between the two extreme groups with intermediate salts having an equilibrium between the two numbers.

Evidence is seen for complexation of anion and cation in the inner hydration sphere of the cation for both heavy rare earth chlorides and nitrates in concentrated solution. The data for the most pronounced example, $Lu(NO_3)_3$, suggest

that in very concentrated aqueous solution, the $Lu(NO_3)_3$ solute may exist as an almost completely complexed and neutrally charged lutetium trinitrate species.

## II. THERMODYNAMIC INTRODUCTION

### A. General Quantities and Definitions

From the first law of thermodynamics for a system of constant composition and mass

$$dE = dQ + dW = dQ - PdV \qquad (2.1)$$

where E is internal energy, W is work done on the system and Q is heat absorbed by the system from its surroundings. The equation includes only pressure(P)-volume(V) work, as other variables such as magnetic and gravitational field strength are held constant in this discussion. Since E has the property that $\Delta E$ for a process depends only on the initial and final states of the system and not on the path between the two states, it is called a "state" function.[1] It is convenient to define another property, enthalpy(H), such that

$$H = E + PV \qquad (2.2)$$

Since E, P and V are state functions, H is also. Considering H as a function of P and T

$$dH = dE + PdV + VdP = dQ + VdP$$

$$= \frac{\partial H}{\partial T}\bigg)_P dT + \frac{\partial H}{\partial P}\bigg)_T dP \qquad (2.3)$$

If system pressure is held constant as in the experiments of this work

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[1] A more complete discussion of this area can be found in a textbook of thermodynamics such as that by Lewis and Randall as revised by Pitzer and Brewer (6).

$$dQ = dQ_p = \frac{\partial H}{\partial T}\Big)_p dT \tag{2.4}$$

The property heat capacity under constant pressure is

$$C_p = \frac{dQ_p}{dT} = \frac{\partial H}{\partial T}\Big)_p \tag{2.5}$$

Thermodynamic properties may be divided into two classes, extensive and intensive. Extensive properties are directly dependent upon the mass included in the system, while intensive properties are independent of this variable. $C_p$ is an extensive property and thus is homogeneous of degree one in the mass of the system. A function f of k variables $x_i$ is homogeneous of degree n if

$$f(ax_1, ax_2, \ldots, ax_k) = a^n f(x_1, x_2, \ldots, x_k) \tag{2.6}$$

Euler's theorem states that for such a function homogeneous of degree one

$$f(x_1, x_2, \ldots, x_k) = \sum_{i=1}^{k} x_i \frac{\partial f}{\partial x_i} \tag{2.7}$$

For an extensive thermodynamic property $G = G(T, P, n_1, n_2, \ldots n_m)$ of an m component system under constant temperature and pressure having $n_i$ moles of component i

$$G = \sum_{i=1}^{m} n_i \frac{\partial G}{\partial n_i}\Big)_{T, P, n_j} \qquad n_j \neq n_i \tag{2.8}$$

$\frac{\partial G}{\partial n_i}\Big)_{T, P, n_j}$ is called the partial molar G of component i or

$\overline{G}_1$ and is an intensive variable. The result for a two compo-
nent system such as solvent, 1, and solute, 2, is

$$G = n_1\overline{G}_1 + n_2\overline{G}_2 \tag{2.9}$$

The quantity $\phi_G$, apparent molar G, may be defined such
that

$$\phi_G = \frac{G - n_1\overline{G}_1^O}{n_2} \tag{2.10}$$

where $\overline{G}_1^O$ is partial molar G of the solvent in its standard
state, usually pure solvent.

### B. Apparent and Partial Molar Heat Capacities

For $C_p$, Equation 2.9 becomes

$$C_p = n_1\overline{C}_{p1} + n_2\overline{C}_{p2} \tag{2.11}$$

while Equation 2.10 becomes

$$\phi_{cp} = \frac{C_p - n_1\overline{C}_{p1}^O}{n_2} \tag{2.12}$$

and

$$C_p = n_2\phi_{cp} + n_1\overline{C}_{p1}^O \tag{2.13}$$

Differentiation of Equation 2.13 with respect to component
two yields

$$\overline{C}_{p2} = \phi_{cp} + n_2\left(\frac{\partial \phi_{cp}}{\partial n_2}\right)_{T,P,n_1} \tag{2.14}$$

The corresponding Equation 2.15 for $\overline{C}_{p1}$ comes from combination

of 2.11, 2.13 and 2.14

$$\overline{C}_{p1} = \overline{C}_{p1}^{o} - \frac{n_2^2}{n_1}\left(\frac{\partial \phi_{cp}}{\partial n_2}\right)_{T,P,n_1} \qquad (2.15)$$

It is convenient to express $\phi_{cp}$ as a function of $m^{1/2}$ since $\phi_{cp}$ is often approximately linear in $m^{1/2}$. Where m is moles solute per 1000 grams solvent and $M_1$ is the molecular weight of the solvent, we have for each 1000 grams of solvent

$$n_1 = 1000/M_1$$

and

$$n_2 = (m^{1/2})^2$$

With this change of variable Equation 2.14 becomes

$$\overline{C}_{p2} = \phi_{cp} + \tfrac{1}{2}m^{1/2}\left(\frac{\partial \phi_{cp}}{\partial m^{1/2}}\right) \qquad (2.16)$$

and Equation 2.15 becomes

$$\overline{C}_{p1} = \overline{C}_{p1}^{o} - \frac{M_1 m^{3/2}}{2000}\left(\frac{\partial \phi_{cp}}{\partial m^{1/2}}\right) \qquad (2.17)$$

$\phi_{cp}$ can be related to specific heat capacity or $C_p$ per unit weight of sample by

$$\phi_{cp} = (\frac{1000}{m} + M_2)S_p - \frac{1000}{m}S_p^o \qquad (2.18)$$

where $S_p$ is the specific heat capacity of a solution of molality m, $S_p^o$ is that for pure solvent and $M_2$ is the formula weight of the solute. Thus, only $S_p$ versus m need be determined to find $\phi_{cp}$, $\overline{C}_{p1}$ and $\overline{C}_{p2}$.

## III. HISTORICAL REVIEW

### A. Early Calorimetry

The history of calorimetric measurement of heat capacity goes back to the 18th century and illustrates that this is one of the earlier areas of chemical endeavor. Many early well known chemists included calorimetry in their interests. Very early quantitative results were the separate determinations of the heats of fusion and vaporization of water by Black (7) and Cavendish (8) around the middle of the century. Interest in calorimetry expanded rapidly so that by 1780 Kirwin as cited in De Magellan (9, p. 167) was able to publish a table of 43 values of specific heat capacities based on water = 1. An ice calorimeter was built by Lavoisier and de Laplace (10a, 10b) at about that time for determination of the heat given off by various processes. DuLong and Petit (11) in the early 19th century made extensive studies including the calculation of specific heat capacities by observation of the cooling of a sample five to ten degrees warmer than the surrounding air. In the 1840's, Joule determined the mechanical and electrical equivalents of heat (12a, 12b, 12c) and thus made possible electrical calibration of calorimeters. At the beginning of the 20th century, Eucken and Nerst (13, 14) developed an isothermally jacketed calorimeter which was soon adapted to the adiabatic variety. Since then the field has expanded rapidly. As a result much thermodynamic data have been accumulated.

Much of this discussion is based on a short history of calorimetry by G. T. Armstrong (15). Five excellent review books which describe calorimeters and give many of their applications in chemistry and physics are by F. D. Rossini (16), H. A. Skinner (17), J. M. Sturtevant (18), W. Swietoslawski (19) and W. P. White (20).

### B. Theory of Heat Capacity as Applied to Aqueous Electrolyte Solutions

While thermodynamic properties of very dilute aqueous electrolyte solutions have been explained by the theories of Milner (21, 22), Debye and Huckel (23)[2] and Mayer (26), there are no good quantitative theories for concentrated aqueous solutions above 0.1 m. Excellent agreement of theory with experimental results in the dilute range has been shown by many workers. Spedding and Miller (27) have shown such agreement for apparent molar heat capacity in the dilute completely ionized aqueous rare earth chlorides. This agreement substantiates the simplifying assumption in the Debye-Huckel theory of complete ionization which is not so for concentrated aqueous solutions. The data of this work are definitely beyond the Debye-Huckel range, therefore the simplifying assumptions do not work.

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[2]Detailed discussion of the Debye-Huckel theory can be found in the ACS monograph of Harned and Owen (24) and in the book on electrolyte solutions by Robinson and Stokes (25).

Quantitative theories for concentrated aqueous solutions of electrolytes will probably have to include consideration of the species present. Fuoss and Onsager (3) have suggested that fused salt theory should be extended down through the concentrated range. The rare earth salts of this work, which form quite concentrated aqueous solutions, are likely candidates for such consideration.

## IV. EXPERIMENTAL

### A. Description of the Calorimeter

The adiabatic single can solution calorimeter used for this work was one built by K. C. Jones (4, 5). In order to reduce thermal contact with its surroundings, the calorimeter was located in an evacuated submarine jacket (Figure 1E) immersed in a well stirred water bath. Adiabatic temperature control was maintained through use of a thermopile. For inertness, the sample container can (Figure 1J) and all other parts coming in contact with solution were made of tantalum. A variable speed stirrer kept sample temperature reasonably uniform.

Since accurate temperature measurement was needed over the range of $24^\circ$ to $26^\circ C$, a wheatstone bridge was constructed (Figure 3) containing a thermistor in one arm. An amplifier and strip chart recorder measured and recorded the imbalance of the bridge. Temperature of the calorimeter system was raised by adding heat electrically with a manganin wire heater powered by an electronic d.c. constant current source. By measuring the time of heating and by measuring the potential drop across a standard resistor in series with the heater, the quantity of heat added could be determined. The over-all accuracy of measurements of specific heat capacity was $\pm 0.0005$ cal $gm^{-1}deg$ $C^{-1}$ which is $\pm 0.05\%$ for dilute solutions.
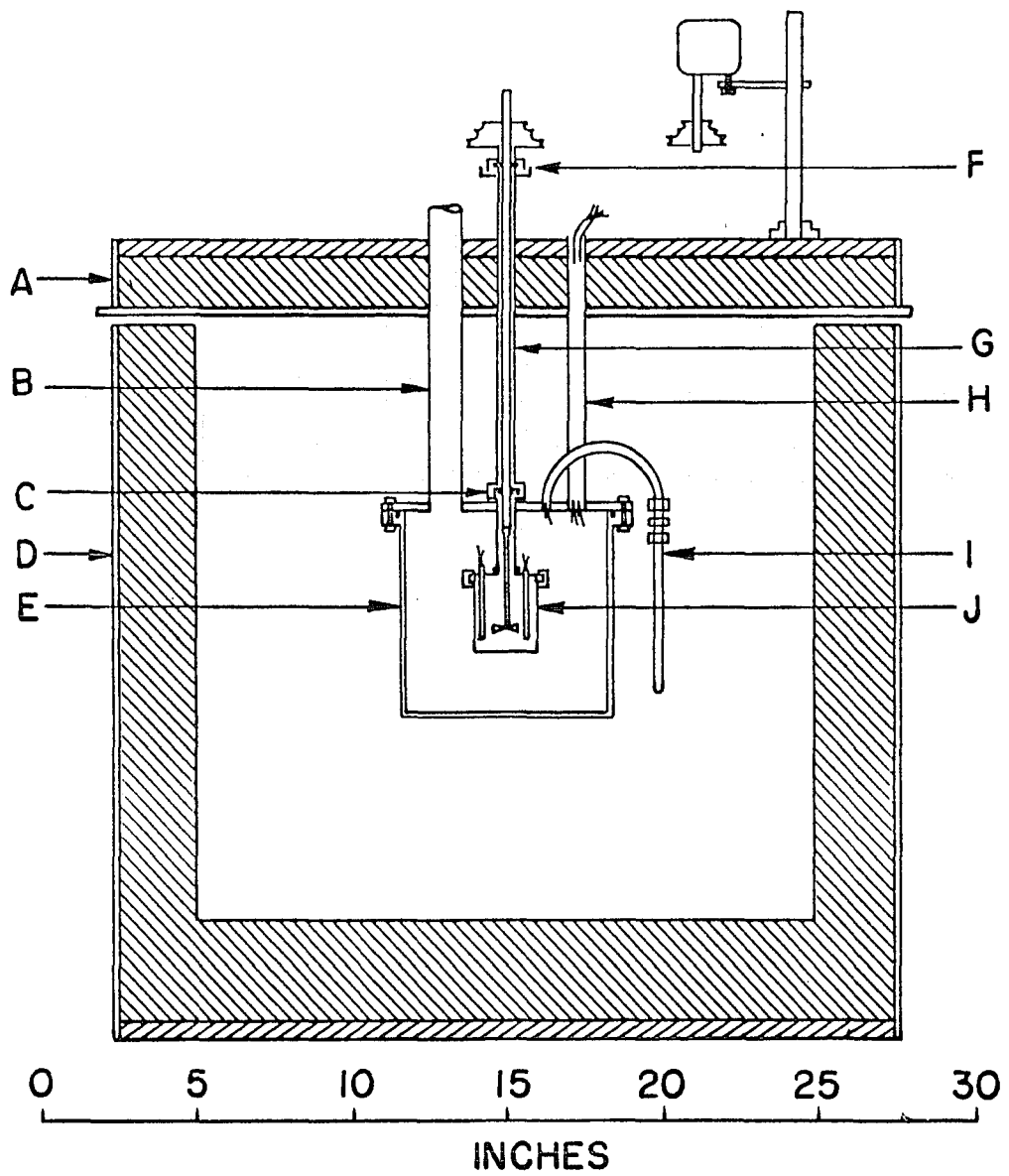
Figure 1.   Single can adiabatic solution calorimeter

1. Water bath

An adiabatic environment for the calorimeter was supplied
by a 22 gallon water bath. A 100 gallon per minute type NSI-
53 Bodine stirrer suspended from the bath lid stirred the
water. By filling the wall (Figure 1D), floor and lid (Fig-
ure 1A) with exploded mica, the bath was insulated. The
bath lid, bath stirrer, submarine lid and calorimeter lid
were attached permanently to a fixed frame. For convenience,
the bath could be lowered from the bath lid by means of a
hydraulic jack. The bath contained two independent heaters
for adjusting temperature against cooling provided by cold
water flowing constantly through a copper coil in the bath.

2. Submarine jacket and vacuum system

The submarine jacket body (Figure 1E) was a monel can
6-1/2 inches in diameter and 6-1/2 inches deep. One-sixteenth
inch plate and 1/8 inch plate formed the side and bottom,
respectively. Silver soldered to the top outside of the
jacket body was a ring machined to hold a 6-7/8 inch by 1/8
inch "O" ring. The submarine body was fastened to its lid
of 1/4 inch monel plate by means of eight bolts in the ring
which fitted through holes in the edge of the lid.

Three half inch diameter tubes suspended the submarine
lid from the water bath lid. Electrical leads from the
calorimeter were housed in two of the tubes (Figure 1H).
The third (Figure 1G), fastened to the center of the lid,

contained the calorimeter stirrer shaft (Figure 2H). Outside the submarine jacket the electrical leads were electrically shielded as were all external portions of calorimeter circuits. The leads left the submarine jacket through vacuum tight seals in the lid. The submarine jacket could be evacuated through a one inch diameter vacuum port in the lid (Figure 1B) by a combination of a model 1400 Duo-Seal mechanical fore pump and a type VMF 20-04 Distillation Products Industries oil diffusion pump. The 8/10 inch diameter pyrex vacuum line connecting the pumps to the vacuum port contained a 10 mm pyrex vacuum stopcock. Vacuum system pressure was measured by a type 507 NRC ionization gauge, run by a type 710 NRC ionization controller and protected from pump oil vapors by a liquid nitrogen cold trap. The pressure during an experimental run was usually better than $1 \times 10^{-5}$ torr and always better than $2 \times 10^{-5}$ torr.

3. Sample container

The samples to be measured were contained by a 110 ml can (Figure 1J), of welded 20 mil tantalum, 1 15/16 inches in diameter and 2 7/16 inches deep. An aluminum "O" ring seat (Figure 2E) was fastened to the outside upper edge of the can by Torr Seal low vapor pressure epoxy resin. Two threaded gold plated rings (Figure 2J and 2K) held the calorimeter can to its tantalum lid when the pair was screwed together. The inner half of the pair was attached to the lid
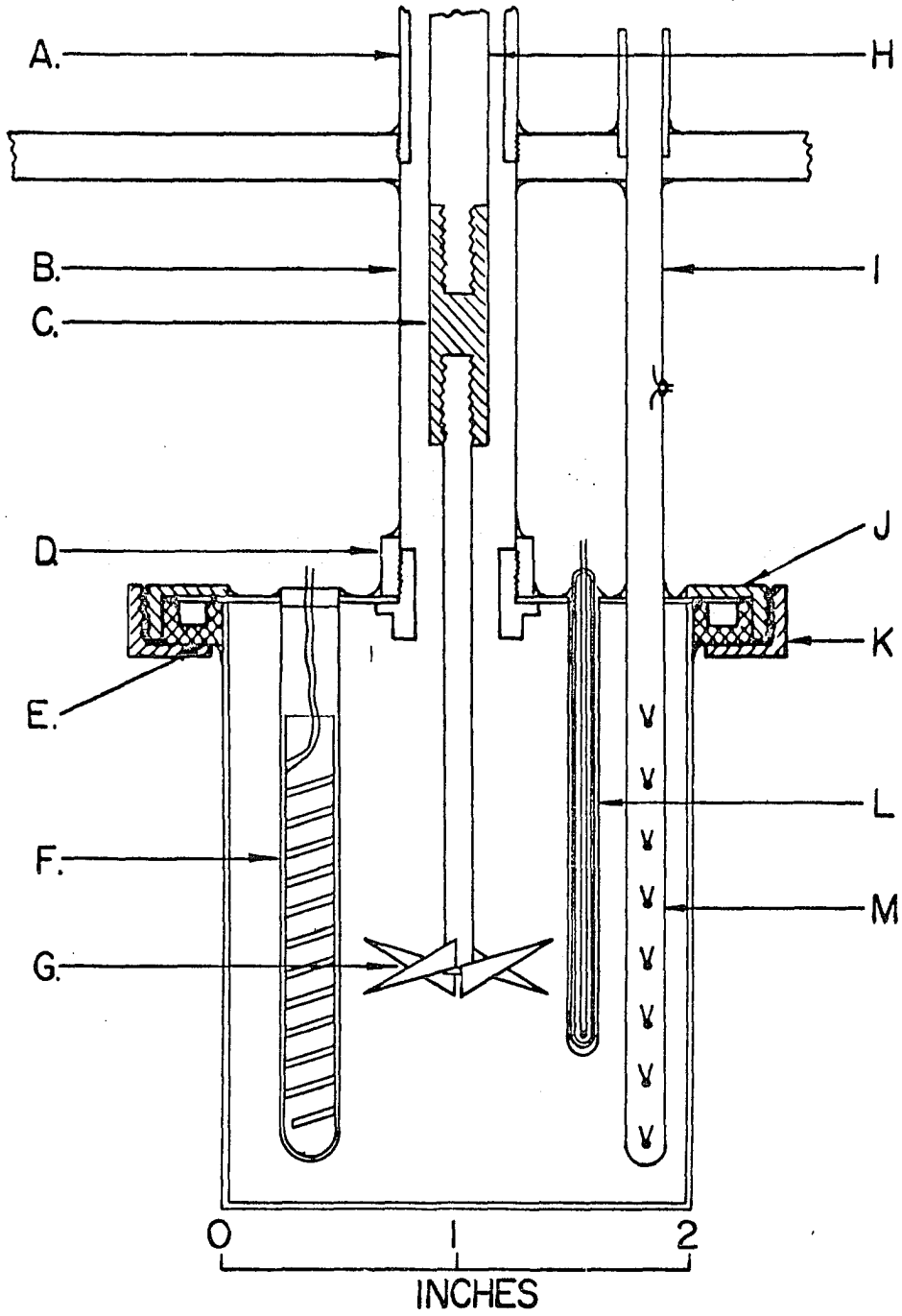
Figure 2.  Sample container

with Torr Seal. At no point did solution in the calorimeter come in contact with anything but tantalum.

Three tantalum wells, sealed at the top with Torr Seal, were welded to the lid and contained the calorimeter heater (Figure 2F), the thermistor (Figure 2L) and the calorimeter half of the thermopile (Figure 2M). The wells were 1/4, 1/8 and 5/32 inch in diameter, respectively, and were formed from tantalum tubing welded shut at the lower end. For suspension from the submarine lid, the calorimeter lid was attached by a threaded lug to a brass flange (Figure 2D) silver soldered to a hanger tube (Figure 2B). The tube, 1/2 inch diameter 6 mil stainless steel 1 3/4 inches in length, was silver soldered at the upper end to the submarine lid and housed the calorimeter stirrer shaft.

4. Temperature control

The temperature of the water bath was controlled by use of an eight junction copper-constantan thermopile. These junctions were spaced at intervals along a tantalum well in the calorimeter (Figure 2M) and also along a copper tube immersed in the water bath. In order to isolate the thermopile from the vacuum, the portion of the thermopile between the calorimeter and the submarine lid was housed in a 1/8 inch diameter stainless steel tube. Six mil tubing was used to minimize heat conduction. The leads to the thermopile entered this tube through a small hole which was made vacuum

tight by Torr Seal.

A controller-amplifier built by the Ames Laboratory electronics shop amplified the thermopile signal by a factor of $10^6$. When the bath was colder than the calorimeter, the controller started current through the 29 ohm water bath control heater by way of a preset variable transformer. An auxiliary 19 ohm bath heater, which could be turned on manually, was powered through another preset variable transformer. This heater was used to supply a fixed amount of extra heating to the water bath while calorimeter system temperature was being raised.

The above system usually maintained bath control within $\pm 0.001^\circ C$ around calorimeter system temperature. During the time the temperature of the calorimeter system was increased, control was $\pm 0.003^\circ C$ or better. The period of oscillation of bath temperature was about one minute.

Assuming Newtonian heat conduction, the net heat leak, $Q_1$, between the bath and the calorimeter is given by the equation

$$Q_1 = A \int (\theta_b - \theta) dt$$

where A is the heat leak constant, $(\theta_b - \theta)$ is the difference between the bath and calorimeter temperatures. The heat leak constant between the calorimeter and its environment was previously found to be 0.3 cal $min^{-1}$ deg $C^{-1}$ by operating the calorimeter isothermally (5). Since the temperature oscil-

lations in control were sinusoidal, yielding nearly equal positive and negative areas in the above integral, the net heat leak was quite small and could be neglected.

5. Stirring

The 7/8 inch diameter four bladed tantalum propellor (Figure 2H), which stirred solutions in the calorimeter, was fixed to the lower end of an 1/8 inch diameter tantalum rod. For reduction of thermal conduction between the calorimeter and its environment, a lucite spacer (Figure 2C) connected the tantalum rod to a 1/4 inch diameter stainless steel shaft (Figure 2H) supported by two bearings (Figure 1C and 1F). A vapor seal (Figure 1F), consisting of an inverted brass cup immersed in dibutyl phthalate, was installed at the top of the shaft. Power to the stirrer came from a 300 rpm type KYC-23RB Bodine motor through two three-gang pulleys connected by a rubber "O" ring drive belt. This yielded nine constant stirring speeds from 105 to 325 rpm.

6. Thermometer

The thermometer in the calorimeter was a glass probe type thermistor (Fenwall number G462) having at 25°C a resistance of 110K ohms and a decrease of 5K ohms per degree C. A new wheatstone bridge containing the thermistor was built as shown in Figure 3. The variable resistance, a six decade type 1432 General Radio Company resistor, had a range of 0 to 111,111 ohms in 0.1 ohm steps. Before installation into

I.35v

I30K Ω    IOOK Ω

AMPLIFIER

IOOK Ω

O-IIIK Ω

THERMOMETER CIRCUIT

TIMER

CALORIMETER HEATER    DUMMY HEATER

Rs

O.IΩ

CONSTANT CURRENT SOURCE    I2Ov A.C.

POTENTIOMETER
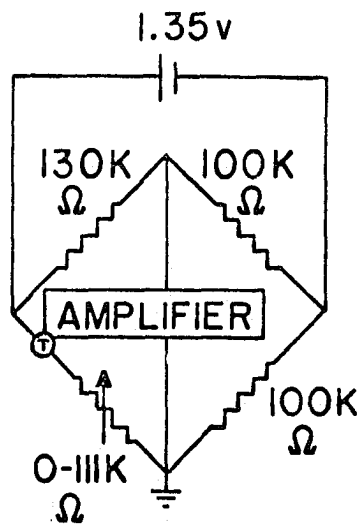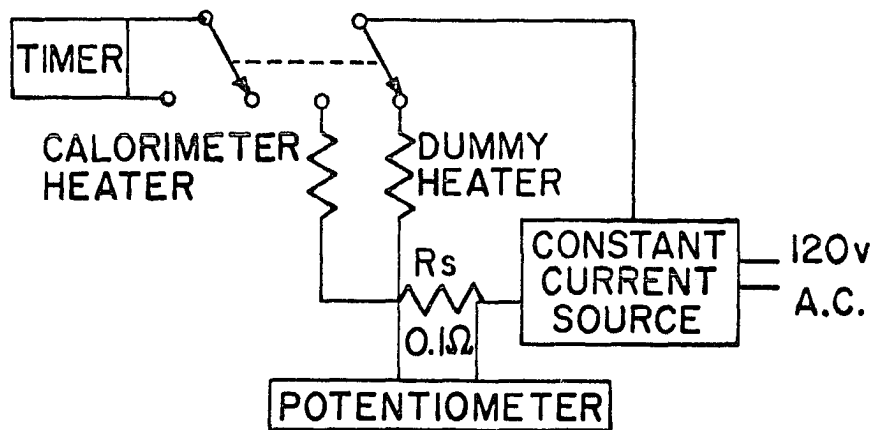
HEATER CIRCUIT

Figure 3. Calorimeter thermometer and heater circuits

the bridge, the decade box was calibrated in each step to the nearest 0.01 ohm. All resistance values below 2,000 ohms were found to be correct as read to the nearest 0.1 ohm. The other resistances in the bridge were type 1441 General Radio Company resistors stable to $\pm$0.003% per year. For stability of the thermistor, the bridge was powered continuously by 1.35 volt mercury cells. A Kintel model 111BF d.c. chopper amplifier, with a set gain of 280, amplified the signal from the bridge. Output of the amplifier was recorded by a Bristol Dynamaster recorder with a 10 mV chart span. Resulting sensitivity was $2 \times 10^{-5}$ deg C, or 0.1 ohm, per mm of chart width.

The thermistor bridge was checked every four to six months against a platinum resistance thermometer calibrated by National Bureau of Standards. In order to have the thermistor and platinum thermometer at the same temperature, both were placed in a 400 ml vessel filled with water and sealed with oil. Temperature, as indicated by the platinum thermometer on a type G-2 Leeds and Northrup mueller bridge, was recorded versus resistance of the wheatstone bridge decade box. Readings were made at $0.1^{\circ}$C intervals from $23^{\circ}$ to $27^{\circ}$C. An IBM 360 computor calculated a fourth order orthogonal polynomial least squares fit of temperature in degrees C versus resistance of the decade box. Temperature as indicated by the thermistor could be calculated from this equation.

The precision of the least squares fits was about $\pm 1 \times 10^{-4}$ deg C for each reading of the thermistor calibrations. The calibrations varied by an average of $\pm 6 \times 10^{-5}$ degrees over fixed resistance intervals corresponding to $0.4^{\circ}C$. The usual magnitude of the temperature rise for an individual measurement of heat capacity was $0.4^{\circ}C$.

### 7. Calorimeter heater

A 63 inch piece of 38 B&S gauge silk covered manganin wire was non-inductively wound on a copper core to form the calorimeter heater. Before being installed in a well in the calorimeter, the heater was annealed at $145^{\circ}C$ for 48 hours (5). The resistance of the heater, which was found to be about 95 ohms, changed less than 0.01% in the time that the experiments of this work were performed.

Figure 3 shows the design of the heater circuit. The solid state d.c. constant current source, built by the Ames Laboratory electronics shop, provided 60 milliamperes current which was stable to better than 0.01 milliampere over a ten minute period. The potential drop across a 0.1 ohm Leeds and Northrup standard resistor ($R_S$) in series with the calorimeter heater was measured with a Leeds and Northrup type K-3 potentiometer. The resistor, calibrated by NBS, was kept in a constant temperature $25^{\circ}C$ oil bath.

In order to keep the output of the constant current source stable, the current was routed through a 95 ohm dummy heater when the calorimeter heater was not being used. The

switch which started current through the calorimeter heater also simultaneously closed a circuit to the timer.

The timer counted the oscillations of a 100K cycles per second quartz crystal in the time interval that the switch was closed. The frequency of the crystal was checked against the ten megacycle WWV standard broadcast through a counter accurate to two parts in $10^7$. The timer was found to be correct within 0.002%.

## B. Experimental Procedure

### 1. Operation of the calorimeter

The following procedure was used for all experimental measurements of heat capacity in this work. The samples, which were weighed to the nearest 0.1 mg in the sample can and corrected for buoyancy in air, were taken from solutions which had been cooled below $24^\circ C$. After the calorimeter containing the sample was put together, the submarine was assembled and opened to the vacuum system. Once the water bath, previously cooled to $24^\circ C$, was raised around the submarine and the calorimeter system temperature was adjusted to that of the water bath, the apparatus was allowed two hours to come to equilibrium. The pressure in the vacuum system was $1 \times 10^{-5}$ torr or better by this time and the drift of calorimeter temperature was constant. A stirring speed was selected such that the drift was $\pm 0.002^\circ C$ or less per hour. Because of an increase in viscosity with concentra-

tion, slower stirring speeds were used for more concentrated solutions. The temperatures of the calorimeter and the water bath were then raised to $24.4^\circ$C, the initial temperature of the first heat capacity measurement.

When a temperature versus time fore slope had been established and the sensitivity of the wheatstone bridge had been checked, the calorimeter heater and the auxiliary bath heater were turned on for the first sample heat. The calorimeter system was heated $0.4^\circ$C in about ten minutes. The system usually took between 15 and 20 minutes to come to equilibrium when heating was terminated. After the temperature slope had been constant for 15 minutes, the next sample heat was initiated. Three measurements of $0.4^\circ$C temperature rise each were made for each run over the range $24.4^\circ$ to $25.6^\circ$C.

Q, the heat added in a measurement, was calculated in defined calories (one calorie = 4.1840 absolute joules) from the equation

$$Q = R_H \mathcal{T} E_s^2 \Big/ (R_s^2 4.1840)$$

where $R_H$ was the calorimeter heater resistance in ohms, $\mathcal{T}$ was the time of heating in seconds, and $R_s$ was the resistance of the 0.1 ohm standard resistor of the heater circuit. The potential drop, $E_s$, across the standard resistor was the average of readings made every half minute during the sample heat. The quantity of heat added for each measurement was

about 50 calories determined to better than 0.01%.

The initial and final temperatures for the measurement
were taken at the start of the heating period and at the time
of coming to equilibrium. Since heat was added continuously
by stirring, a correction to the temperature change had to
be made. The fore and after slopes in degrees C per minute
were averaged, multiplied by the time interval between ini-
tial and final temperature, and subtracted from the total
temperature change to yield a corrected temperature rise $\Delta\theta$.
The correction was usually less than $0.001^{\circ}C$.

The total heat capacity of the system was found when Q
was divided by $\Delta\theta$. By subtracting the heat capacity of
the calorimeter, the heat capacity of the sample was calcu-
lated. Since some of the heat added during a measurement was
absorbed by evaporation of solvent as solvent vapor pressure
increased with temperature, the sample heat capacity had to
be corrected by the method of Hoge (28). The resulting heat
capacity of the sample under its saturated vapor, when divided
by sample weight, yielded specific heat capacity.

2. <u>Heat capacity of the calorimeter and accuracy of results</u>

In order to determine the heat capacity of the calorimeter
(W), the total heat capacity of the calorimeter with a sample
of air saturated conductivity water was measured. W was the
difference between the total heat capacity and the heat capac-
ity of the water sample. The specific heat capacity of the

water was assumed to be 0.9989 cal $gm^{-1}$ deg $C^{-1}$ (29). In terms of the system heat capacity, about 120 cal deg $C^{-1}$ with a water sample, W was reproducible to within 0.02%. The value of W was about 16.75 cal deg $C^{-1}$. This changed slightly whenever a calorimeter part was changed and had to be redetermined then. Several successive runs on water were used for each determination.

Because W was found to vary with volume of sample, due to the indefinite nature of the boundary of the calorimeter, all sample volumes were kept within 0.5 ml of 105 ml.

For a check of the accuracy of the calorimeter, results of measurements of specific heat capacities of NaCl solutions were compared with results of Randall and Rossini (30). Their results, reportedly accurate to 0.01%, were recalculated with $C^{12}$ based atomic weights and defined calories. A fourth order least squares fit was made in specific heat capacity versus molality of their recalculated results. Table 1 shows the comparison. From these results it is inferred that the calorimeter is accurate within 0.0005 cal $gm^{-1}$ deg $C^{-1}$.

C. Preparation and Analysis of Solutions

1. Preparation of solutions

The rare earth chloride, nitrate and perchlorate stock solutions were prepared by dissolving the pure rare earth oxides in the appropriate Baker & Adamson C. P. acid. All water used in preparation of stock solutions, dilutions and

Table 1.  Specific heat capacities of aqueous NaCl solutions
at 25°C

| m | # of determinations | $S_p$ this work | $S_p$ R&R |
|---|---|---|---|
| 0.099582 | 3 | $0.9909 \pm 0.0002$[a] | 0.9912 |
| 0.36622 | 3 | $0.9721 \pm 0.0001$ | 0.9726 |
| 0.50022 | 3 | $0.9635 \pm 0.0002$ | 0.9639 |
| 0.81349 | 6 | $0.9446 \pm 0.0001$ | 0.9450 |
| 1.0050 | 9 | $0.9344 \pm 0.0001$ | 0.9344 |
| 1.4402 | 12 | $0.9120 \pm 0.0002$ | 0.9125 |
| 1.5059 | 6 | $0.9090 \pm 0.0001$ | 0.9094 |
| 1.9618 | 3 | $0.8891 \pm 0.0001$ | 0.8896 |

[a]Average deviation from the mean.

water samples was prepared by distillation from a solution of
$KMnO_4$ and KOH.  The water prepared in this manner, called
"conductivity water", had a specific conductance of less
than $1 \times 10^{-6}$ mho per cm.

The freshly prepared hot stock solution was filtered
from excess oxide through a sintered glass funnel.  In order
to determine the equivalence pH for rare earth hydrolysis
equilibrium, 25 ml samples of the cooled solution were titrated
with dilute acid.  The stock solution, when adjusted to this

pH to avoid colloidal hydrolysis products and to assure a three to one ratio of anion to cation, was kept in a well stoppered Pyrex flask.

Dilutions were made at intervals of 0.1 in square root of molality with weighed portions of stock solution and water. All weights were corrected for buoyancy in air. The saturated solutions, prepared by concentrating 500 ml portions of stock solution over $Mg(ClO_4)_2$, were placed in stoppered Pyrex flasks and allowed to come to equilibrium with the crystals formed during saturation. Samples of saturated solution were taken after the flasks had been fixed on a rocker arm in a $25^{\circ}C$ water bath for two weeks or more.

## 2. Analysis for concentration

Four methods were used for analysis of the concentrations of the rare earth stock and saturated solutions. The methods for rare earth cation were EDTA titration, oxide weight and sulfate weight. Chloride ion concentrations in the rare earth chloride solutions were determined by titration with $AgNO_3$ solution.

A standard for the EDTA titration method was a $Zn^{+2}$ solution prepared from electrolytic zinc. End points were found by use of xylenol orange as an indicator and $H^+$ concentration was kept constant with a pH 5 buffer (31). End points in the chloride titration method were determined potentiometrically. The $AgNO_3$ solution was standardized with a solution of known concentration prepared from anhydrous KCl. In these methods,

portions of solutions were measured by weight.

For the other two methods, weighed portions of rare earth solutions were precipitated as oxalate or sulfate and taken to dryness. The rare earth oxalates were ignited at $800^\circ$ to $900^\circ$C and weighed as anhydrous rare earth oxides. After ignition at $550^\circ$C, the rare earth sulfates were weighed as anhydrous rare earth sulfates.

The methods used for each type of solution are summarized in Table 2. The average of results of the methods used for each solution was taken as the concentration. The average deviation from the mean was always 0.1% or less.

Table 2. Methods of analysis for concentrations of solutions

| Type of solution | Methods used | Notes |
| --- | --- | --- |
| $Cl^-$ stock | oxide weight<br>sulfate weight<br>$Cl^-$ titration<br>EDTA titration | two or more of the<br>four methods used<br>for each solution |
| $Cl^-$ saturated | -- | previously determined<br>by co-workers |
| $NO_3^-$ stock | oxide weight<br>sulfate weight<br>EDTA titration | two or more methods |
| $NO_3^-$ saturated | oxide weight<br>sulfate weight<br>EDTA titration | one or more methods |
| $ClO_4^-$ stock | sulfate weight and<br>sometimes EDTA titration | |
| $ClO_4^-$ saturated | sulfate weight<br>EDTA titration | one or both methods |

## 3.  Analysis for impurities

Oxide samples prepared from each of the rare earth stock solutions by ignition of precipitated oxalate were analyzed for impurities by an emission spectrographic method.  Results are shown in Table 3.

Table 3.  Results of spectrographic analyses for impurities

| Oxide | Stock solution | Analyses in per cent[a] | | |
|-------|----------------|------------------------|---|---|
| $La_2O_3$ | $NO_3^-$ | Fe: | $< 0.004$ | |
| | | Ca: | $0.002$ | |
| | | Ce: | $< 0.035$ | undetected |
| | | Pr: | $< 0.015$ | " |
| $La_2O_3$ | $ClO_4^-$ | Fe: | $< 0.004$ | |
| | | Ca: | $0.002$ | |
| | | Ce: | $< 0.035$ | undetected |
| | | Pr: | $< 0.015$ | " |
| $Pr_6O_{11}$ | $Cl^-$ | Fe: | $< 0.009$ | |
| | | Ca: | $< 0.020$ | |
| | | La: | $< 0.040$ | undetected |
| | | Ce: | $< 0.100$ | " |
| | | Nd: | $< 0.100$ | " |
| | | Sm: | $< 0.020$ | " |
| $Nd_2O_3$ | $NO_3^-$ | Fe: | $< 0.009$ | |
| | | Ca: | $< 0.020$ | |
| | | Ce: | undetected | |
| | | Pr: | $< 0.100$ | undetected |
| | | Sm: | $0.020$ | |
| | | Eu: | undetected | |

[a]Since a result reported as $<$ (less than) reflects
the lower limit of the analytical method, the actual amount
of impurity present may be much less than the value reported.

Table 3. (Continued)

| Oxide | Stock solution | Analyses in per cent[a] | |
|-------|----------------|-------------------------|---|
| $Nd_2O_3$ | $ClO_4^-$ | Fe: | < 0.009 |
| | | Ca: | < 0.020 |
| | | Ce: | undetected |
| | | Pr: | < 0.100 undetected |
| | | Sm: | < 0.010 " |
| | | Eu: | undetected |
| $Sm_2O_3$ | $Cl^-$ | Fe: | ⋜ 0.002 |
| | | Ca: | 0.040 |
| | | Pr: | undetected |
| | | Nd: | < 0.020 undetected |
| | | Eu: | < 0.010 " |
| | | Gd: | < 0.010 " |
| $Eu_2O_3$ | $Cl^-$ | Fe: | ⋜ 0.002 |
| | | Ca: | ⋜ 0.002 |
| | | Nd: | undetected |
| | | Sm: | < 0.015 undetected |
| | | Gd: | < 0.025 |
| | | Tb: | undetected |
| $Gd_2O_3$ | $Cl^-$ | Fe: | 0.002 |
| | | Ca: | 0.004 |
| | | Sm: | < 0.020 undetected |
| | | Eu: | < 0.001 " |
| | | Tb: | < 0.010 |
| | | Y: | < 0.002 undetected |

Table 3. (Continued)

| Oxide | Stock solution | Analyses in per cent[a] | | |
|---|---|---|---|---|
| $Gd_2O_3$ | $NO_3^-$ | Fe: | 0.001 | |
| | | Ca: | < 0.005 | |
| | | Sm: | < 0.020 | undetected |
| | | Eu: | < 0.001 | " |
| | | Tb: | < 0.020 | " |
| | | Y: | < 0.002 | " |
| | | Dy: | < 0.010 | " |
| $Gd_2O_3$ | $ClO_4^-$ | Fe: | 0.001 | |
| | | Ca: | < 0.005 | |
| | | Sm: | < 0.020 | undetected |
| | | Eu: | < 0.001 | " |
| | | Tb: | < 0.020 | " |
| | | Y: | < 0.002 | " |
| | | Dy: | < 0.010 | " |
| $Tb_4O_7$ | $Cl^-$ | Fe: | < 0.002 | |
| | | Ca: | 0.008 | |
| | | Eu: | undetected | |
| | | Gd: | < 0.020 | undetected |
| | | Y: | < 0.008 | " |
| | | Dy: | < 0.010 | " |
| | | Ho: | undetected | |
| $Ho_2O_3$ | $Cl^-$ | Fe: | < 0.005 | |
| | | Ca: | 0.004 | |
| | | Tb: | undetected | |
| | | Y: | < 0.001 | undetected |
| | | Dy: | 0.020 | |
| | | Er: | < 0.050 | undetected |
| | | Tm: | < 0.020 | " |
| | | Yb: | 0.005 | |

Table 3. (Continued)

| Oxide | Stock solution | Analyses in per cent[a] |
|-------|----------------|-------------------------|
| $Er_2O_3$ | $NO_3^-$ | Fe: $\lessapprox 0.002$<br>Ca: $\phantom{<} 0.020$<br>Dy: $< 0.010$ undetected<br>Ho: $< 0.005$ "<br>Tm: $< 0.001$ "<br>Yb: $< 0.001$ "<br>Cu: $< 0.050$<br>Zn: undetected |
| $Tm_2O_3$ | $Cl^-$ | Fe: $< 0.005$<br>Ca: $\phantom{<} 0.001$<br>Ho: $< 0.020$ undetected<br>Er: $< 0.003$ "<br>Yb: $< 0.001$<br>Lu: $< 0.020$ undetected<br>Cu: trace<br>Zn: undetected |
| $Lu_2O_3$ | $Cl^-$ | Fe: $\lessapprox 0.003$<br>Ca: $\phantom{<} 0.015$<br>Tm: $\phantom{<} 0.010$<br>Yb: $\phantom{<} 0.005$<br>Cu: $< 0.001$<br>Zn: undetected |
| $Lu_2O_3$ | $NO_3^-$ | Fe: $\lessapprox 0.003$<br>Ca: $< 0.002$<br>Tm: $< 0.001$ undetected<br>Yb: $\phantom{<} 0.003$<br>Cu: $< 0.001$<br>Zn: undetected |

Table 3. (Continued)

| Oxide | Stock solution | Analyses in per cent[a] |
|-------|----------------|--------------------------|
| $Lu_2O_3$ | $ClO_4^-$ | Fe: $< 0.003$<br>Ca: $< 0.002$<br>Tm: $< 0.001$ undetected<br>Yb: $0.003$<br>Cu: $< 0.001$<br>Zn: undetected |

## V.  CALCULATIONS AND RESULTS

### A.  Calculation of Heat Capacity Properties

Since an expression of $\phi_{cp}$ as a function of concentration is needed to calculate $\overline{C}_{p1}$ and $\overline{C}_{p2}$, least squares fits of $\phi_{cp}$ versus $m^{1/2}$ were made on an IBM 360 computor for each rare earth salt of this work. The $\phi_{cp}$ points were weighted proportionally to $(P_{\phi_{cp}})^{-2}$ where $P_{\phi_{cp}}$ is the probable error in $\phi_{cp}$ which is discussed later in the error analysis section. Each $\phi_{cp}$ was the average of three results as calculated from the equation

$$\phi_{cp} = (\frac{1000}{m} + M_2)S_p - \frac{1000}{m} S_p^o \qquad (2.18)$$

using the three $S_p$ results from one run on the calorimeter and $M_2$ values based on $C^{12}$. The first through sixth order fits calculated for each salt could be expressed in the form

$$\phi_{cp} = \sum_{k=0}^{n} A_k m^{k/2} \qquad (5.1)$$

where n is the order of fit and the $A_k$ are the coefficients for each term. Fourth order fits were used for all cases except $Lu(NO_3)_3$ and the rare earth perchlorates. Since the shape of the curve for $Lu(NO_3)_3$ was difficult to fit because of the constant portion near saturation, a sixth order fit had to be used. Third order fits gave sufficient precision for the perchlorates. $\overline{C}_{p1}$ was calculated from Equation 5.2

while Equation 5.3 was used for $\overline{C}_{p2}$. The $A_k$ are those from the least squares fits.

$$\overline{C}_{p1} = \overline{C}_{p1}^{0} - \frac{M_1}{2000} \sum_{k=0}^{n} kA_k m^{(k+2)/2}$$

$$= 17.9955 - (9.00767 \times 10^{-3}) \sum_{k=0}^{n} kA_k m^{(k+2)/2}$$

$$\text{(5.2)}$$

$$\overline{C}_{p2} = \sum_{k=0}^{n} (1+k/2)A_k m^{k/2} \qquad \text{(5.3)}$$

## B. Tables and Graphs of Properties

Tables 4 through 20 contain the experimental results of this work and show the molality, square root of molality, specific heat capacity ($S_p$), apparent molar heat capacity ($\phi_{cp}$) and least squares apparent molar heat capacity ($\phi_{cp}$L.S.) for each concentration of the salts measured. The difference between the two $\phi_{cp}$ quantities is $\triangle$. Apparent molar heat capacity, and the partial molar heat capacities of solvent and solute ($\overline{C}_{p1}$ and $\overline{C}_{p2}$) at rounded square roots of molalities as calculated from the least squares coefficients ($A_k$) are shown in Tables 21 through 29. Table 30 gives the $A_k$ for each salt. Results of the rare earth chlorides determined by K. C. Jones (4, 5) are included in Tables 21 through

Table 4. Specific heat capacities and apparent molar heat capacities of aqueous solutions of $PrCl_3$ at 25°C

| m | $m^{1/2}$ | $S_p$ | $-\phi_{cp}$ | $-\phi_{cp}^a$ L. S. | $\Delta$ |
|---|---|---|---|---|---|
| 0.098520 | 0.31388 | 0.9660 | 95.3 | 96.6 | -1.3 |
| 0.15257 | 0.39060 | 0.9492 | 91.3 | 91.9 | -0.6 |
| 0.24614 | 0.49613 | 0.9216 | 86.0 | 85.9 | 0.1 |
| 0.35914 | 0.59928 | 0.8908 | 80.9 | 80.5 | 0.4 |
| 0.48193 | 0.69421 | 0.8597 | 76.2 | 75.7 | 0.5 |
| 0.63989 | 0.79993 | 0.8236 | 70.2 | 70.2 | 0.0 |
| 0.82159 | 0.90642 | 0.7864 | 64.2 | 64.6 | -0.4 |
| 1.0092 | 1.0046 | 0.7518 | 58.9 | 59.2 | -0.3 |
| 1.2262 | 1.1073 | 0.7164 | 53.3 | 53.1 | 0.2 |
| 1.4537 | 1.2057 | 0.6845 | 47.0 | 47.0 | 0.0 |
| 1.7123 | 1.3085 | 0.6534 | 40.2 | 40.3 | -0.1 |
| 1.9836 | 1.4084 | 0.6255 | 33.6 | 33.5 | 0.1 |
| 2.1601 | 1.4697 | 0.6100 | 29.2 | 29.1 | 0.1 |
| 2.5708 | 1.6034 | 0.5802 | 19.4 | 19.5 | -0.1 |
| 2.9010 | 1.7032 | 0.5611 | 12.2 | 12.2 | 0.0 |
| 3.2339 | 1.7983 | 0.5453 | 5.4 | 5.4 | 0.0 |
| 3.5595 | 1.8867 | 0.5324 | -0.6 | -0.6 | 0.0 |
| 3.7936 | 1.9477 | 0.5244 | -4.6 | -4.6 | 0.0 |
| 3.8910[b] | 1.9725 | 0.5212 | -6.1 | -6.1 | 0.0 |

Average ±0.2

[a]Calculated from Equation 5.1 using coefficients given in Table 30.

[b]Saturated solution.

Table 5.  Specific heat capacities and apparent molar heat
capacities of aqueous solutions of $SmCl_3$ at 25°C

| m | $m^{1/2}$ | $S_p$ | $-\phi_{cp}$ | $-\phi_{cp}^a$ L.S. | $\Delta$ |
|---|---|---|---|---|---|
| 0.097114 | 0.31163 | 0.9658 | 92.5 | 94.4 | -1.9 |
| 0.15957 | 0.39946 | 0.9460 | 88.1 | 88.8 | -0.7 |
| 0.26869 | 0.51836 | 0.9137 | 82.4 | 82.1 | 0.3 |
| 0.36036 | 0.60030 | 0.8884 | 78.6 | 78.0 | 0.6 |
| 0.51578 | 0.71818 | 0.8491 | 72.5 | 72.2 | 0.3 |
| 0.67020 | 0.81866 | 0.8139 | 67.0 | 67.3 | -0.3 |
| 0.85276 | 0.92345 | 0.7760 | 62.2 | 61.9 | 0.3 |
| 1.0625 | 1.0308 | 0.7383 | 55.7 | 56.1 | -0.4 |
| 1.1372 | 1.0664 | 0.7256 | 54.1 | 54.0 | 0.1 |
| 1.4371 | 1.1988 | 0.6817 | 45.8 | 46.0 | -0.2 |
| 1.6664 | 1.2909 | 0.6532 | 39.8 | 39.9 | -0.1 |
| 1.9453 | 1.3947 | 0.6237 | 32.8 | 32.6 | 0.2 |
| 2.1161 | 1.4547 | 0.6082 | 28.5 | 28.2 | 0.3 |
| 2.5233 | 1.5885 | 0.5785 | 18.1 | 18.3 | -0.2 |
| 2.8645 | 1.6925 | 0.5583 | 10.5 | 10.6 | -0.1 |
| 3.1788 | 1.7829 | 0.5429 | 4.1 | 4.1 | 0.0 |
| 3.5070 | 1.8727 | 0.5293 | -2.0 | -2.0 | 0.0 |
| 3.6414[b] | 1.9082 | 0.5242 | -4.2 | -4.2 | 0.0 |

Average $\pm$0.3

[a]Calculated from Equation 5.1 using coefficients given
in Table 30.

[b]Saturated solution.

Table 6. Specific heat capacities and apparent molar heat
capacities of aqueous solutions of $EuCl_3$ at 25° C

| m | $m^{1/2}$ | $S_p$ | $-\phi_{cp}$ | $-\phi_{cp}$ [a] L.S. | $\Delta$ |
|---|---|---|---|---|---|
| 0.10020 | 0.31654 | 0.9652 | 87.4 | 87.6 | -0.2 |
| 0.16044 | 0.40055 | 0.9464 | 82.6 | 82.7 | -0.1 |
| 0.25091 | 0.50091 | 0.9199 | 77.0 | 77.6 | -0.6 |
| 0.36158 | 0.60132 | 0.8893 | 73.3 | 72.9 | +0.4 |
| 0.49249 | 0.70178 | 0.8560 | 69.0 | 68.5 | 0.5 |
| 0.64460 | 0.80287 | 0.8209 | 64.1 | 64.1 | 0.0 |
| 0.81986 | 0.90546 | 0.7842 | 59.3 | 59.3 | 0.0 |
| 1.0099 | 1.0050 | 0.7488 | 54.3 | 54.4 | -0.1 |
| 1.2233 | 1.1060 | 0.7138 | 48.7 | 48.9 | -0.2 |
| 1.4406 | 1.2002 | 0.6825 | 43.4 | 43.4 | 0.0 |
| 1.7008 | 1.3041 | 0.6504 | 36.9 | 36.9 | 0.0 |
| 1.9595 | 1.3998 | 0.6232 | 30.7 | 30.5 | 0.2 |
| 2.2674 | 1.5058 | 0.5969 | 23.1 | 23.1 | 0.0 |
| 2.5784 | 1.6057 | 0.5750 | 15.8 | 16.1 | -0.3 |
| 2.8731 | 1.6950 | 0.5571 | 9.9 | 9.9 | 0.0 |
| 3.2423 | 1.8006 | 0.5383 | 3.0 | 3.0 | 0.0 |
| 3.4579 | 1.8595 | 0.5283 | -0.4 | -0.6 | +0.2 |
| 3.5889[b] | 1.8944 | 0.5232 | -2.6 | -2.5 | -0.1 |

Average ±0.2

[a]Calculated from Equation 5.1 using coefficients given
in Table 30.

[b]Saturated solution.

Table 7.  Specific heat capacities and apparent molar heat
capacities of aqueous solutions of $GdCl_3$ at $25°C$

| m | $m^{1/2}$ | $S_p$ | $-\phi_{cp}$ | $-\phi_{cp}$ [a] L.S. | $\triangle$ |
|---|---|---|---|---|---|
| 0.099125 | 0.31484 | 0.9648 | 89.5 | 89.9 | -0.4 |
| 0.15933 | 0.39916 | 0.9457 | 84.6 | 84.7 | -0.1 |
| 0.24836 | 0.49836 | 0.9190 | 79.5 | 79.4 | 0.1 |
| 0.35899 | 0.59916 | 0.8881 | 74.5 | 74.4 | 0.1 |
| 0.44484 | 0.66696 | 0.8657 | 71.3 | 71.3 | 0.0 |
| 0.63895 | 0.79934 | 0.8192 | 65.2 | 65.2 | 0.0 |
| 0.80874 | 0.89930 | 0.7830 | 60.5 | 60.5 | 0.0 |
| 0.97562 | 0.98773 | 0.7510 | 56.1 | 56.2 | -0.1 |
| 1.2282 | 1.1082 | 0.7084 | 49.8 | 49.8 | 0.0 |
| 1.5239 | 1.2344 | 0.6661 | 42.8 | 42.6 | 0.2 |
| 1.8584 | 1.3632 | 0.6273 | 34.6 | 34.8 | -0.2 |
| 2.1480 | 1.4656 | 0.5987 | 28.5 | 28.3 | 0.2 |
| 2.5512 | 1.5972 | 0.5670 | 19.8 | 19.8 | 0.0 |
| 2.8683 | 1.6936 | 0.5463 | 13.8 | 13.8 | 0.0 |
| 3.2006 | 1.7890 | 0.5276 | 8.2 | 8.1 | 0.1 |
| 3.4360 | 1.8536 | 0.5159 | 4.6 | 4.6 | 0.0 |
| 3.5898[b] | 1.8947 | 0.5084 | 2.6 | 2.6 | 0.0 |

Average $^+_-0.1$

[a]Calculated from Equation 5.1 using coefficients given
in Table 30.

[b]Saturated solution.

Table 8. Specific heat capacities and apparent molar heat capacities of aqueous solutions of $TbCl_3$ at 25°C

| m | $m^{1/2}$ | $S_p$ | $-\phi_{cp}$ | $-\phi_{cp}{}^a$ L.S. | $\triangle$ |
|---|---|---|---|---|---|
| 0.10034 | 0.31677 | 0.9646 | 86.1 | 85.4 | 0.7 |
| 0.16149 | 0.40186 | 0.9457 | 78.4 | 80.4 | -2.0 |
| 0.25153 | 0.50153 | 0.9185 | 76.0 | 75.2 | 0.8 |
| 0.35847 | 0.59872 | 0.8889 | 71.0 | 70.7 | 0.3 |
| 0.48992 | 0.69995 | 0.8552 | 66.3 | 66.2 | 0.1 |
| 0.63592 | 0.79744 | 0.8209 | 62.1 | 61.8 | 0.3 |
| 0.80884 | 0.89935 | 0.7844 | 57.0 | 57.2 | -0.2 |
| 1.0146 | 1.0073 | 0.7457 | 51.8 | 52.1 | -0.3 |
| 1.2118 | 1.1008 | 0.7126 | 47.2 | 47.3 | -0.1 |
| 1.4563 | 1.2068 | 0.6768 | 41.6 | 41.6 | 0.0 |
| 1.6991 | 1.3035 | 0.6463 | 36.0 | 36.0 | 0.0 |
| 1.9484 | 1.3959 | 0.6192 | 30.6 | 30.6 | 0.0 |
| 2.1513 | 1.4668 | 0.5998 | 26.4 | 26.3 | 0.1 |
| 2.5622 | 1.6007 | 0.5669 | 18.2 | 18.3 | -0.1 |
| 2.8898 | 1.6999 | 0.5449 | 12.6 | 12.7 | -0.1 |
| 3.2270 | 1.7964 | 0.5246 | 7.8 | 7.8 | 0.0 |
| 3.4756 | 1.8643 | 0.5110 | 4.8 | 4.8 | 0.0 |
| 3.5713[b] | 1.8898 | 0.5061 | 3.7 | 3.8 | -0.1 |

Average ±0.3

[a]Calculated from Equation 5.1 using coefficients given in Table 30.

[b]Saturated solution.

Table 9. Specific heat capacities and apparent molar heat capacities of aqueous solutions of $HoCl_3$ at 25°C

| m | $m^{1/2}$ | $S_p$ | $-\phi_{cp}$ | $-\phi_{cp}^{a}$ L.S. | $\Delta$ |
|---|---|---|---|---|---|
| 0.099954 | 0.31616 | 0.9641 | 86.6 | 85.8 | 0.8 |
| 0.16025 | 0.40031 | 0.9450 | 80.0 | 80.8 | -0.8 |
| 0.25166 | 0.50166 | 0.9173 | 75.4 | 75.4 | 0.0 |
| 0.36253 | 0.60211 | 0.8860 | 71.0 | 70.6 | 0.4 |
| 0.49258 | 0.70184 | 0.8524 | 66.3 | 66.1 | 0.2 |
| 0.64614 | 0.80383 | 0.8162 | 61.4 | 61.5 | -0.1 |
| 0.81608 | 0.90337 | 0.7798 | 57.0 | 56.9 | 0.1 |
| 0.99374 | 0.99686 | 0.7459 | 52.3 | 52.4 | -0.1 |
| 1.2201 | 1.1406 | 0.7073 | 47.1 | 46.9 | 0.2 |
| 1.4517 | 1.2049 | 0.6735 | 41.5 | 41.5 | 0.0 |
| 1.6980 | 1.3031 | 0.6423 | 35.7 | 35.9 | -0.2 |
| 1.9640 | 1.4014 | 0.6131 | 30.1 | 30.0 | 0.1 |
| 2.2617 | 1.5039 | 0.5855 | 24.0 | 23.9 | 0.1 |
| 2.5616 | 1.6005 | 0.5618 | 18.2 | 18.2 | 0.0 |
| 2.9039 | 1.7041 | 0.5387 | 12.3 | 12.4 | -0.1 |
| 3.2267 | 1.7963 | 0.5194 | 7.7 | 7.7 | 0.0 |
| 3.6942[b] | 1.9220 | 0.4941 | 2.6 | 2.6 | 0.0 |

Average $\pm$0.2

[a]Calculated from Equation 5.1 using coefficients given in Table 30.

[b]Saturated solution.

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Table 10. Specific heat capacities and apparent molar heat
capacities of aqueous solutions of $TmCl_3$ at 25°C

| m | $m^{1/2}$ | $S_p$ | $-\phi_{cp}$ | $-\phi_{cp}$ [a] L.S. | $\triangle$ |
|---|---|---|---|---|---|
| 0.10495 | 0.32396 | 0.9625 | 81.6 | 83.4 | -1.8 |
| 0.16011 | 0.40014 | 0.9444 | 80.3 | 79.4 | 0.9 |
| 0.24731 | 0.49731 | 0.9180 | 74.2 | 74.8 | -0.6 |
| 0.39110 | 0.62538 | 0.8772 | 69.6 | 69.1 | 0.5 |
| 0.49598 | 0.70426 | 0.8504 | 65.4 | 65.6 | -0.2 |
| 0.65425 | 0.80886 | 0.8124 | 61.4 | 60.9 | 0.5 |
| 0.82134 | 0.90628 | 0.7773 | 55.8 | 56.4 | -0.6 |
| 1.0153 | 1.0076 | 0.7399 | 51.4 | 51.4 | 0.0 |
| 1.2310 | 1.1095 | 0.7037 | 46.1 | 46.1 | 0.0 |
| 1.4710 | 1.2129 | 0.6686 | 40.5 | 40.4 | 0.1 |
| 1.7124 | 1.3086 | 0.6383 | 34.8 | 34.9 | -0.1 |
| 1.9612 | 1.4004 | 0.6111 | 29.5 | 29.5 | 0.0 |
| 2.2716 | 1.5072 | 0.5820 | 23.3 | 23.2 | 0.1 |
| 2.5915 | 1.6098 | 0.5571 | 17.1 | 17.2 | -0.1 |
| 2.9278 | 1.7111 | 0.5345 | 11.5 | 11.7 | -0.2 |
| 3.2822 | 1.8117 | 0.5130 | 6.8 | 6.8 | 0.0 |
| 3.7003 | 1.9236 | 0.4903 | 2.5 | 2.3 | 0.2 |
| 3.8773[b] | 1.9691 | 0.4818 | 0.7 | 0.9 | -0.2 |

Average $\pm$0.3

[a]Calculated from Equation 5.1 using coefficients given in Table 30.

[b]Saturated solution.

Table 11. Specific heat capacities and apparent molar heat capacities of aqueous solutions of $LuCl_3$ at 25°C

| m | $m^{1/2}$ | $S_p$ | $-\phi_{cp}$ | $-\phi_{cp}$ [a] L.S. | $\triangle$ |
|---|---|---|---|---|---|
| 0.10054 | 0.31708 | 0.9632 | 84.1 | 83.9 | 0.2 |
| 0.16291 | 0.40362 | 0.9427 | 79.6 | 79.8 | -0.2 |
| 0.25369 | 0.50368 | 0.9146 | 75.1 | 75.3 | -0.2 |
| 0.39432 | 0.62795 | 0.8743 | 69.9 | 70.0 | -0.1 |
| 0.49699 | 0.70498 | 0.8470 | 67.4 | 66.7 | 0.7 |
| 0.64895 | 0.80558 | 0.8106 | 62.1 | 62.3 | -0.2 |
| 0.81360 | 0.90200 | 0.7746 | 57.8 | 57.8 | 0.0 |
| 1.0084 | 1.0042 | 0.7368 | 52.6 | 52.9 | -0.3 |
| 1.2296 | 1.1089 | 0.6989 | 47.3 | 47.5 | -0.2 |
| 1.4663 | 1.2109 | 0.6634 | 42.2 | 41.9 | 0.3 |
| 1.7189 | 1.3111 | 0.6312 | 36.4 | 36.3 | 0.1 |
| 1.9822 | 1.4079 | 0.6021 | 30.8 | 30.7 | 0.1 |
| 2.2850 | 1.5116 | 0.5738 | 24.6 | 24.7 | -0.1 |
| 2.5862 | 1.6082 | 0.5496 | 19.1 | 19.2 | -0.1 |
| 2.9136 | 1.7069 | 0.5269 | 13.8 | 13.9 | -0.1 |
| 3.3110 | 1.8196 | 0.5025 | 8.6 | 8.5 | 0.1 |
| 3.6023 | 1.8980 | 0.4864 | 5.5 | 5.3 | 0.2 |
| 4.1165[b] | 2.0289 | 0.4601 | 1.5 | 1.5 | 0.0 |

Average $\pm$0.2

[a]Calculated from Equation 5.1 using coefficients given in Table 30.

[b]Saturated solution.

Table 12. Specific heat capacities and apparent molar heat capacities of aqueous solutions of $La(NO_3)_3$ at $25^\circ C$

| m | $m^{1/2}$ | $S_p$ | $+\phi_{cp}$ | $+\phi_{cp}{}^a$ L.S. | $\triangle$ |
|---|---|---|---|---|---|
| 0.098972 | 0.31460 | 0.9634 | -46.0 | -46.9 | -0.9 |
| 0.15991 | 0.39989 | 0.9434 | -40.5 | -40.4 | 0.1 |
| 0.24983 | 0.49983 | 0.9162 | -33.2 | -32.8 | 0.4 |
| 0.35981 | 0.59984 | 0.8863 | -24.8 | -25.2 | -0.4 |
| 0.48912 | 0.69937 | 0.8544 | -17.9 | -17.6 | 0.3 |
| 0.63972 | 0.79983 | 0.8216 | - 9.9 | -10.1 | -0.2 |
| 0.81007 | 0.90004 | 0.7889 | - 2.9 | - 2.8 | 0.1 |
| 1.0003 | 1.0002 | 0.7571 | 4.2 | 4.1 | -0.1 |
| 1.2076 | 1.0989 | 0.7265 | 10.5 | 10.6 | 0.1 |
| 1.3405 | 1.1578 | 0.7092 | 14.4 | 14.3 | -0.1 |
| 1.6943 | 1.3017 | 0.6692 | 22.9 | 22.8 | -0.1 |
| 1.9598 | 1.3999 | 0.6439 | 28.1 | 28.0 | -0.1 |
| 2.0915 | 1.4462 | 0.6324 | 30.3 | 30.3 | 0.0 |
| 2.5574 | 1.5992 | 0.5975 | 37.2 | 37.3 | 0.1 |
| 2.8925 | 1.7007 | 0.5766 | 41.3 | 41.2 | -0.1 |
| 3.2392 | 1.7998 | 0.5572 | 44.7 | 44.7 | 0.0 |
| 3.6055 | 1.8988 | 0.5393 | 47.8 | 47.8 | 0.0 |
| 3.9997 | 1.9999 | 0.5222 | 50.5 | 50.5 | 0.0 |
| 4.4561 | 2.1110 | 0.5047 | 53.1 | 53.1 | 0.0 |
| 4.6084[b] | 2.1467 | 0.4992 | 53.8 | 53.8 | 0.0 |

Average $\pm 0.2$

[a]Calculated from Equation 5.1 using coefficients given in Table 30.

[b]Saturated solution.

Table 13. Specific heat capacities and apparent molar heat capacities of aqueous solutions of $Nd(NO_3)_3$ at $25°C$

| $m$ | $m^{1/2}$ | $S_p$ | $+\phi_{cp}$ | $+\phi_{cp}{}^a$ L.S. | $\triangle$ |
|---|---|---|---|---|---|
| 0.10235 | 0.31992 | 0.9618 | -44.4 | -43.0 | 1.4 |
| 0.16385 | 0.40479 | 0.9420 | -36.0 | -36.9 | -0.9 |
| 0.25617 | 0.50613 | 0.9138 | -30.5 | -29.7 | 0.8 |
| 0.36966 | 0.60800 | 0.8830 | -22.0 | -22.4 | -0.4 |
| 0.50312 | 0.70931 | 0.8498 | -15.7 | -15.3 | 0.4 |
| 0.65951 | 0.81210 | 0.8162 | - 7.4 | - 8.3 | -0.9 |
| 0.83422 | 0.91336 | 0.7820 | - 1.8 | - 1.5 | 0.3 |
| 1.0319 | 1.0158 | 0.7490 | 5.2 | 5.1 | -0.1 |
| 1.2503 | 1.1182 | 0.7170 | 11.3 | 11.5 | 0.2 |
| 1.4910 | 1.2211 | 0.6868 | 17.5 | 17.6 | 0.1 |
| 1.7550 | 1.3248 | 0.6585 | 23.5 | 23.4 | -0.1 |
| 2.0330 | 1.4258 | 0.6326 | 28.8 | 28.8 | 0.0 |
| 2.3452 | 1.5314 | 0.6078 | 34.0 | 34.0 | 0.0 |
| 2.6621 | 1.6316 | 0.5862 | 38.6 | 38.5 | -0.1 |
| 3.0361 | 1.7424 | 0.5642 | 43.1 | 43.1 | 0.0 |
| 3.3940 | 1.8423 | 0.5460 | 46.9 | 46.8 | -0.1 |
| 3.7928 | 1.9475 | 0.5277 | 50.0 | 50.2 | 0.2 |
| 4.1440 | 2.0357 | 0.5137 | 52.5 | 52.6 | 0.1 |
| 4.5990[b] | 2.1445 | 0.4973 | 55.2 | 55.1 | -0.1 |
| | | | | Average | ±0.3 |

[a]Calculated from Equation 5.1 using coefficients given in Table 30.

[b]Saturated solution.

Table 14. Specific heat capacities and apparent molar heat capacities of aqueous solutions of $Gd(NO_3)_3$ at $25^\circ C$

| m | $m^{1/2}$ | $S_p$ | $+\phi_{cp}$ | $+\phi_{cp}$[a] L.S. | $\triangle$ |
|---|---|---|---|---|---|
| 0.099982 | 0.31620 | 0.9618 | -40.7 | -39.3 | 1.4 |
| 0.15663 | 0.39577 | 0.9427 | -35.5 | -34.4 | 1.1 |
| 0.25001 | 0.50001 | 0.9136 | -27.4 | -27.9 | -0.5 |
| 0.35970 | 0.59975 | 0.8824 | -21.1 | -21.6 | -0.5 |
| 0.49084 | 0.70060 | 0.8485 | -15.3 | -15.3 | 0.0 |
| 0.64170 | 0.80106 | 0.8139 | - 8.9 | - 9.1 | -0.2 |
| 0.81139 | 0.90077 | 0.7794 | - 2.9 | - 3.0 | -0.1 |
| 1.0044 | 1.0022 | 0.7450 | 2.9 | 3.1 | 0.2 |
| 1.2106 | 1.1003 | 0.7130 | 8.6 | 8.9 | 0.3 |
| 1.4396 | 1.1998 | 0.6827 | 14.7 | 14.5 | -0.2 |
| 1.6917 | 1.3007 | 0.6533 | 20.0 | 20.1 | 0.1 |
| 1.9667 | 1.4024 | 0.6263 | 25.5 | 25.4 | -0.1 |
| 2.2544 | 1.5015 | 0.6016 | 30.3 | 30.4 | 0.1 |
| 2.5658 | 1.6018 | 0.5791 | 35.1 | 35.0 | -0.1 |
| 2.8961 | 1.7018 | 0.5581 | 39.4 | 39.3 | -0.1 |
| 3.2383 | 1.7995 | 0.5393 | 43.2 | 43.2 | 0.0 |
| 3.6224 | 1.9033 | 0.5208 | 46.8 | 46.8 | 0.0 |
| 3.9515 | 1.9878 | 0.5066 | 49.3 | 49.4 | 0.1 |
| 4.3996[b] | 2.0975 | 0.4896 | 52.3 | 52.2 | -0.1 |
| | | | | Average | $\pm0.3$ |

[a]Calculated from Equation 5.1 using coefficients given in Table 30.

[b]Saturated solution.

Table 15.  Specific heat capacities and apparent molar heat capacities of aqueous solutions of $Er(NO_3)_3$ at 25°C

| m | $m^{1/2}$ | $S_p$ | $+\phi_{cp}$ | $+\phi_{cp}^{a}$ L.S. | $\triangle$ |
|---|---|---|---|---|---|
| 0.10110 | 0.31797 | 0.9600 | -45.2 | -39.6 | 5.6 |
| 0.25464 | 0.50462 | 0.9093 | -30.6 | -30.0 | 0.6 |
| 0.36194 | 0.60162 | 0.8782 | -23.1 | -23.9 | -0.8 |
| 0.49086 | 0.70061 | 0.8444 | -16.5 | -17.1 | -0.6 |
| 0.64281 | 0.80175 | 0.8090 | - 9.6 | - 9.9 | -0.3 |
| 0.81380 | 0.90211 | 0.7742 | - 2.6 | - 2.6 | 0.0 |
| 1.0045 | 1.0023 | 0.7408 | 4.7 | 4.6 | -0.1 |
| 1.2041 | 1.0973 | 0.7100 | 11.0 | 11.2 | 0.2 |
| 1.5061 | 1.2272 | 0.6714 | 19.7 | 19.9 | 0.2 |
| 1.7119 | 1.3084 | 0.6488 | 24.7 | 24.9 | 0.2 |
| 1.9765 | 1.4059 | 0.6237 | 30.5 | 30.4 | -0.1 |
| 2.2625 | 1.5042 | 0.5998 | 35.5 | 35.5 | 0.0 |
| 2.5868 | 1.6084 | 0.5763 | 40.2 | 40.2 | 0.0 |
| 2.9168 | 1.7079 | 0.5556 | 44.3 | 44.2 | -0.1 |
| 3.2417 | 1.8005 | 0.5372 | 47.4 | 47.3 | -0.1 |
| 3.6571 | 1.9124 | 0.5166 | 50.6 | 50.5 | -0.1 |
| 4.0010 | 2.0002 | 0.5008 | 52.4 | 52.5 | 0.1 |
| 4.4498 | 2.1095 | 0.4827 | 54.5 | 54.7 | 0.2 |
| 4.8837 | 2.2099 | 0.4674 | 56.3 | 56.3 | 0.0 |
| 5.1793 | 2.2758 | 0.4577 | 57.2 | 57.3 | 0.1 |
| 5.4560[b] | 2.3358 | 0.4501 | 58.4 | 58.2 | -0.2 |

Average $\pm0.5$

[a]Calculated from Equation 5.1 using coefficients given in Table 30.

[b]Saturated solution.

Table 16. Specific heat capacities and apparent molar heat capacities of aqueous solutions of $Lu(NO_3)_3$ at $25^\circ C$

| m | $m^{1/2}$ | $S_p$ | $+\phi_{cp}$ | $+\phi_{cp}^{a}$ L.S. | $\triangle$ |
|---|---|---|---|---|---|
| 0.099670 | 0.31571 | 0.9597 | -47.1 | -46.8 | 0.3 |
| 0.16035 | 0.40044 | 0.9386 | -37.4 | -38.6 | -1.2 |
| 0.25023 | 0.50023 | 0.9092 | -30.3 | -30.8 | -0.5 |
| 0.35993 | 0.59994 | 0.8761 | -24.9 | -23.9 | 1.0 |
| 0.50098 | 0.70780 | 0.8386 | -17.3 | -16.8 | 0.5 |
| 0.64031 | 0.80020 | 0.8059 | -10.5 | -10.5 | 0.0 |
| 0.80962 | 0.89979 | 0.7711 | - 3.0 | - 3.4 | -0.4 |
| 0.99165 | 0.99582 | 0.7385 | 4.0 | 3.8 | -0.2 |
| 1.2053 | 1.0979 | 0.7058 | 11.7 | 11.7 | 0.0 |
| 1.4403 | 1.2001 | 0.6759 | 19.8 | 19.6 | -0.2 |
| 1.6907 | 1.3003 | 0.6488 | 27.1 | 27.2 | 0.1 |
| 1.9762 | 1.4058 | 0.6231 | 34.7 | 34.8 | 0.1 |
| 2.2610 | 1.5037 | 0.6009 | 40.9 | 41.1 | 0.2 |
| 2.5802 | 1.6063 | 0.5797 | 46.8 | 46.9 | 0.1 |
| 2.8851 | 1.6986 | 0.5620 | 51.4 | 51.3 | -0.1 |
| 3.2462 | 1.8017 | 0.5427 | 55.4 | 55.2 | -0.2 |
| 3.6145 | 1.9012 | 0.5242 | 57.9 | 57.9 | 0.0 |
| 4.0569 | 2.0142 | 0.5043 | 60.1 | 60.0 | -0.1 |
| 4.5525 | 2.1337 | 0.4832 | 61.1 | 61.3 | 0.2 |
| 4.9609 | 2.2273 | 0.4674 | 61.6 | 61.7 | 0.1 |
| 5.4126 | 2.3265 | 0.4517 | 62.0 | 61.9 | -0.1 |
| 5.8903 | 2.4270 | 0.4365 | 62.1 | 62.0 | -0.1 |
| 6.4138 | 2.5325 | 0.4213 | 62.0 | 62.0 | 0.0 |
| 6.8206[b] | 2.6116 | 0.4108 | 62.0 | 62.1 | 0.1 |

Average $\pm 0.2$

[a]Calculated from Equation 5.1 using coefficients given in Table 30.

[b]Saturated solution.

Table 17.  Specific heat capacities and apparent molar heat
capacities of aqueous solutions of $La(ClO_4)_3$ at
25°C

| m | $m^{1/2}$ | $S_p$ | $+\phi_{cp}$ | $+\phi_{cp}$[a] L.S. | $\triangle$ |
|---|---|---|---|---|---|
| 0.089116 | 0.29852 | 0.9593 | -25.0 | -27.6 | -2.6 |
| 0.16111 | 0.40139 | 0.9303 | -19.0 | -21.1 | -2.1 |
| 0.25001 | 0.50001 | 0.8968 | -16.3 | -15.3 | 1.0 |
| 0.35039 | 0.59194 | 0.8629 | -10.9 | -10.3 | 0.6 |
| 0.49386 | 0.70275 | 0.8193 | - 5.5 | - 4.8 | 0.7 |
| 0.64477 | 0.80298 | 0.7791 | - 0.2 | - 0.2 | 0.0 |
| 0.81666 | 0.90370 | 0.7384 | 3.9 | 4.1 | 0.2 |
| 1.0063 | 1.0032 | 0.6995 | 8.4 | 8.0 | -0.4 |
| 1.2134 | 1.1015 | 0.6621 | 11.9 | 11.6 | -0.3 |
| 1.4617 | 1.2090 | 0.6234 | 15.7 | 15.4 | -0.3 |
| 1.7340 | 1.3168 | 0.5868 | 18.9 | 19.0 | 0.1 |
| 1.9875 | 1.4098 | 0.5576 | 21.8 | 22.0 | 0.2 |
| 2.2696 | 1.5065 | 0.5299 | 25.0 | 25.0 | 0.0 |
| 2.5422 | 1.5944 | 0.5061 | 27.5 | 27.8 | 0.3 |
| 2.9044 | 1.7042 | 0.4798 | 31.1 | 31.3 | 0.2 |
| 3.3033 | 1.8175 | 0.4560 | 35.0 | 34.9 | -0.1 |
| 3.5779 | 1.8915 | 0.4418 | 37.5 | 37.4 | -0.1 |
| 4.0777 | 2.0193 | 0.4204 | 42.0 | 41.9 | -0.1 |
| 4.4645 | 2.1129 | 0.4072 | 45.5 | 45.4 | -0.1 |
| 4.7908[b] | 2.1888 | 0.3973 | 48.1 | 48.4 | 0.3 |

Average ±0.5

[a]Calculated from Equation 5.1 using coefficients given
in Table 30.

[b]Saturated solution.

Table 18.  Specific heat capacities and apparent molar heat
capacities of aqueous solutions of $Nd(ClO_4)_3$ at
$25^\circ C$

| m | $m^{1/2}$ | $S_p$ | $+\phi_{cp}$ | $+\phi_{cp}{}^a$ L.S. | $\triangle$ |
|---|---|---|---|---|---|
| 0.10040 | 0.31686 | 0.9539 | -25.8 | -28.1 | -2.3 |
| 0.15994 | 0.39992 | 0.9295 | -22.7 | -22.4 | -0.3 |
| 0.24961 | 0.49961 | 0.8960 | -15.8 | -16.1 | -0.3 |
| 0.36060 | 0.60050 | 0.8582 | -10.5 | -10.3 | 0.2 |
| 0.48492 | 0.69636 | 0.8204 | - 4.9 | - 5.2 | -0.3 |
| 0.63899 | 0.79937 | 0.7780 | - 1.3 | - 0.2 | 1.1 |
| 0.80591 | 0.89773 | 0.7390 | 4.6 | 4.2 | -0.4 |
| 0.99386 | 0.99693 | 0.6995 | 8.3 | 8.3 | 0.0 |
| 1.2091 | 1.0996 | 0.6606 | 12.5 | 12.3 | -0.2 |
| 1.4382 | 1.1992 | 0.6244 | 16.0 | 15.9 | -0.1 |
| 1.6913 | 1.3005 | 0.5900 | 19.3 | 19.4 | 0.1 |
| 1.9641 | 1.4015 | 0.5585 | 23.0 | 22.8 | -0.2 |
| 2.2484 | 1.4995 | 0.5300 | 26.0 | 26.1 | 0.1 |
| 2.5510 | 1.5972 | 0.5044 | 29.4 | 29.3 | -0.1 |
| 2.8869 | 1.6991 | 0.4800 | 32.7 | 32.8 | 0.1 |
| 3.2116 | 1.7921 | 0.4601 | 35.9 | 36.0 | 0.1 |
| 3.6192 | 1.9024 | 0.4397 | 40.1 | 40.0 | -0.1 |
| 4.0735 | 2.0183 | 0.4211 | 44.6 | 44.5 | -0.1 |
| 4.5091 | 2.1235 | 0.4071 | 48.9 | 48.9 | 0.0 |
| 4.6849[b] | 2.1645 | 0.4022 | 50.6 | 50.7 | 0.1 |

Average $\pm 0.3$

[a]Calculated from Equation 5.1 using coefficients given
in Table 30.

[b]Saturated solution.

Table 19. Specific heat capacities and apparent molar heat capacities of aqueous solutions of $Gd(ClO_4)_3$ at $25^\circ C$

| m | $m^{1/2}$ | $S_p$ | $+\phi_{cp}$ | $+\phi_{cp}$ [a] L.S. | $\Delta$ |
|---|---|---|---|---|---|
| 0.10126 | 0.31822 | 0.9529 | -20.2 | -19.2 | 1.0 |
| 0.16030 | 0.40038 | 0.9290 | -12.9 | -14.3 | -1.4 |
| 0.25286 | 0.50286 | 0.8937 | - 8.9 | - 8.6 | 0.3 |
| 0.35979 | 0.59982 | 0.8567 | - 5.0 | - 3.8 | 1.2 |
| 0.48895 | 0.69925 | 0.8172 | 0.6 | 0.8 | 0.2 |
| 0.64056 | 0.80035 | 0.7757 | 5.0 | 5.0 | 0.0 |
| 0.81081 | 0.90045 | 0.7349 | 9.2 | 8.9 | -0.3 |
| 1.0033 | 1.0017 | 0.6944 | 12.9 | 12.6 | -0.3 |
| 1.2155 | 1.1025 | 0.6556 | 16.2 | 16.0 | -0.2 |
| 1.4451 | 1.2021 | 0.6192 | 19.3 | 19.2 | -0.1 |
| 1.6943 | 1.3017 | 0.5849 | 22.2 | 22.3 | 0.1 |
| 1.9663 | 1.4022 | 0.5531 | 25.3 | 25.4 | 0.1 |
| 2.2551 | 1.5017 | 0.5241 | 28.2 | 28.4 | 0.2 |
| 2.5731 | 1.6041 | 0.4970 | 31.4 | 31.5 | 0.1 |
| 2.8874 | 1.6992 | 0.4744 | 34.5 | 34.6 | 0.1 |
| 3.2331 | 1.7981 | 0.4533 | 37.7 | 37.8 | 0.1 |
| 3.5946 | 1.8959 | 0.4352 | 41.4 | 41.2 | -0.2 |
| 3.9858 | 1.9964 | 0.4187 | 45.2 | 45.0 | -0.2 |
| 4.2046 | 2.0505 | 0.4108 | 47.3 | 47.2 | -0.1 |
| 4.6088[b] | 2.1468 | 0.3981 | 51.0 | 51.2 | 0.2 |
| | | | | Average | $\pm$0.3 |

[a]Calculated from Equation 5.1 using coefficients given in Table 30.

[b]Saturated solution.

Table 20. Specific heat capacities and apparent molar heat capacities of aqueous solutions of $Lu(ClO_4)_3$ at $25°C$

| m | $m^{1/2}$ | $S_p$ | $+\phi_{cp}$ | $+\phi_{cp}{}^a$ L.S. | $\Delta$ |
|---|---|---|---|---|---|
| 0.098796 | 0.31432 | 0.9527 | -16.8 | -17.6 | -0.8 |
| 0.15456 | 0.39314 | 0.9289 | -13.2 | -12.8 | 0.4 |
| 0.24963 | 0.49963 | 0.8917 | - 7.3 | - 6.7 | 0.6 |
| 0.35855 | 0.59879 | 0.8534 | - 1.9 | - 1.4 | 0.5 |
| 0.48974 | 0.69981 | 0.8121 | 3.0 | 3.5 | 0.5 |
| 0.64086 | 0.80054 | 0.7705 | 8.2 | 8.1 | -0.1 |
| 0.80679 | 0.89822 | 0.7301 | 12.4 | 12.2 | -0.2 |
| 0.99149 | 0.99574 | 0.6910 | 16.6 | 16.1 | -0.5 |
| 1.2113 | 1.1006 | 0.6505 | 20.2 | 20.0 | -0.2 |
| 1.4426 | 1.2011 | 0.6139 | 23.7 | 23.4 | -0.3 |
| 1.6960 | 1.3023 | 0.5793 | 26.8 | 26.8 | 0.0 |
| 1.9629 | 1.4010 | 0.5480 | 29.7 | 29.9 | 0.2 |
| 2.2405 | 1.4968 | 0.5200 | 32.4 | 32.9 | 0.5 |
| 2.5458 | 1.5956 | 0.4942 | 35.7 | 35.8 | 0.1 |
| 2.8864 | 1.6989 | 0.4695 | 38.8 | 38.9 | 0.1 |
| 3.2070 | 1.7908 | 0.4501 | 41.9 | 41.7 | -0.2 |
| 3.6036 | 1.8983 | 0.4293 | 45.1 | 45.0 | -0.1 |
| 4.0392 | 2.0098 | 0.4104 | 48.5 | 48.5 | 0.0 |
| 4.3816 | 2.0932 | 0.3981 | 51.3 | 51.2 | -0.1 |
| 4.6334[b] | 2.1525 | 0.3896 | 52.9 | 53.2 | - 0.3 |
|  |  |  |  | Average | ±0.3 |

[a]Calculated from Equation 5.1 using coefficients given in Table 30.

[b]Saturated solution.

Table 21.  Apparent molar heat capacities of aqueous rare
           earth chloride solutions at 25°C

| $m^{1/2}$ | $-\phi_{cp}$ LaCl$_3$[a] | PrCl$_3$ | NdCl$_3$[a] | SmCl$_3$ | EuCl$_3$ | GdCl$_3$ |
|---|---|---|---|---|---|---|
| 0.3 | 93.6 | 97.4 | 95.2 | 95.2 | 88.7 | 90.9 |
| 0.4 | 88.7 | 91.3 | 89.9 | 88.8 | 82.7 | 84.7 |
| 0.5 | 84.0 | 85.7 | 84.8 | 83.1 | 77.6 | 79.3 |
| 0.6 | 79.3 | 80.5 | 79.9 | 78.0 | 73.0 | 74.4 |
| 0.7 | 74.5 | 75.4 | 74.9 | 73.1 | 68.6 | 69.8 |
| 0.8 | 69.6 | 70.2 | 69.9 | 68.2 | 64.2 | 65.2 |
| 0.9 | 64.4 | 65.0 | 64.6 | 63.2 | 59.6 | 60.5 |
| 1.0 | 59.0 | 59.4 | 59.1 | 57.8 | 54.6 | 55.5 |
| 1.1 | 53.3 | 53.6 | 53.2 | 52.1 | 49.3 | 50.3 |
| 1.2 | 47.3 | 47.4 | 47.0 | 45.9 | 43.4 | 44.7 |
| 1.3 | 41.0 | 40.9 | 40.4 | 39.2 | 37.1 | 38.7 |
| 1.4 | 34.6 | 34.0 | 33.5 | 32.2 | 30.4 | 32.5 |
| 1.5 | 28.2 | 27.0 | 26.4 | 24.9 | 23.5 | 26.1 |
| 1.6 | 21.7 | 19.7 | 19.0 | 17.4 | 16.5 | 19.7 |
| 1.7 | 15.5 | 12.5 | 11.5 | 10.0 | 9.6 | 13.4 |
| 1.8 | 9.6 | 5.3 | 4.0 | 2.9 | 3.0 | 7.5 |
| 1.85 | 6.9 | 1.9 | 0.3 | -0.5 | 0.0 | 4.8 |
| 1.9 | 4.3 | -1.5 | -3.3 | -3.7 | | |
| 1.95 | 2.0 | -4.7 | -6.9 | | | |

[a]Determined by K. C. Jones (4).

Table 21. (Continued)

| $m^{1/2}$ | $-\phi_{cp}$ | | | | | | |
|---|---|---|---|---|---|---|---|
| | $TbCl_3$ | $DyCl_3$[a] | $HoCl_3$ | $ErCl_3$[a] | $TmCl_3$ | $YbCl_3$[a] | $LuCl_3$ |
| 0.3 | 86.5 | 85.4 | 86.9 | 85.7 | 84.7 | 84.8 | 84.7 |
| 0.4 | 80.5 | 80.0 | 80.8 | 79.9 | 79.4 | 79.8 | 79.9 |
| 0.5 | 75.3 | 75.2 | 75.5 | 74.9 | 74.7 | 75.2 | 75.5 |
| 0.6 | 70.6 | 70.7 | 70.7 | 70.4 | 70.2 | 70.8 | 71.2 |
| 0.7 | 66.2 | 66.3 | 66.2 | 66.0 | 65.8 | 66.5 | 66.9 |
| 0.8 | 61.7 | 61.9 | 61.7 | 61.7 | 61.3 | 62.0 | 62.5 |
| 0.9 | 57.2 | 57.3 | 57.1 | 57.2 | 56.7 | 57.4 | 57.9 |
| 1.0 | 52.4 | 52.4 | 52.3 | 52.4 | 51.8 | 52.5 | 53.1 |
| 1.1 | 47.3 | 47.2 | 47.2 | 47.4 | 46.6 | 47.4 | 48.0 |
| 1.2 | 41.9 | 41.7 | 41.7 | 42.0 | 41.1 | 41.9 | 42.6 |
| 1.3 | 36.2 | 36.0 | 36.0 | 36.3 | 35.4 | 36.2 | 36.9 |
| 1.4 | 30.3 | 30.1 | 30.1 | 30.4 | 29.5 | 30.4 | 31.2 |
| 1.5 | 24.3 | 24.1 | 24.1 | 24.4 | 23.6 | 24.5 | 25.4 |
| 1.6 | 18.4 | 18.2 | 18.2 | 18.5 | 17.8 | 18.7 | 19.7 |
| 1.7 | 12.7 | 12.6 | 12.6 | 12.8 | 12.3 | 13.2 | 14.3 |
| 1.8 | 7.6 | 7.5 | 7.6 | 7.8 | 7.3 | 8.2 | 9.4 |
| 1.85 | 5.4 | 5.2 | 5.3 | 5.6 | 5.1 | 6.0 | 7.2 |
| 1.9 | | 3.2 | 3.4 | 3.7 | 3.1 | 4.0 | 5.3 |
| 1.95 | | | | | 1.4 | 2.2 | 3.6 |
| 2.0 | | | | | | 0.8 | 2.2 |

Table 22.  Apparent molar heat capacities of aqueous rare earth nitrate solutions at 25°C

| $m^{1/2}$ | $+\phi'_{cp}$ | | | | |
| --- | --- | --- | --- | --- | --- |
| | $La(NO_3)_3$ | $Nd(NO_3)_3$ | $Gd(NO_3)_3$ | $Er(NO_3)_3$ | $Lu(NO_3)_3$ |
| 0.3 | -47.9 | -44.5 | -40.3 | -40.3 | -48.5 |
| 0.4 | -40.4 | -37.3 | -34.1 | -35.8 | -38.7 |
| 0.5 | -32.8 | -30.1 | -27.9 | -30.3 | -30.8 |
| 0.6 | -25.1 | -23.0 | -21.6 | -24.0 | -23.9 |
| 0.7 | -17.5 | -16.0 | -15.4 | -17.2 | -17.3 |
| 0.8 | -10.1 | - 9.1 | - 9.2 | -10.0 | -10.5 |
| 0.9 | - 2.8 | - 2.4 | - 3.0 | - 2.8 | - 3.4 |
| 1.0 | 4.1 | 4.1 | 3.0 | 4.4 | 4.1 |
| 1.1 | 10.7 | 10.4 | 8.8 | 11.4 | 11.9 |
| 1.2 | 16.9 | 16.4 | 14.6 | 18.1 | 19.6 |
| 1.3 | 22.7 | 22.1 | 20.0 | 24.4 | 27.2 |
| 1.4 | 28.0 | 27.4 | 25.3 | 30.1 | 34.4 |
| 1.5 | 32.9 | 32.5 | 30.3 | 35.3 | 40.9 |
| 1.6 | 37.3 | 37.1 | 35.0 | 39.9 | 46.6 |
| 1.7 | 41.2 | 41.4 | 39.3 | 43.9 | 51.3 |
| 1.8 | 44.7 | 45.3 | 43.2 | 47.3 | 55.1 |
| 1.9 | 47.8 | 48.7 | 46.7 | 50.1 | 57.9 |
| 2.0 | 50.5 | 51.7 | 49.7 | 52.5 | 59.8 |
| 2.1 | 52.8 | 54.2 | 52.3 | 54.5 | 61.0 |
| 2.15 | 53.9 | 55.2 | | 55.4 | 61.4 |
| 2.2 | | | | 56.2 | 61.6 |
| 2.3 | | | | 57.7 | 61.9 |
| 2.4 | | | | | 62.0 |
| 2.5 | | | | | 62.0 |
| 2.6 | | | | | 62.1 |

Table 23. Apparent molar heat capacities of aqueous rare
earth perchlorate solutions at 25°C

| $m^{1/2}$ | $+\phi_{cp}$ | | | |
| | $La(ClO_4)_3$ | $Nd(ClO_4)_3$ | $Gd(ClO_4)_3$ | $Lu(ClO_4)_3$ |
|---|---|---|---|---|
| 0.3 | -27.5 | -29.3 | -20.4 | -18.6 |
| 0.4 | -21.1 | -22.4 | -14.3 | -12.4 |
| 0.5 | -15.3 | -16.0 | - 8.8 | - 6.6 |
| 0.6 | - 9.9 | -10.3 | - 3.8 | - 1.4 |
| 0.7 | - 4.9 | - 5.0 | 0.8 | 3.6 |
| 0.8 | - 0.3 | - 0.2 | 5.0 | 8.1 |
| 0.9 | 3.9 | 4.3 | 8.9 | 12.3 |
| 1.0 | 7.9 | 8.4 | 12.5 | 16.2 |
| 1.1 | 11.6 | 12.3 | 15.9 | 19.9 |
| 1.2 | 15.1 | 15.9 | 19.2 | 23.4 |
| 1.3 | 18.4 | 19.4 | 22.3 | 26.7 |
| 1.4 | 21.7 | 22.8 | 25.3 | 29.9 |
| 1.5 | 24.8 | 26.1 | 28.3 | 33.0 |
| 1.6 | 28.0 | 29.4 | 31.4 | 36.0 |
| 1.7 | 31.1 | 32.8 | 34.6 | 39.0 |
| 1.8 | 34.4 | 36.3 | 37.9 | 42.0 |
| 1.9 | 37.7 | 39.9 | 41.4 | 45.0 |
| 2.0 | 41.2 | 43.8 | 45.2 | 48.1 |
| 2.1 | 44.9 | 47.9 | 49.2 | 51.4 |
| 2.15 | 46.8 | 50.0 | 51.4 | 53.1 |

Table 24.  Partial molar heat capacities of aqueous rare
earth chloride solutions at 25°C

| | | | $\overline{C}_{p2}$ | | | |
|---|---|---|---|---|---|---|
| $m^{\frac{1}{2}}$ | $LaCl_3$[a] | $PrCl_3$ | $NdCl_3$[a] | $SmCl_3$ | $EuCl_3$ | $GdCl_3$ |
| 0.3 | -86.0 | -87.7 | -86.9 | -84.7 | -78.9 | -80.8 |
| 0.4 | -79.1 | -79.7 | -79.5 | -76.7 | -71.7 | -73.2 |
| 0.5 | -72.3 | -72.3 | -72.4 | -69.8 | -65.6 | -66.6 |
| 0.6 | -65.2 | -65.0 | -65.1 | -63.1 | -59.6 | -60.2 |
| 0.7 | -57.6 | -57.5 | -57.5 | -56.1 | -53.3 | -53.8 |
| 0.8 | -49.5 | -49.5 | -49.3 | -48.5 | -46.3 | -46.7 |
| 0.9 | -40.6 | -40.7 | -40.4 | -39.8 | -38.2 | -38.8 |
| 1.0 | -31.1 | -31.0 | -30.6 | -30.1 | -28.9 | -30.0 |
| 1.1 | -21.0 | -20.5 | -20.0 | -19.2 | -18.4 | -20.4 |
| 1.2 | -10.5 | - 9.3 | - 8.6 | - 7.4 | - 7.0 | -10.0 |
| 1.3 | 0.1 | 2.6 | 3.4 | 5.2 | 5.1 | 0.9 |
| 1.4 | 10.6 | 14.8 | 15.8 | 18.1 | 17.4 | 11.8 |
| 1.5 | 20.4 | 26.9 | 28.3 | 30.7 | 29.2 | 22.2 |
| 1.6 | 29.2 | 38.5 | 40.6 | 42.4 | 39.7 | 31.4 |
| 1.7 | 36.2 | 49.0 | 52.3 | 52.3 | 48.0 | 38.5 |
| 1.8 | 40.9 | 57.8 | 62.9 | 59.4 | 53.1 | 42.7 |
| 1.85 | 42.2 | 61.3 | 67.6 | 61.6 | 54.0 | 43.3 |
| 1.9 | 42.5 | 64.1 | 71.8 | 62.7 | | |
| 1.95 | 41.9 | 66.0 | 75.4 | | | |
| 2.0 | | | | | | |

[a]Determined by K. C. Jones (4).

Table 24. (Continued)

| | | | | $\bar{C}_{p2}$ | | | |
|---|---|---|---|---|---|---|---|
| $m^{1/2}$ | $TbCl_3$ | $DyCl_3{}^a$ | $HoCl_3$ | $ErCl_3{}^a$ | $TmCl_3$ | $YbCl_3{}^a$ | $LuCl_3$ |
| 0.3 | -76.7 | -76.8 | -77.0 | -76.3 | -76.3 | -76.8 | -77.1 |
| 0.4 | -69.4 | -70.0 | -69.5 | -69.3 | -69.5 | -70.2 | -70.7 |
| 0.5 | -63.1 | -63.7 | -63.0 | -63.1 | -63.2 | -64.0 | -64.6 |
| 0.6 | -57.0 | -57.5 | -56.8 | -57.2 | -56.9 | -57.8 | -58.4 |
| 0.7 | -50.7 | -51.0 | -50.5 | -50.9 | -50.3 | -51.2 | -51.8 |
| 0.8 | -43.9 | -43.8 | -43.6 | -44.1 | -43.1 | -44.0 | -44.6 |
| 0.9 | -36.3 | -35.9 | -36.0 | -36.5 | -35.2 | -36.1 | -36.7 |
| 1.0 | -27.8 | -27.3 | -27.5 | -27.9 | -26.6 | -27.4 | -28.1 |
| 1.1 | -18.5 | -17.9 | -18.2 | -18.6 | -17.2 | -18.1 | -19.0 |
| 1.2 | - 8.6 | - 8.0 | - 8.3 | - 8.6 | - 7.5 | - 8.4 | - 9.4 |
| 1.3 | 1.6 | 2.0 | 1.8 | 1.6 | 2.4 | 1.4 | 0.2 |
| 1.4 | 11.6 | 11.8 | 11.7 | 11.5 | 11.9 | 10.9 | 9.5 |
| 1.5 | 20.8 | 20.7 | 20.7 | 20.6 | 20.6 | 19.5 | 17.9 |
| 1.6 | 28.4 | 28.1 | 28.2 | 28.0 | 27.8 | 26.7 | 24.9 |
| 1.7 | 33.4 | 33.2 | 33.2 | 32.8 | 32.6 | 31.7 | 29.7 |
| 1.8 | 34.9 | 35.1 | 34.6 | 34.0 | 34.3 | 33.7 | 31.5 |
| 1.85 | 34.0 | 34.5 | 33.6 | 32.9 | 33.6 | 33.2 | 31.0 |
| 1.9 | | 32.7 | 31.3 | 30.4 | 31.8 | 31.7 | 29.4 |
| 1.95 | | | | | 28.5 | 28.8 | 26.6 |
| 2.0 | | | | | | 24.6 | 22.4 |

Table 25. Partial molar heat capacities of aqueous rare
earth nitrate solutions at 25°C

| $m^{1/2}$ | $\overline{C}_{p2}$ | | | | |
|---|---|---|---|---|---|
| | $La(NO_3)_3$ | $Nd(NO_3)_3$ | $Gd(NO_3)_3$ | $Er(NO_3)_3$ | $Lu(NO_3)_3$ |
| 0.3 | -36.8 | -33.7 | -31.0 | -34.5 | -31.5 |
| 0.4 | -25.3 | -22.9 | -21.6 | -25.7 | -21.4 |
| 0.5 | -13.6 | -12.2 | -12.2 | -15.4 | -12.8 |
| 0.6 | - 2.2 | - 1.8 | - 2.8 | - 4.2 | - 3.9 |
| 0.7 | 8.9 | 8.3 | 6.4 | 7.4 | 6.0 |
| 0.8 | 19.4 | 18.1 | 15.5 | 18.9 | 17.3 |
| 0.9 | 29.1 | 27.3 | 24.3 | 29.9 | 29.6 |
| 1.0 | 38.0 | 36.0 | 32.7 | 40.1 | 42.3 |
| 1.1 | 46.0 | 44.1 | 40.7 | 49.2 | 54.7 |
| 1.2 | 52.9 | 51.5 | 48.2 | 57.0 | 66.0 |
| 1.3 | 58.8 | 58.1 | 55.0 | 63.4 | 75.4 |
| 1.4 | 63.7 | 63.9 | 61.2 | 68.4 | 82.4 |
| 1.5 | 67.6 | 68.9 | 66.5 | 72.0 | 86.8 |
| 1.6 | 70.6 | 72.9 | 70.9 | 74.2 | 88.5 |
| 1.7 | 72.8 | 76.0 | 74.4 | 75.3 | 87.6 |
| 1.8 | 74.2 | 78.0 | 76.7 | 75.4 | 84.6 |
| 1.9 | 75.1 | 79.0 | 77.9 | 74.9 | 80.2 |
| 2.0 | 75.6 | 79.0 | 77.7 | 74.1 | 75.1 |
| 2.1 | 75.9 | 77.8 | 76.1 | 73.5 | 70.1 |
| 2.15 | 76.1 | 76.8 | | 73.4 | 67.9 |
| 2.2 | | | | 73.6 | 66.0 |
| 2.3 | | | | 75.0 | 63.4 |
| 2.4 | | | | | 62.5 |
| 2.5 | | | | | 62.8 |
| 2.6 | | | | | 63.2 |

Table 26.  Partial molar heat capacities of aqueous rare
earth perchlorate solutions at 25°C

| $m^{1/2}$ | $\overline{C}_{p2}$ | | | |
| | $La(ClO_4)_3$ | $Nd(ClO_4)_3$ | $Gd(ClO_4)_3$ | $Lu(ClO_4)_3$ |
|---|---|---|---|---|
| 0.3 | -17.6 | -18.4 | -10.9 | - 8.9 |
| 0.4 | - 8.9 | - 9.2 | - 2.8 | - 0.5 |
| 0.5 | - 1.2 | - 1.0 | 4.3 | 7.1 |
| 0.6 | 5.6 | 6.3 | 10.6 | 13.9 |
| 0.7 | 11.8 | 12.7 | 16.2 | 20.0 |
| 0.8 | 17.3 | 18.4 | 21.2 | 25.6 |
| 0.9 | 22.3 | 23.6 | 25.8 | 30.6 |
| 1.0 | 27.0 | 28.4 | 30.0 | 35.3 |
| 1.1 | 31.4 | 32.9 | 34.1 | 39.6 |
| 1.2 | 35.6 | 37.3 | 38.1 | 43.7 |
| 1.3 | 39.8 | 41.6 | 42.2 | 47.7 |
| 1.4 | 44.0 | 46.1 | 46.5 | 51.7 |
| 1.5 | 48.4 | 50.9 | 51.2 | 55.7 |
| 1.6 | 53.1 | 56.1 | 56.3 | 59.9 |
| 1.7 | 58.2 | 61.8 | 62.0 | 64.3 |
| 1.8 | 63.8 | 68.2 | 68.5 | 69.1 |
| 1.9 | 70.0 | 75.4 | 75.8 | 74.3 |
| 2.0 | 77.0 | 83.5 | 84.1 | 80.1 |
| 2.1 | 84.8 | 92.8 | 93.6 | 86.4 |
| 2.15 | 89.0 | 97.8 | 98.8 | 89.9 |

Table 27.   Partial molar heat capacities of aqueous rare
earth chloride solutions at 25°C

| $m^{1/2}$ | $\overline{C}_{p1}$ | | | |
|---|---|---|---|---|
| | $LaCl_3$[a] | $PrCl_3$ | $NdCl_3$[a] | $SmCl_3$ |
| 0.3 | 17.983 | 17.980 | 17.982 | 17.978 |
| 0.4 | 17.968 | 17.962 | 17.966 | 17.961 |
| 0.5 | 17.943 | 17.935 | 17.940 | 17.935 |
| 0.6 | 17.904 | 17.895 | 17.900 | 17.899 |
| 0.7 | 17.846 | 17.838 | 17.842 | 17.846 |
| 0.8 | 17.764 | 17.756 | 17.758 | 17.768 |
| 0.9 | 17.648 | 17.641 | 17.641 | 17.655 |
| 1.0 | 17.493 | 17.484 | 17.482 | 17.496 |
| 1.1 | 17.292 | 17.275 | 17.271 | 17.280 |
| 1.2 | 17.042 | 17.006 | 17.000 | 16.997 |
| 1.3 | 16.742 | 16.672 | 16.663 | 16.642 |
| 1.4 | 16.398 | 16.272 | 16.256 | 16.220 |
| 1.5 | 16.026 | 15.813 | 15.781 | 15.742 |
| 1.6 | 15.648 | 15.311 | 15.248 | 15.237 |
| 1.7 | 15.303 | 14.796 | 14.674 | 14.752 |
| 1.8 | 15.045 | 14.312 | 14.091 | 14.359 |
| 1.85 | 14.970 | 14.102 | 13.810 | 14.228 |
| 1.9 | 14.947 | 13.926 | 13.543 | 14.159 |
| 1.95 | 14.987 | 13.796 | 13.301 | |
| 2.0 | | | | |

[a]Determined by K. C. Jones (4).

Table 27.  (Continued)

| $m^{1/2}$ | $\overline{C}_{p1}$ | | | |
| --- | --- | --- | --- | --- |
| | $EuCl_3$ | $GdCl_3$ | $TbCl_3$ | $DyCl_3$ [a] |
| 0.3 | 17.980 | 17.979 | 17.980 | 17.982 |
| 0.4 | 17.964 | 17.962 | 17.964 | 17.966 |
| 0.5 | 17.941 | 17.938 | 17.940 | 17.944 |
| 0.6 | 17.909 | 17.904 | 17.907 | 17.910 |
| 0.7 | 17.861 | 17.854 | 17.860 | 17.860 |
| 0.8 | 17.789 | 17.782 | 17.790 | 17.787 |
| 0.9 | 17.683 | 17.680 | 17.690 | 17.684 |
| 1.0 | 17.531 | 17.536 | 17.552 | 17.543 |
| 1.1 | 17.323 | 17.344 | 17.367 | 17.356 |
| 1.2 | 17.050 | 17.095 | 17.130 | 17.121 |
| 1.3 | 16.710 | 16.789 | 16.843 | 16.838 |
| 1.4 | 16.307 | 16.430 | 16.515 | 16.518 |
| 1.5 | 15.861 | 16.037 | 16.168 | 16.180 |
| 1.6 | 15.406 | 15.641 | 15.842 | 15.859 |
| 1.7 | 14.998 | 15.292 | 15.595 | 15.610 |
| 1.8 | 14.721 | 15.064 | 15.514 | 15.508 |
| 1.85 | 14.667 | 15.028 | 15.570 | 15.544 |
| 1.9 | | | | 15.658 |
| 1.95 | | | | |
| 2.0 | | | | |

Table 27.  (Continued)

| | | | $\overline{C}_{p1}$ | | |
|---|---|---|---|---|---|
| $m^{1/2}$ | $HoCl_3$ | $ErCl_3{}^a$ | $TmCl_3$ | $YbCl_3{}^a$ | $LuCl_3$ |
| 0.3 | 17.979 | 17.980 | 17.982 | 17.983 | 17.983 |
| 0.4 | 17.963 | 17.965 | 17.967 | 17.968 | 17.969 |
| 0.5 | 17.939 | 17.942 | 17.944 | 17.946 | 17.947 |
| 0.6 | 17.906 | 17.910 | 17.910 | 17.911 | 17.913 |
| 0.7 | 17.857 | 17.862 | 17.859 | 17.861 | 17.862 |
| 0.8 | 17.787 | 17.793 | 17.786 | 17.788 | 17.789 |
| 0.9 | 17.687 | 17.693 | 17.682 | 17.684 | 17.686 |
| 1.0 | 17.549 | 17.554 | 17.541 | 17.543 | 17.546 |
| 1.1 | 17.364 | 17.368 | 17.356 | 17.359 | 17.363 |
| 1.2 | 17.129 | 17.130 | 17.124 | 17.127 | 17.136 |
| 1.3 | 16.843 | 16.844 | 16.846 | 16.851 | 16.864 |
| 1.4 | 16.518 | 16.517 | 16.532 | 16.539 | 16.560 |
| 1.5 | 16.176 | 16.174 | 16.203 | 16.211 | 16.241 |
| 1.6 | 15.854 | 15.855 | 15.894 | 15.900 | 15.940 |
| 1.7 | 15.612 | 15.619 | 15.657 | 15.656 | 15.705 |
| 1.8 | 15.536 | 15.555 | 15.568 | 15.550 | 15.607 |
| 1.85 | 15.596 | 15.623 | 15.609 | 15.578 | 15.637 |
| 1.9 | 15.743 | 15.781 | 15.728 | 15.678 | 15.738 |
| 1.95 | | | 15.942 | 15.869 | 15.927 |
| 2.0 | | | | 16.168 | 16.222 |

Table 28. Partial molar heat capacities of aqueous rare
earth nitrate solutions at 25°C

| | $\overline{C}_{p1}$ | | | | |
|---|---|---|---|---|---|
| $m^{1/2}$ | $La(NO_3)_3$ | $Nd(NO_3)_3$ | $Gd(NO_3)_3$ | $Er(NO_3)_3$ | $Lu(NO_3)_3$ |
| 0.3 | 17.978 | 17.978 | 17.980 | 17.986 | 17.968 |
| 0.4 | 17.952 | 17.954 | 17.960 | 17.966 | 17.946 |
| 0.5 | 17.909 | 17.915 | 17.925 | 17.929 | 17.914 |
| 0.6 | 17.847 | 17.858 | 17.874 | 17.867 | 17.866 |
| 0.7 | 17.762 | 17.781 | 17.803 | 17.779 | 17.790 |
| 0.8 | 17.656 | 17.682 | 17.711 | 17.662 | 17.675 |
| 0.9 | 17.530 | 17.562 | 17.597 | 17.519 | 17.514 |
| 1.0 | 17.385 | 17.420 | 17.460 | 17.354 | 17.307 |
| 1.1 | 17.227 | 17.260 | 17.301 | 17.173 | 17.062 |
| 1.2 | 17.062 | 17.084 | 17.123 | 16.987 | 16.794 |
| 1.3 | 16.895 | 16.898 | 16.931 | 16.806 | 16.530 |
| 1.4 | 16.734 | 16.707 | 16.729 | 16.643 | 16.299 |
| 1.5 | 16.587 | 16.520 | 16.528 | 16.509 | 16.133 |
| 1.6 | 16.458 | 16.346 | 16.336 | 16.412 | 16.063 |
| 1.7 | 16.353 | 16.196 | 16.167 | 16.361 | 16.107 |
| 1.8 | 16.275 | 16.083 | 16.038 | 16.354 | 16.273 |
| 1.9 | 16.221 | 16.021 | 15.968 | 16.386 | 16.547 |
| 2.0 | 16.186 | 16.027 | 15.980 | 16.439 | 16.897 |
| 2.1 | 16.160 | 16.118 | 16.100 | 16.484 | 17.273 |
| 2.15 | 16.144 | 16.201 | | 16.491 | 17.450 |
| 2.2 | | | | 16.476 | 17.610 |
| 2.3 | | | | 16.352 | 17.846 |
| 2.4 | | | | | 17.941 |
| 2.5 | | | | | 17.908 |
| 2.6 | | | | | 17.860 |

Table 29.  Partial molar heat capacities of aqueous rare
earth perchlorate solutions at 25°C

| $m^{1/2}$ | $\overline{C}_{p1}$ | | | |
| | $La(ClO_4)_3$ | $Nd(ClO_4)_3$ | $Gd(ClO_4)_3$ | $Lu(ClO_4)_3$ |
|---|---|---|---|---|
| 0.3 | 17.979 | 17.978 | 17.980 | 17.980 |
| 0.4 | 17.960 | 17.957 | 17.962 | 17.961 |
| 0.5 | 17.932 | 17.928 | 17.936 | 17.934 |
| 0.6 | 17.895 | 17.888 | 17.902 | 17.896 |
| 0.7 | 17.848 | 17.839 | 17.860 | 17.850 |
| 0.8 | 17.792 | 17.781 | 17.809 | 17.794 |
| 0.9 | 17.727 | 17.714 | 17.750 | 17.728 |
| 1.0 | 17.651 | 17.636 | 17.681 | 17.653 |
| 1.1 | 17.564 | 17.547 | 17.600 | 17.567 |
| 1.2 | 17.463 | 17.442 | 17.504 | 17.469 |
| 1.3 | 17.346 | 17.320 | 17.388 | 17.356 |
| 1.4 | 17.206 | 17.172 | 17.247 | 17.226 |
| 1.5 | 17.039 | 16.991 | 17.070 | 17.073 |
| 1.6 | 16.836 | 16.766 | 16.848 | 16.892 |
| 1.7 | 16.585 | 16.486 | 16.567 | 16.674 |
| 1.8 | 16.276 | 16.133 | 16.210 | 16.410 |
| 1.9 | 15.892 | 15.688 | 15.757 | 16.088 |
| 2.0 | 15.414 | 15.129 | 15.186 | 15.695 |
| 2.1 | 14.823 | 14.429 | 14.470 | 15.213 |
| 2.15 | 14.478 | 14.016 | 14.047 | 14.932 |

Table 30. Coefficients from least squares fits of apparent molal heat capacity versus square root of molality of aqueous rare earth chlorides, nitrates and perchlorates at 25°C

| Salt | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $A_4$ |
|---|---|---|---|---|---|
| LaCl$_3$[a] | -111.349 | 71.2191 | - 52.4529 | 44.7680 | - 11.2039 |
| PrCl$_3$ | -121.817 | 102.448 | - 87.6668 | 60.8124 | - 13.1959 |
| NdCl$_3$[a] | -115.069 | 80.1360 | - 59.0444 | 44.6258 | - 9.73198 |
| SmCl$_3$ | -123.684 | 126.191 | -129.562 | 88.6098 | - 19.3688 |
| EuCl$_3$ | -115.999 | 123.889 | -136.416 | 95.1106 | - 21.2164 |
| GdCl$_3$ | -118.024 | 120.092 | -122.232 | 83.1823 | - 18.5525 |
| TbCl$_3$ | -112.962 | 118.150 | -123.507 | 85.5140 | - 19.6105 |
| DyCl$_3$[a] | -107.702 | 97.0327 | - 94.9199 | 69.7377 | - 16.5392 |
| HoCl$_3$ | -113.764 | 119.462 | -123.546 | 85.0621 | - 19.4911 |
| ErCl$_3$[a] | -110.930 | 112.856 | -118.806 | 83.8887 | - 19.4660 |
| TmCl$_3$ | -106.284 | 93.0684 | - 88.8468 | 66.1776 | - 15.8716 |
| YbCl$_3$[a] | -104.836 | 85.8065 | - 79.7611 | 61.0751 | - 14.8224 |

[a]Data of K. C. Jones (4).

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Table 30. (Continued)

| Salt | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $A_4$ |
|---|---|---|---|---|---|
| $LuCl_3$ | -103.665 | 80.1594 | - 72.5455 | 57.0143 | - 14.0479 |
| $La(ClO_4)_3$ | - 50.1801 | 85.2638 | - 34.6529 | 7.43040 | |
| $Nd(ClO_4)_3$ | - 54.1563 | 94.3404 | - 40.8012 | 9.05382 | |
| $Gd(ClO_4)_3$ | - 42.2177 | 83.2694 | - 37.2393 | 8.72292 | |
| $Lu(ClO_4)_3$ | - 40.3633 | 81.3709 | - 30.9580 | 6.19899 | |
| $La(NO_3)_3$ | - 68.3906 | 60.3704 | 33.2025 | - 25.3240 | 4.24424 |
| $Nd(NO_3)_3$ | - 65.8295 | 69.7385 | 7.02587 | - 7.41643 | 0.577240 |
| $Gd(NO_3)_3$ | - 58.4257 | 58.6040 | 7.17477 | - 4.03456 | - 0.341266 |
| $Er(NO_3)_3$ | - 44.4499 | - 15.8027 | 116.711 | - 61.7769 | 9.74630 |
| $Lu(NO_3)_3$[b] | -108.276 | 324.542 | -576.936 | 622.654 | -335.504 |

$(A_5 = 86.1295, \quad A_6 = -8.47733)$

[b] Note that a fit of order six was used for $Lu(NO_3)_3$.

30 and in Figures 4 through 10. In Figures 4 and 5, specific heat capacities of the rare earth chlorides, nitrates and perchlorates are plotted versus molality. Figures 6 through 11 represent apparent and partial molar heat capacities against square root of molality. Specific heat capacity is cal $gm^{-1}deg$ $C^{-1}$ and apparent and partial molar heat capacities are cal $mole^{-1}deg$ $C^{-1}$ where cal is defined calories (one calorie = 4.1840 absolute joules).

## C. Error Analysis

Since $\phi_{cp}$ is a function of the two measurable quantities $S_p$ and molality, errors in either of them cause error in $\phi_{cp}$. Also, errors in $S_p$ and m are independent of each other. The principle of propagation of precision indices (32) predicts the probable error in $\phi_{cp}$ ($P_{\phi_{cp}}$) to be given by the equation

$$(P_{\phi_{cp}})^2 = \left(\frac{\partial \phi_{cp}}{\partial m}\right)^2 (P_m)^2 + \left(\frac{\partial \phi_{cp}}{\partial S_p}\right)^2 (P_s)^2$$

$$(5.4)$$

where $P_m$ and $P_s$ are the probable errors in molality and specific heat capacity, respectively. In conjunction with Equation 2.18, Equation 5.4 becomes

$$(P_{\phi_{cp}})^2 = \left(\frac{1000(S_p^o - S_p)}{m^2}\right)^2 (P_m)^2$$

$$+ \left(\frac{1000}{m} + M_2\right)^2 (P_s)^2 \qquad (5.5)$$
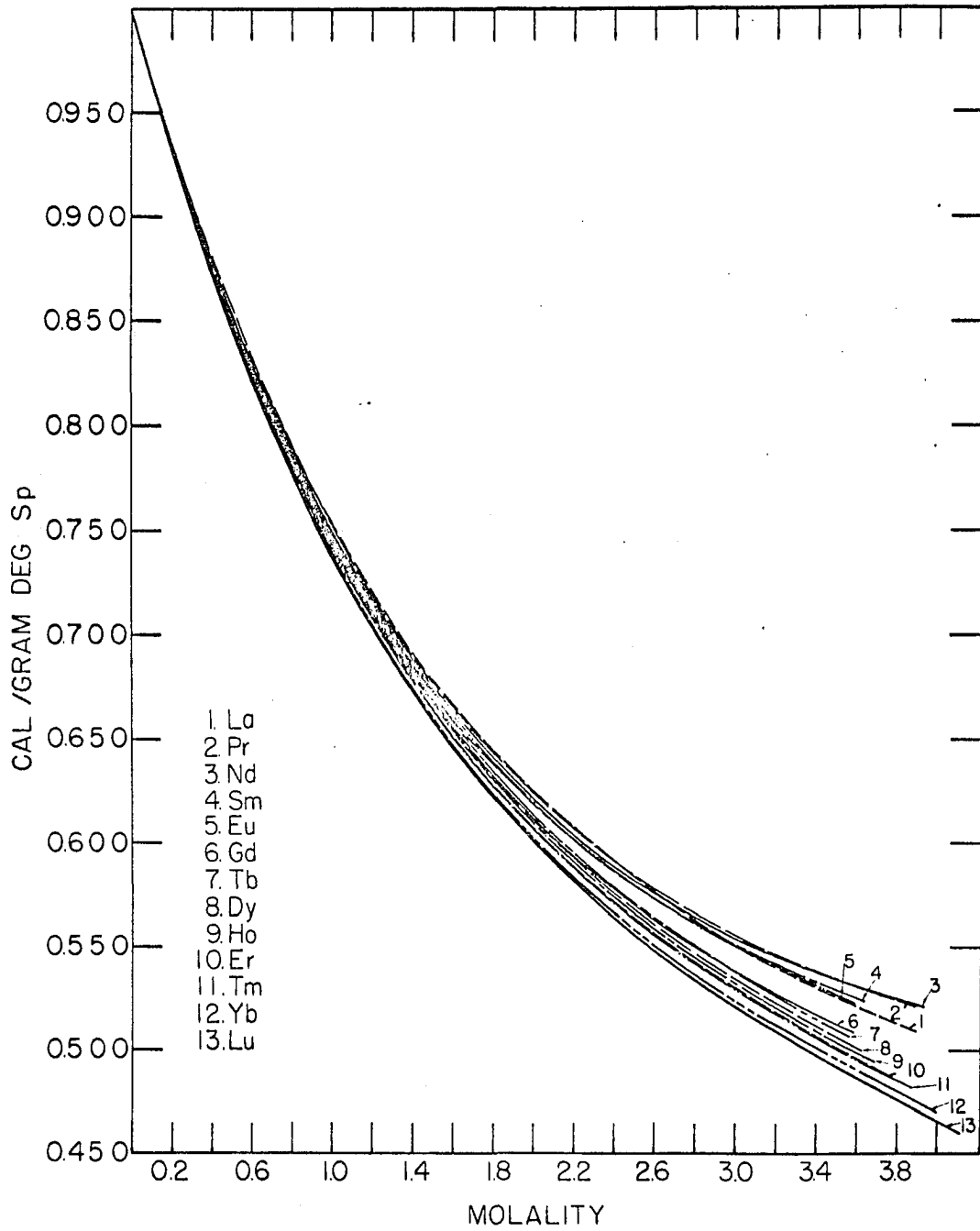
Figure 4. Specific heat capacities of some aqueous rare earth chloride solutions at 25°C
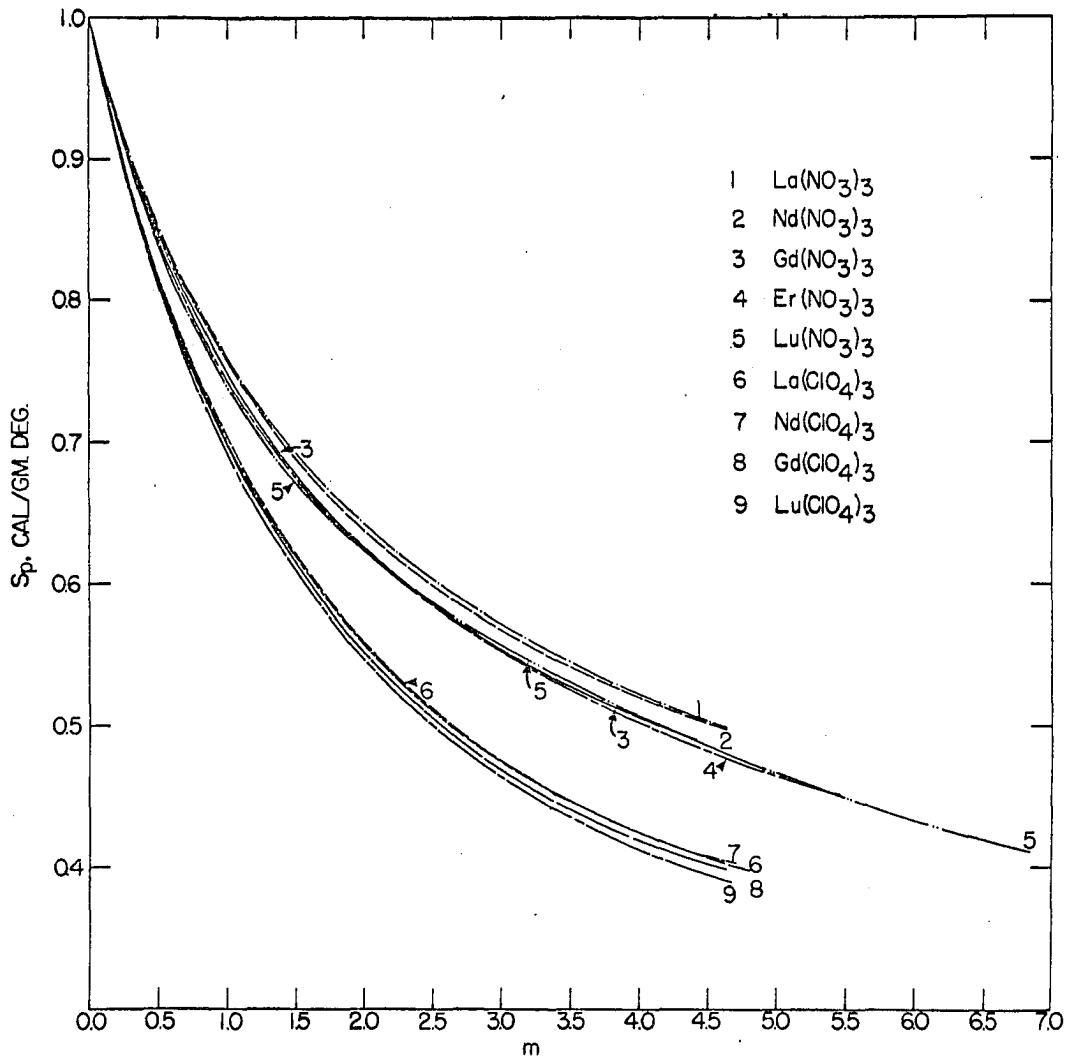
Figure 5. Specific heat capacities of some aqueous rare earth nitrate and perchlorate solutions at 25°C
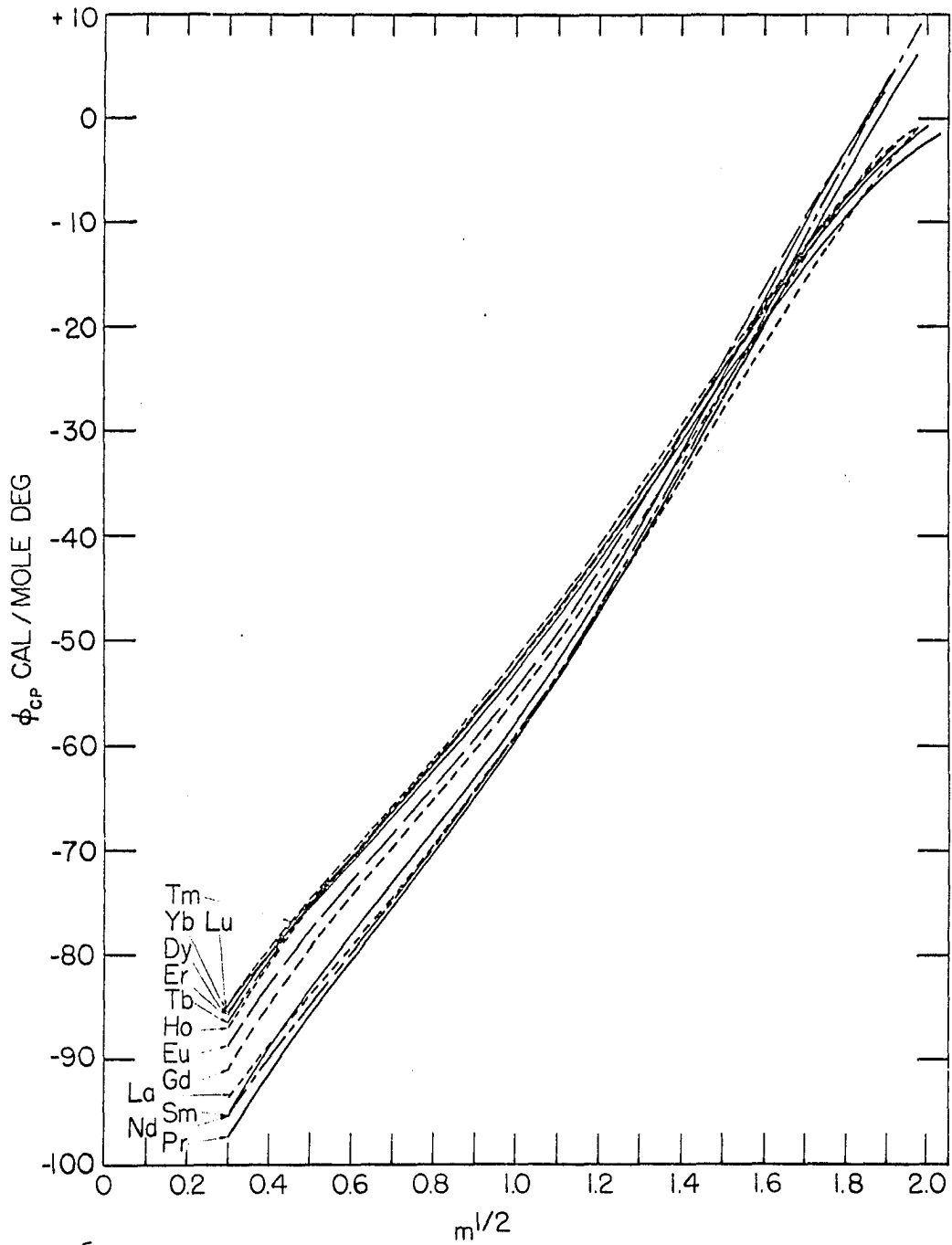
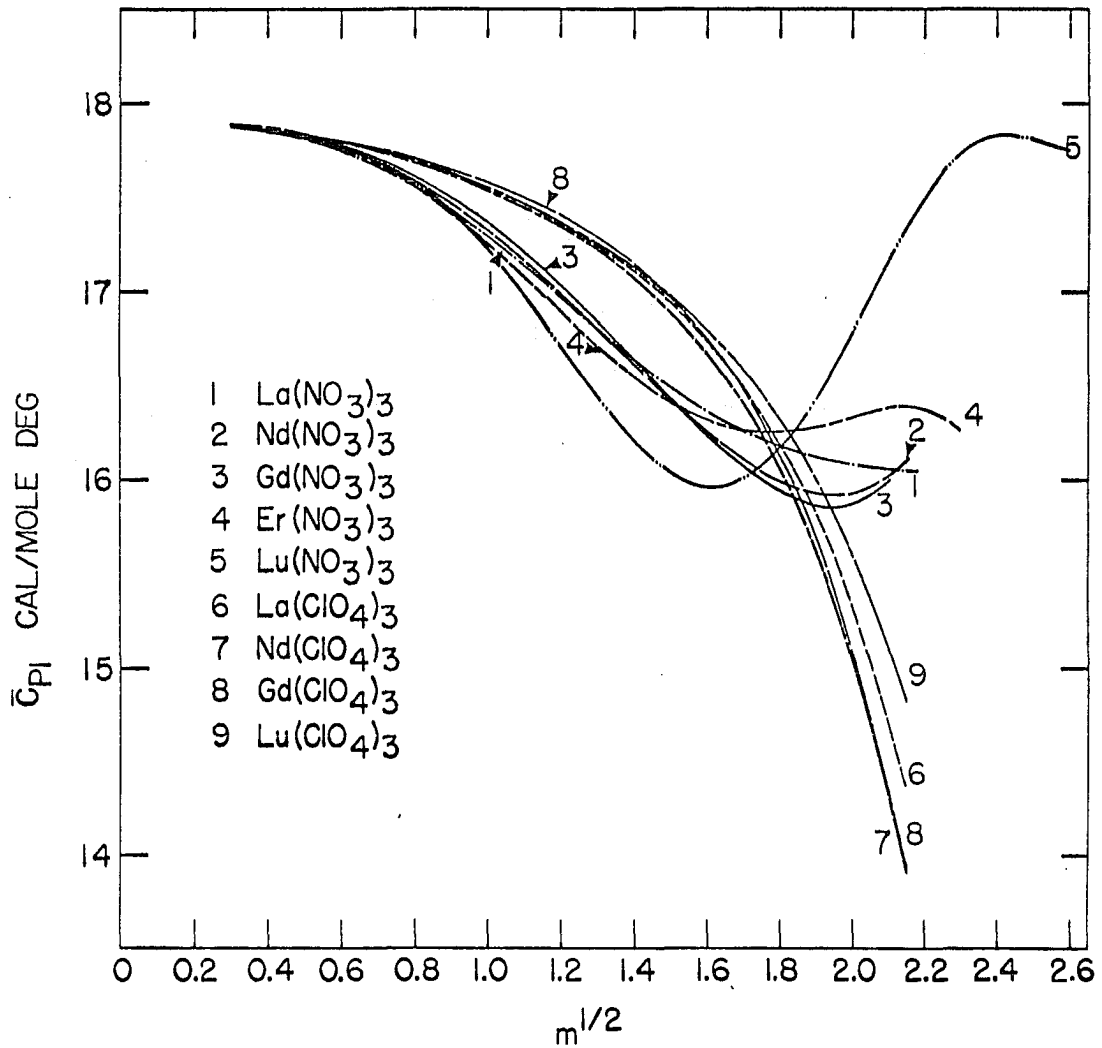Figure 6.  Apparent molar heat capacities of some aqueous rare earth chloride solutions at 25°C
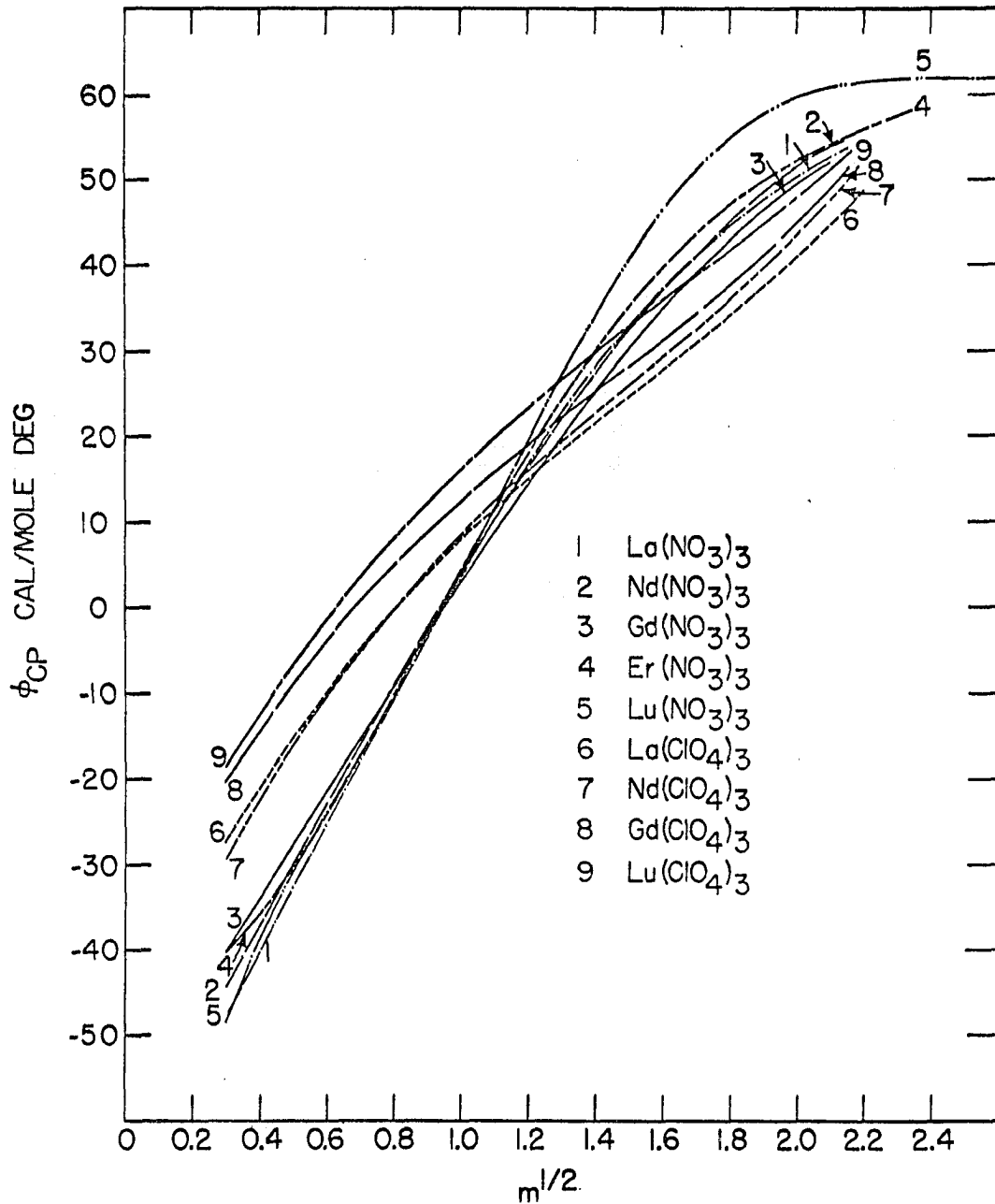
Figure 7. Apparent molar heat capacities of some aqueous rare earth nitrate and perchlorate solutions at 25°C
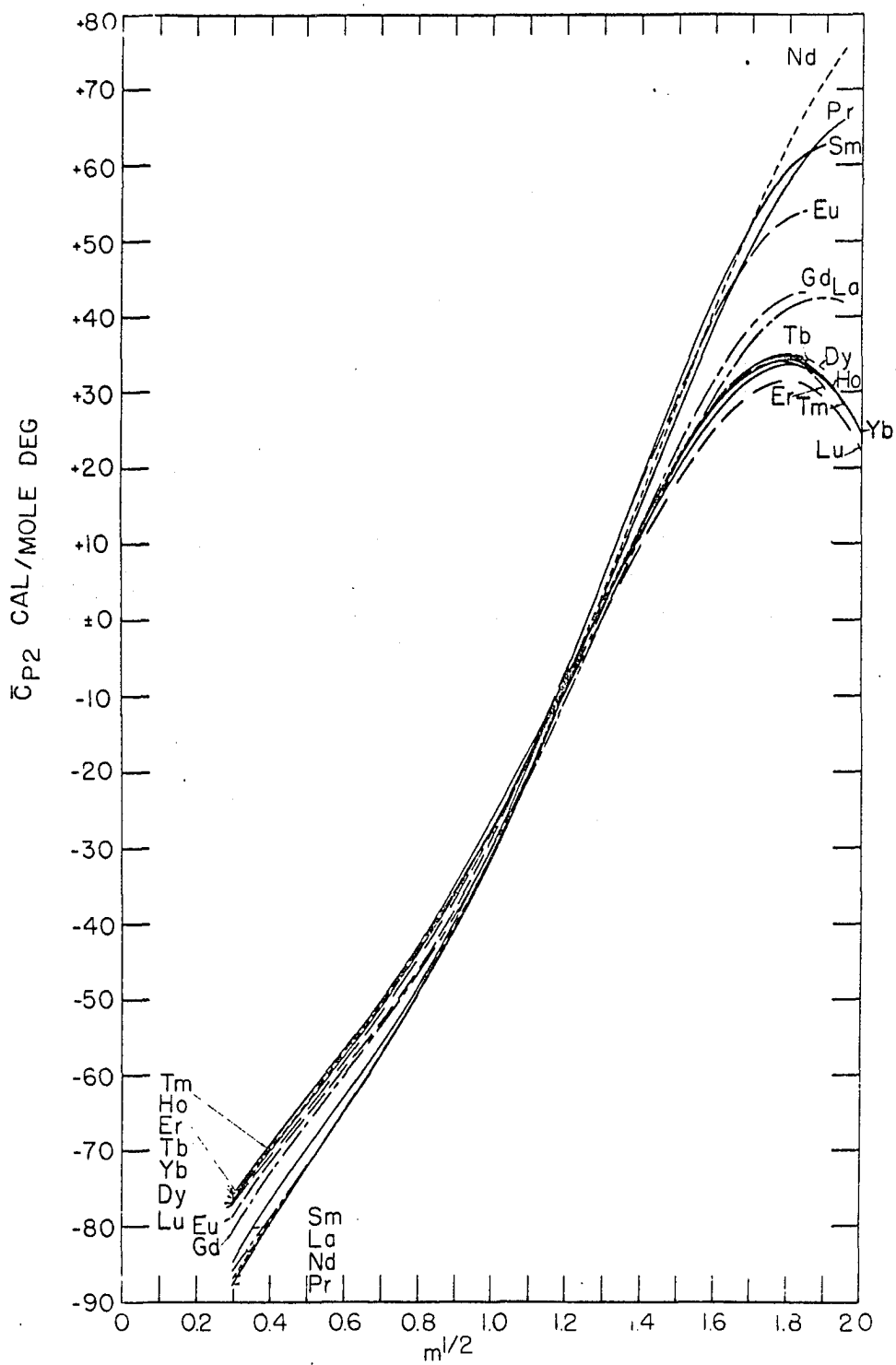
Figure 8. Partial molar heat capacities of the solute for some aqueous rare earth chloride solutions at 25°C
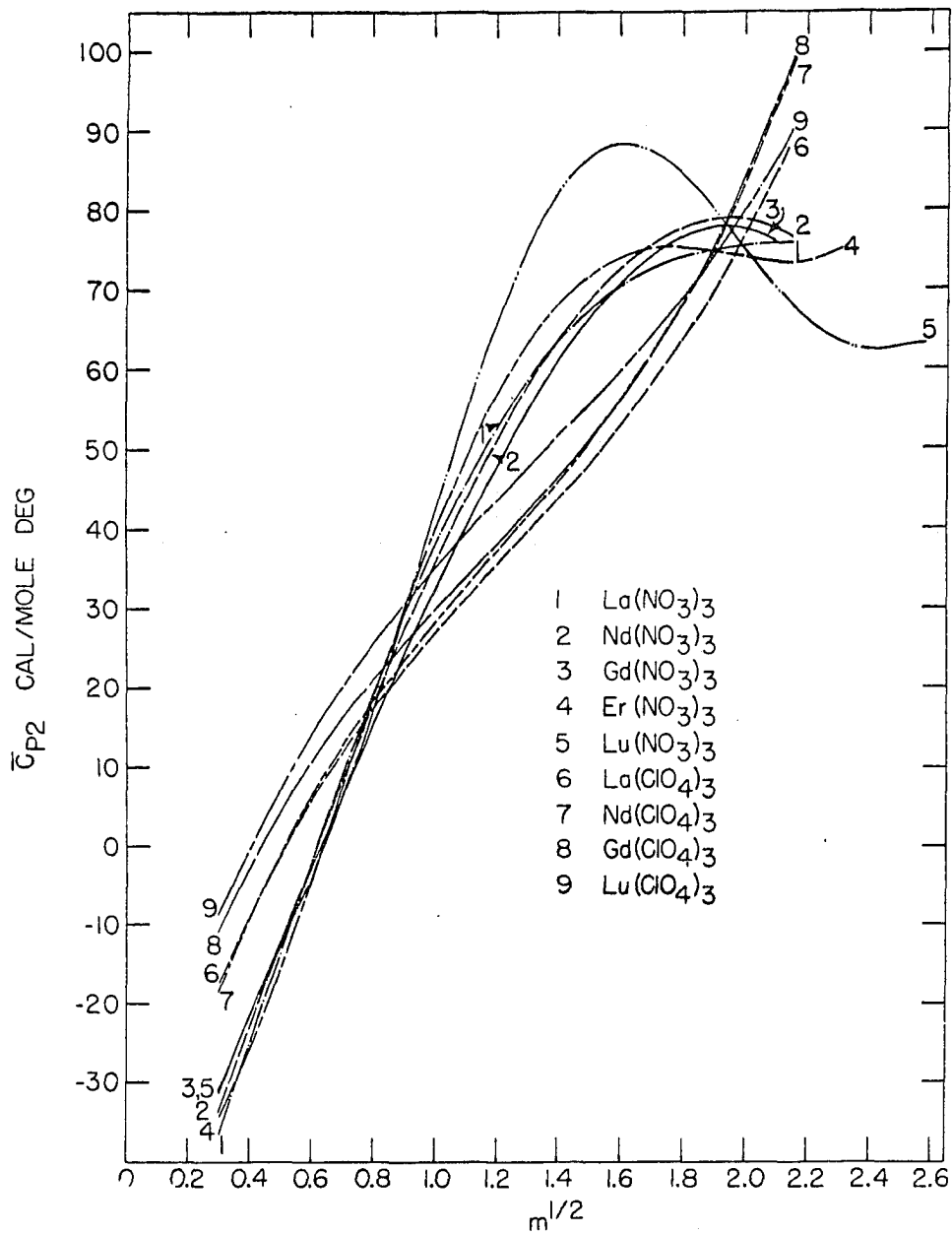
Figure 9. Partial molar heat capacities of the solute for some aqueous rare earth nitrate and perchlorate solutions at 25°C
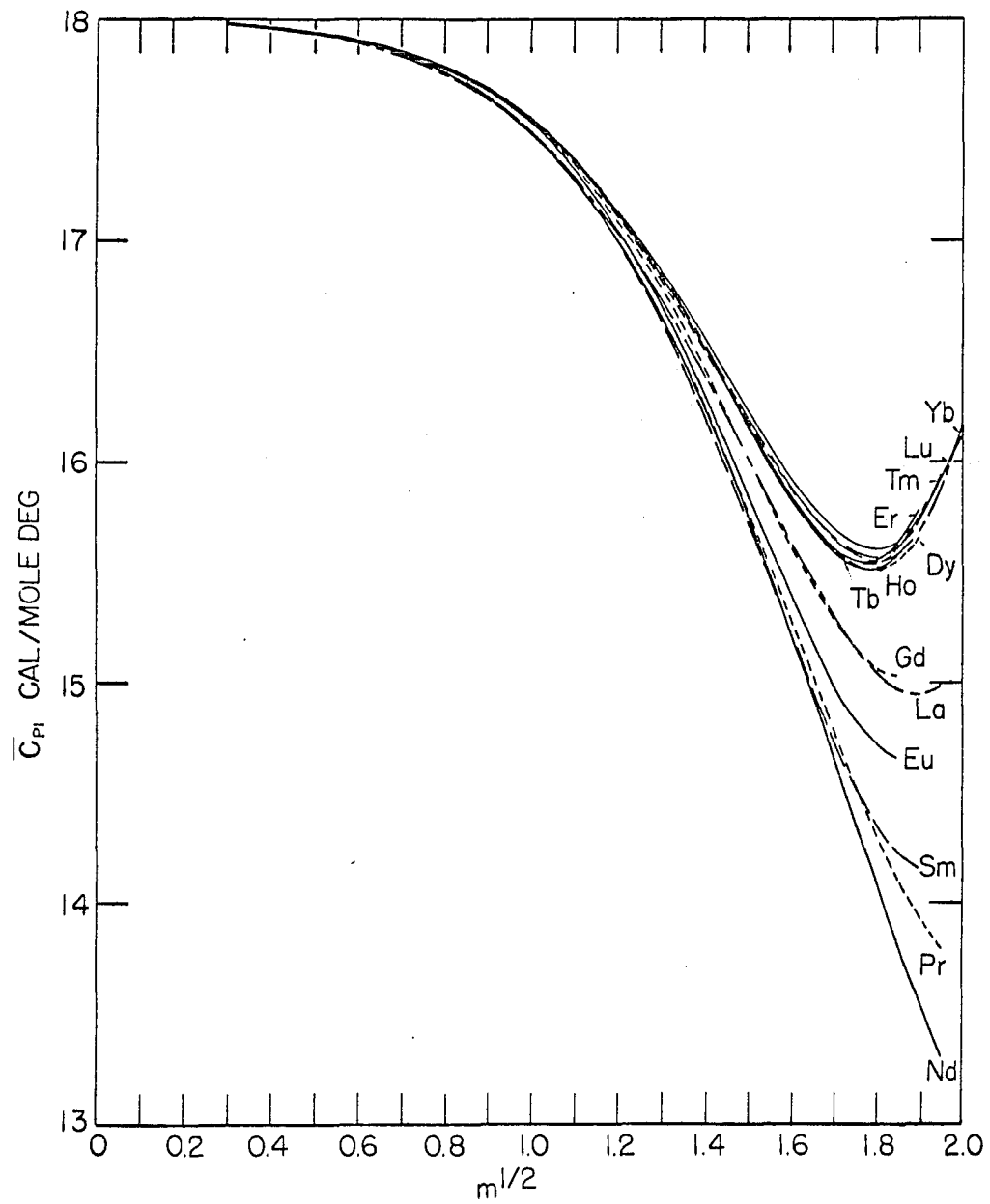
Figure 10. Partial molar heat capacities of the solvent for some aqueous rare earth chloride solutions at 25°C

Figure 11. Partial molar heat capacities of the solvent
for some aqueous rare earth nitrate and
perchlorate solutions at 25°C

$P_m$ is estimated to be 0.1% or less of molality while $P_s$ is assumed to be 0.0005 cal gm$^{-1}$deg C$^{-1}$ or less. The examples of GdCl$_3$, Gd(ClO$_4$)$_3$ and Gd(NO$_3$)$_3$ are shown in Table 31. It is obvious that the major source of uncertainty in $\phi_{cp}$ is uncertainty in $S_p$.

For the partial molar quantities $\overline{C}_{p2}$ and $\overline{C}_{p1}$, which involve a derivative term of $\phi_{cp}$, it is difficult to make a quantitative statement about errors. However, since uncertainty in slope of a least squares fit increases near the upper and lower ends of the data, there will be more uncertainty in the derivative of $\phi_{cp}$ in these regions. Consequently, the accuracies of both of the partial molar quantities drop at the high concentration end of the data. Because they must approach the known value of $\overline{C}_{p1}^{0}$ in Equation 5.2 as solute concentration becomes zero, experimental values of $\overline{C}_{p1}$ are fairly accurate at the lower end of the data. Experimental values of $\overline{C}_{p2}$ decrease in accuracy at the dilute end of the data since both $\phi_{cp}$ and its derivative become more uncertain there.

Table 31. Probable error in apparent molal heat capacity of gadolinium chloride, perchlorate, and nitrate solutions

| m | $m^{\frac{1}{2}}$ | $GdCl_3$ | | | $Gd(ClO_4)_3$ | | | $Gd(NO_3)_3$ | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $\left(\dfrac{\partial \phi_{cp}}{\partial m}\right)P_m$ | $\left(\dfrac{\partial \phi_{cp}}{\partial S_p}\right)P_s$ | $P_{\phi_{cp}}$ | $\left(\dfrac{\partial \phi_{cp}}{\partial m}\right)P_m$ | $\left(\dfrac{\partial \phi_{cp}}{\partial S_p}\right)P_s$ | $P_{\phi_{cp}}$ | $\left(\dfrac{\partial \phi_{cp}}{\partial m}\right)P_m$ | $\left(\dfrac{\partial \phi_{cp}}{\partial S_p}\right)P_s$ | $P_{\phi_{cp}}$ |
| 0.09 | 0.3 | 0.34 | 5.68 | 5.7 | 0.45 | 5.78 | 5.8 | 0.37 | 5.72 | 5.7 |
| 0.16 | 0.4 | 0.33 | 3.26 | 3.3 | 0.44 | 3.35 | 3.4 | 0.35 | 3.30 | 3.3 |
| 0.25 | 0.5 | 0.32 | 2.13 | 2.2 | 0.42 | 2.23 | 2.3 | 0.34 | 2.17 | 2.2 |
| 0.36 | 0.6 | 0.31 | 1.52 | 1.6 | 0.40 | 1.62 | 1.7 | 0.32 | 1.56 | 1.6 |
| 0.49 | 0.7 | 0.30 | 1.15 | 1.2 | 0.37 | 1.25 | 1.3 | 0.31 | 1.19 | 1.2 |
| 0.64 | 0.8 | 0.28 | 0.91 | 1.0 | 0.35 | 1.01 | 1.1 | 0.29 | 0.95 | 1.0 |
| 0.81 | 0.9 | 0.27 | 0.75 | 0.8 | 0.32 | 0.84 | 0.9 | 0.27 | 0.79 | 0.8 |
| 1.00 | 1.0 | 0.25 | 0.63 | 0.7 | 0.30 | 0.73 | 0.8 | 0.25 | 0.67 | 0.7 |
| 1.21 | 1.1 | 0.24 | 0.54 | 0.6 | 0.28 | 0.64 | 0.7 | 0.24 | 0.58 | 0.6 |
| 1.44 | 1.2 | 0.22 | 0.48 | 0.5 | 0.26 | 0.58 | 0.6 | 0.22 | 0.52 | 0.6 |
| 1.69 | 1.3 | 0.21 | 0.43 | 0.5 | 0.24 | 0.52 | 0.6 | 0.20 | 0.47 | 0.5 |
| 1.96 | 1.4 | 0.20 | 0.39 | 0.4 | 0.23 | 0.48 | 0.5 | 0.19 | 0.43 | 0.5 |
| 2.25 | 1.5 | 0.19 | 0.35 | 0.4 | 0.21 | 0.45 | 0.5 | 0.18 | 0.40 | 0.4 |
| 2.56 | 1.6 | 0.17 | 0.33 | 0.4 | 0.20 | 0.42 | 0.5 | 0.16 | 0.37 | 0.4 |
| 2.89 | 1.7 | 0.16 | 0.30 | 0.4 | 0.18 | 0.40 | 0.4 | 0.15 | 0.34 | 0.4 |
| 3.24 | 1.8 | 0.15 | 0.29 | 0.3 | 0.17 | 0.38 | 0.4 | 0.14 | 0.33 | 0.4 |
| 3.61 | 1.9 | 0.14 | 0.27 | 0.3 | 0.16 | 0.37 | 0.4 | 0.13 | 0.31 | 0.3 |
| 4.00 | 2.0 | | | | 0.15 | 0.35 | 0.4 | 0.12 | 0.30 | 0.3 |
| 4.41 | 2.1 | | | | 0.14 | 0.34 | 0.4 | 0.12 | 0.28 | 0.3 |

## VI.  DISCUSSION

Most dilute aqueous salt solutions, including those of the rare earths in this work, have negative apparent molar heat capacities.  This can be attributed to the breakdown of the structure of water and the restriction of some of the rotational degrees of freedom of water as it is strongly oriented in the first hydration sphere of the metal cation. The rare earth ions, having high charge densities, hydrate very strongly and consequently have quite negative $\phi_{cp}$'s in dilute solution.  In solutions of higher concentration the heat capacity of the rare earth solute will become more important, thus $\phi_{cp}$ is more positive in nature there.

From the data of this work it is noted that the $\phi_{cp}$'s of the rare earth salts, in the concentration range less than 1.5 molal, are in the order $ClO_4^- > NO_3^- > Cl^-$ with $Cl^-$ most negative.  This is in agreement with the heat capacity data of Randall and Rossini for NaCl and $NaNO_3$ (30) and the data of Ferrer for $NaClO_4$ (33).  This order is to be expected as perchlorate ion has more internal vibrational degrees of freedom than nitrate while chloride has none.

Jekel et al. (34) have measured the heat of solution of anhydrous $GdCl_3$ as a function of temperature and extrapolated to infinite dilution from about $4 \times 10^{-4}$ molal.  From these results they have derived $\phi_{cp}$ of $GdCl_3$ at infinite dilution and found $-104 \pm 5$ cal mole$^{-1}$deg$^{-1}$ at 25°C.  For com-

parison it was necessary in the present work to extrapolate from 0.1 molal to infinite dilution which introduces some uncertainty. A value of $-110\pm10$ cal mole$^{-1}$deg$^{-1}$ was found for GdCl$_3$ which is very good agreement considering the extrapolations involved.

While the crystalographic radii of the rare earth tripositive cations form a rather smooth monotonic function versus atomic number, the apparent molar heat capacities of the aqueous chlorides and perchlorates do not. Figure 12, which shows $\phi_{cp}$ at one molal, indicates that the rare earth chlorides form two series, one for heavy rare earths and one for light, with Sm, Eu and Gd intermediate. The perchlorates show similar behavior. This phenomenon can be explained by assuming different first sphere coordination numbers for the light and heavy series. As the rare earth cations become smaller with increasing atomic number, the number of waters which can be accommodated in the inner hydration sphere shifts to a lower value. At a given concentration, the heavy rare earths have fewer tightly bound waters of hydration with the resultant more positive $\phi_{cp}$. The intermediate salts have an equilibrium between the two coordination numbers and thus have $\phi_{cp}$'s with values between that found at the light and heavy ends.. With increasing concentration, the equilibrium shifts toward the lower coordination number and $\phi_{cp}$ becomes more positive more rapidly as observed in Pr, Nd, Sm and
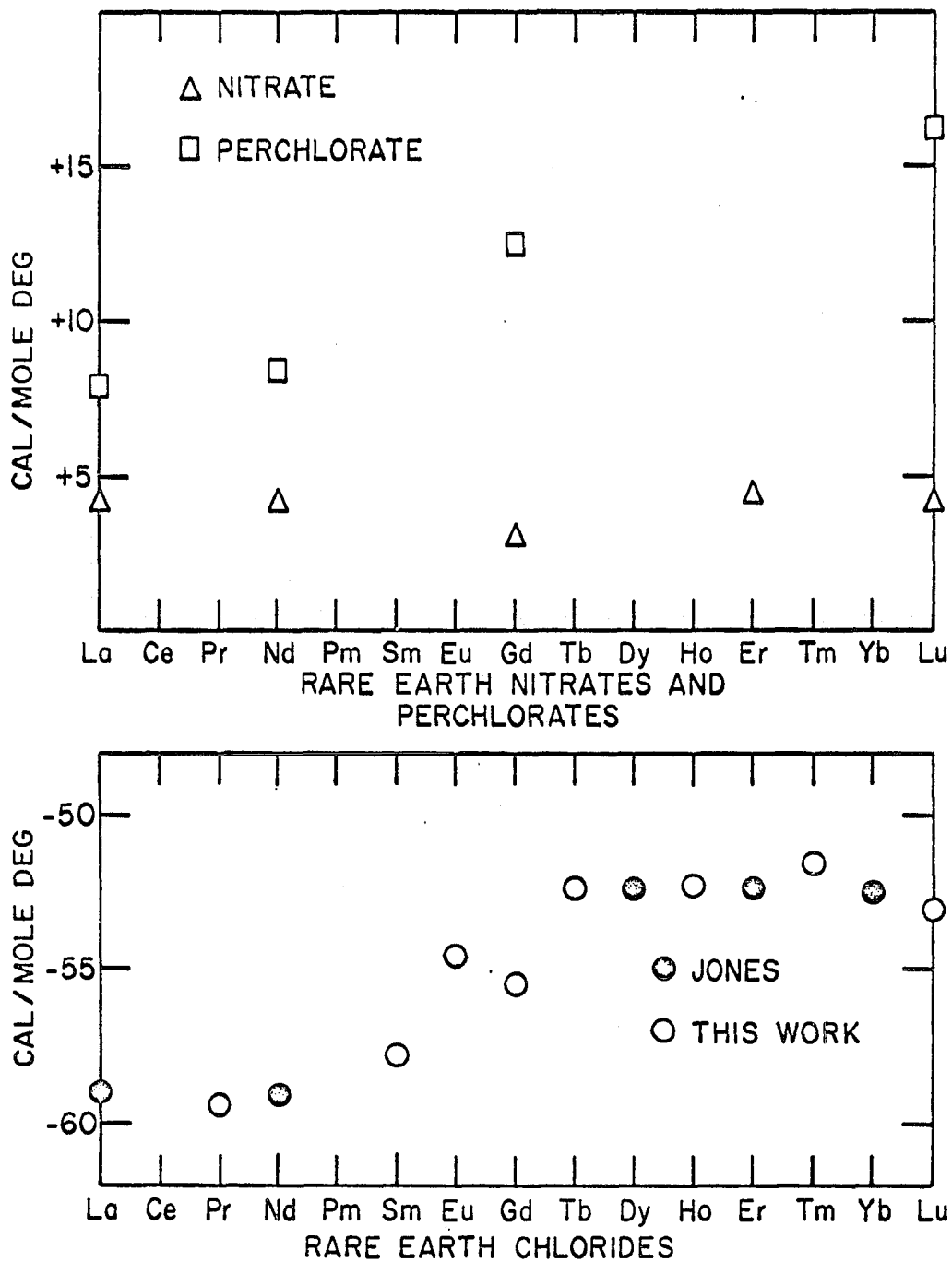
Figure 12.  Apparent molar heat capacities at one molal for some aqueous rare earth chloride, nitrate and perchlorate solutions at 25°C

$EuCl_3$ as well as in $Nd(ClO_4)_3$.

In dilute aqueous solution, nitrate ion has been observed to complex rare earth ion more strongly than does chloride ion (2). Probably due to the higher degree of complexation in the nitrates, the double series effect is obscured. Perchlorate ion is usually assumed to form no complexes with rare earth ions.

The double series effect has been observed and explained in a similar manner in other $\phi_{cp}$ data (4, 5), apparent molar volume data[3] (35) and relative apparent molar heat content data (36, 37). The same effect has been observed for the heats of formation of some rare earth chelates (38, 39, 40). Also, La and $PrCl_3$ are reported to form heptahydrate crystals at $25°C$ while heavier rare earth chlorides form hexahydrates (37, 41).

Below a concentration of one molal, $EuCl_3$, $TmCl_3$ and $LuCl_3$ fall slightly off a smooth curve which could be drawn through the chloride points of Figure 12. Eu and $TmCl_3$ are somewhat more positive while $LuCl_3$ is less positive. These differences can be explained by consideration of electronic heat capacities. All the tripositive rare earth ions except La, Eu, Gd and Lu have highly degenerate ground state elec-

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[3]Spedding, F. H., Brown, M. and Gray, K., Ames Laboratory of the A.E.C., Ames, Iowa. Apparent molal volumes of some aqueous rare earth chloride solutions at $25°C$. Private communication. 1964.

tronic energy levels which are split in the presence of ligand fields. This leads to significant electronic heat capacities, due to shifts in populations of energy levels with increase in temperature, for these rare earth ions at $25^{\circ}C$. In various crystalline compounds, due to this phenomenon, Pr through Sm have a heat capacity contribution on the order of a half cal mole$^{-1}$deg$^{-1}$ while Tb through Yb vary from approximately 0.1 to 0.5 or more cal mole$^{-1}$deg$^{-1}$ as atomic number increases. La, Gd and Lu ions have no electronic heat capacity, thus it is not surprising that LuCl$_3$ has a $\phi_{cp}$ less positive than the other heavy rare earth chlorides. Since the electronic heat capacity resulting from ligand field split ground states is quite sensitive to the nature of the ligands of the rare earth ions and the crystal field splittings in solution are not known, no quantitative calculations are possible for this type of contribution. The only data available for low lying electronic energy levels of rare earth ions are for various crystalline compounds.

In the case of Eu$^{+3}$ there are several low lying electronic energy levels, arising from spin-orbit coupling, above the singly degenerate ground state. The electronic term in the heat capacities of various europium salts (42, 43, 44) is in the range 2.0-2.2 cal mole$^{-1}$deg$^{-1}$ at $25^{\circ}C$. Since the positions of the levels are fairly insensitive to

the ligands around the europium ion, a similar term must be present in the $\phi_{cp}$ of aqueous $EuCl_3$ solutions. As determined in this work, the $\phi_{cp}$ is 2.0 cal mole$^{-1}$deg$^{-1}$ more positive than the above mentioned smooth curve through the $\phi_{cp}$'s of the other rare earths in Figure 12. Upon taking into account the heat capacity due to the split ground state of $Sm^{+3}$ which is probably present in aqueous solution, the difference would still be about 2.3 cal mole$^{-1}$deg$^{-1}$.

The partial molar heat capacity data of this work are evidence for very strong interaction between cation and anion in concentrated solutions of heavy rare earth nitrates and chlorides. $Lu(NO_3)_3$ is the most extreme sample of this. Rumanova et al. (45) have reported three nitrate ions and four waters in the first coordination sphere of praseodymium from their structural studies of $Pr(NO_3)_3 \cdot 6H_2O$. Their data show two oxygens of each nitrate adjacent to the $Pr^{+3}$ ion. Marezio et al. (46) in similar studies of $GdCl_3 \cdot 6H_2O$ have shown that there are two chloride ions along with six waters in the first coordination sphere of gadolinium. In very concentrated aqueous erbium nitrate solutions, Abrahamer and Marcus (1) claim that nitrate ions enter the inner hydration sphere of erbium ion. With this type of behavior increasing with higher concentration in aqueous solution, $\overline{C}_{p1}$ would show an upturn while $\overline{C}_{p2}$ would have a corresponding downturn as observed in the heavy rare earth nitrates and chlorides

of this work. An anion entering the inner sphere of hydration would eject a water molecule which would become less tightly bound. Furthermore the anion would cause the net charge density of the rare earth complex to decrease, yielding yet more freedom for the water. Greater upturn and increase in $\overline{C}_{p1}$ would be correlated with higher degree of inner hydration sphere complexation. The $\overline{C}_{p1}$ of $Lu(NO_3)_3$ more concentrated than 5.5 molal is within experimental accuracy of that for free water, $\overline{C}_{p1}^{o}$. This implies a very high degree of complexation, perhaps as much as all three anions entering the hydration sphere of $Lu^{+3}$ thus producing a neutrally charged species. Kapustinskii and Stakhanova (47) have reported similar behavior, $\overline{C}_{p1}$ approaching that of free water, for supersaturated $Cu(NO_3)_2$, $NaC_2H_3O_2$ and $Na_2S_2O_3$.

The concentrated heavy rare earth chlorides show a lower degree of this type of behavior, implying less inner hydration sphere complexation. The data for the perchlorates show no evidence for such ionic interaction.

It must be emphasized that the above discussion is very qualitative in nature. Much more must be known of the species in solution before any quantitative discussion is possible. From further studies being made at this time of $\phi_{cp}$'s for the rare earth nitrates, it is expected that other heavy rare earth nitrates will show evidence for inner hydra-

tion sphere complexation, the degree increasing with atomic number. Partial molar volume studies of heavy rare earth nitrates should show a correlation.

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# VIII. ACKNOWLEDGEMENTS