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THE HIGH TEMPERATURE HEAT CAPACITY AND RELATED

THERMODYNAMIC FUNCTIONS OF SOME RARE EARTH METALS

by

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INTRODUCTION

The rare earths occupy a unique position in the periodic classification of the elements. They are usually listed at the bottom of our modern periodic tables and the series is placed under lanthanum which is in group IIIA. Lanthanum is often considered the first member of the rare earth series with no electrons in the characteristic 4f orbital. It is followed by cerium which has one 4f electron, praseodymium with two and so forth up to lutecium with a filled orbital containing 14 4f electrons. Some authors refer to the rare earths as "lanthanons" or "lanthanides" after the first member of the series.

Although these elements were discovered in the 1700's, it was not until recently that they have become available in high purity in reasonable quantities. Because of this, the determination of physical and chemical properties of these elements is in its early stage. Accurate data on properties such as melting point, boiling point, density, crystal structure, resistivity, magnetic susceptibility, compressibility, dilatometric study, and low temperature heat capacity have recently become available for some of these metals.

In the investigation of some of these properties, an anomalous behavior has been observed in the vicinity of the melting point for some of these metals. Thermal analyses

have indicated a first order transition occurring from 20 to
250 degrees below their respective melting points of six of
the rare earth metals and dilatometric studies (Barson et al.,
1957) and measurement of the temperature coefficients of re-
sistivity (Spedding et al., 1957a) have verified this obser-
vation. Dilatometric studies also indicated a plastic flow
phenomenon for lanthanum, cerium, praseodymium and neodymium
above their transition temperatures. Attempts to quench this
phase and high temperature x-rays studies·by members of this
laboratory have been unsuccessful in establishing the form of
this intermediate phase.

By thermal analyses, comparisons of the lengths of
the isothermal plateaus obtained at the solid transition
temperatures and at the melting points indicate that the
heats of transition are equal to about 1/2 of the heats of
fusion. A comparison of this ratio for other metals that
exhibit solid to solid transitions indicates that this is
an abnormally high ratio for the rare earth metals. It thus
becomes evident that the accurate measurements of the heat
of transition and the heat of fusion are necessary to gain a
greater insight into the nature of this phenomenon. High
temperature heat capacity data would add to the accumulation
of data on physical properties from which a theory of rare
earth metals might be formulated. High temperature enthalpy

as a function of temperature studies would furnish us with the necessary data.

The high temperature heat capacity and related thermodynamic functions would be of considerable value when examining this group of elements for some practical applications. It is through the use of thermodynamics that many possible uses are judged. Thermodynamics is one of the general fields of science that is utilized by the chemist, physicist and engineer. It is the study of temperature, energy and related functions.

It is the tool of the engineer to enable him to theoretically design and construct more efficient engines. He uses thermodynamics to study the efficiency of various fuels. These are but a few of the many applications that thermodynamics has in engineering.

The physicists employ thermodynamics in their study of electricity, magnetism and radiation. It enables them to forgo many experimental difficulties by means of a few calculations. Heat capacity data give the solid state physicists a greater insight into the nature of solids. It is partially due to thermodynamics that physics has advanced in its many different fields.

A chemist utilizes thermodynamic calculations to advise him of the feasibility of reactions. By carrying out a series of calculations, he can determine whether or not a

reaction is spontaneous and if so, what yields he can expect. It is through such uses of thermodynamics that we are often able to save both time and money for the benefit of all.

So as to determine the high temperature thermodynamic functions, a method must be chosen for making the necessary measurements. The three general methods presently employed are:

(1) The adiabatic method in which a known quantity of heat is added to the sample and the resulting temperature rise measured.

(2) The thermal analytical methods in which the heat capacity is determined by an inspection of the heating or cooling curves and a comparison with a standard.

(3) The so called "drop" methods in which the heat content, relative to a fixed temperature, is measured by dropping a sample at a known temperature into a calorimeter.

An investigation of the literature indicated that the "drop" methods are the most accurate. Since the high temperature thermodynamic quantities are desired for all of the rare earths, the Bunsen ice calorimetric method, as described in the literature, has been modified to facilitate the obtaining of the necessary data.

HISTORICAL

Method

In 1870 Robert Bunsen invented what is now known as the Bunsen ice calorimeter. He devised the scheme which enables one to measure a quantity of heat by observing the volume change it produces in melting ice in a glass chamber. The method he chose to measure this volume change was to weigh the amount of mercury drawn into the chamber to compensate for this volume change. To insulate his calorimeter from the surroundings, he packed snow about it. The apparatus consisted of two coaxial glass tubes. The inside one was open at the top and closed at the bottom. The outer tube was about three times the diameter of the center tube and was sealed to the outside of the center tube about six inches from its top. The bottom of the outside tube was connected to a capillary tube which led outside the constant temperature bath to a weighing bottle. The space between these two tubes was filled with distilled water except for a small pool of mercury at the bottom and the capillary tube. Bunsen utilized the heat given up by a known weight of water when it was cooled from a higher temperature to the temperature of the calorimeter to obtain the heat equivalence of his mercury intake.

Dieterici (1905) employed essentially Bunsen's original design but performed the calibration by two methods. He used the water calibration of Bunsen and an electrical calibration. He inserted a known resistance into the center tube and passed a constant current through this resistance for a specified time. He measured the voltage drop across this resistance element and determined the current independently. The consistency of his electrical calibrations was quite good.

Griffiths's (1913) contribution to the field of ice calorimetry was an investigation of the heat leak of the calorimeter. The heat leak is the rate at which the ice melts due to the flow of heat in from the warmer surroundings. He found the heat leak could be reduced a factor of ten by surrounding the calorimeter with another closed bottom coaxial tube which fitted about the calorimeter proper except for a portion of the center tube which extended through the top of it. The space between this tube and the calorimeter proper contained dry air. Thus, the calorimeter was insulated from local temperature variations in the constant temperature bath. He also electrically calibrated his calorimeter and found his value to agree within experimental error with the value determined electrically by Dieterici.

Sachse (1929) attempted to improve the sensitivity of the calorimeter by employing diphenyl ether which melts at

$27^{\circ}C$. Theoretically, this would improve the sensitivity of the calorimeter as the calibration factor is about 1/3 the calibration factor of an ice calorimeter. It would also have the advantage of making the data obtained relative to $27^{\circ}C$ which is closer to $25^{\circ}C$, the temperature relative to which most thermodynamic data is recorded. More recent investigators (Giguere et al., 1955) have not exceeded the reproducibility of the ice calorimeter by this method.

Zmaczynski et al. (1933) took special care to place the ice calorimeter deeper in the ice bath and to eliminate the pressure of the mercury by extending the mercury capillary tube from the top if the ice bath down to the level of the mercury in the bottom of the glass chamber. They contended that this reduced the heat leak to a minimum and permitted better results.

Ginnings and Corruccini (1947a) revived interest in the Bunsen ice calorimeter by introducing modifications which improved its precision. They constructed their model from glass and metal which made it more durable. The space between the calorimeter proper and the outermost glass tube could be evacuated and then filled with dry carbon dioxide to improve the insulation. A gate was introduced above the calorimeter proper and served the purpose of preventing radiation from the furnace, in which a sample was suspended, from adding to the heat leak of the calorimeter. They con-

structed the center well from thin copper and additionally increased the rate of heat dissipation from the sample by surrounding this well with copper vanes on which the ice mantle could be frozen. They attached a small diameter copper tube to the bottom of the well while the other end of the copper tube led out of the constant temperature bath, admitting a slow stream of dry carbon dioxide which prevented the condensation of water in the center well. The electrical calibration of this calorimeter agreed within the limit of error with those previously determined by Dieterici and Griffiths.

Leake and Turkdogan (1954) contributed improvements to facilitate the functioning of an ice calorimeter. They permanently evacuated the space between the glass chamber and the outer flask. They explained that this aided in better insulation and does not require the time-consuming task of evacuating this space and refilling it with carbon dioxide; after the introduction of carbon dioxide, time was required for the carbon dioxide and the glass chamber to come to equilibrium. Their electrical calibration agreed with that obtained by Ginnings and Corruccini (1947a).

Smith (1955) improved the technique of freezing the ice mantle about the center tube. The technique that had been previously employed was to fill a closed-bottom, cylindrical, copper tube with dry ice and to obtain the desired

shape of the ice mantle by adjusting the thermal contact of the cold tube with the inside of the well. They employed the simple device of passing air through copper coils cooled in dry ice and allowing the cooled air to pass down a tube inserted in their calorimeter well. They could control the shape of the ice mantle by adjusting the height of this inserted tube and the rate of freezing by controlling the rate of flow of the air.

Cerium

Hillebrand (1876) determined the mean specific heat of two grams of 95.1% cerium between $0^\circ C$ and $100^\circ C$ using an ice calorimeter. The value which he obtained was 0.04479 calories per degree per gram.

Hirsch (1912) determined the mean specific heat of 98% cerium between $20^\circ C$ and $100^\circ C$. He reported the melting point to be $635^\circ C$ and found the value of 0.05112 calories per degree per gram for the mean specific heat.

Jaeger and Rosenbohm (1934) carried out high temperature measurements of the heat capacity of cerium from $310^\circ C$ to $550^\circ C$. They employed a "drop" method using a copper block calorimeter. They found a variation of the heat capacity over the temperature range studied which they attributed to a transition occurring in the temperature interval

$360^{\circ}C$ to $370^{\circ}C$. They used a platinum jacket to protect the cerium from oxidation, with the weight of platinum being about twice the weight of cerium employed.

Jaeger et al. (1936, 1938b) redetermined the heat capacity of cerium over the temperature interval $300^{\circ}C$ to $550^{\circ}C$. The weight of cerium employed was 22.2098 grams while the platinum jacket weighed 28.0393 grams. The cerium sample was reported to be 98.8% pure with the major impurity being iron. The melting point of the cerium was reported as $635^{\circ}C$. They reported two transitions in this range, one at $362^{\circ}C$ and the other at $502^{\circ}C$. They found that their heat capacity could be expressed as a function of temperature by the equation:

$$Cp = 7.3377 + .43493 \times 10^{-2}(t-380), \qquad (1)$$

where Cp is the heat capacity (calories degree^{-1} mole^{-1}) and t is the temperature ($^{\circ}C$). This equation was valid only in the temperature range of $380^{\circ}C$ to $480^{\circ}C$. The remainder of their heat capacity data was too sporadic to be fit by a simple equation.

Cavallaro (1943) determined the heat of fusion of cerium by a thermal analytical technique. He accomplished this by determining the heat capacity of his system and measuring the slope and the length of the isothermal plateau in a temperature versus time curve for cerium. He obtained the

value of 5.5 kilocalories per mole for the heat of fusion of cerium.

Kelley (1949) compiled the high temperature thermodynamic functions available for miscellaneous substances and estimated data when it had not been determined experimentally. He gave the following equation to express enthalpy as a function of temperature for cerium:

$$H_T - H_{298.2} = 4.40T + 3.00 \times 10^{-3} T^2 - 1579. \tag{2}$$

For this equation, H_T is the enthalpy of cerium in calories per mole at some absolute temperature T. He stated that this equation is valid for the temperature range $298.2^{\circ}K$ to $800^{\circ}K$ with a limit of error of 3%.

Brewer (1950) has estimated some thermodynamic quantities for various materials. He estimated the heat of fusion of cerium to be 2.2 kilocalories per mole.

Parkinson et al. (1951) determined the low temperature heat capacity of cerium. They obtained erratic results in the temperature region of $135^{\circ}K$ to $170^{\circ}K$. They reported the heat capacity equal to 6.90 calories per degree per mole at $200^{\circ}K$.

Kojama and Kikuchi (1953) estimated the heat of fusion of cerium from phase diagram studies. Their estimate was 3.09 kilocalories per mole.

Stull and Sinke (1955) compiled high temperature thermodynamic data available for the elements and included

estimated data where none was available. They reported the
heat capacity of cerium as 6.90 calories per degree per mole
at 300°K and estimated the heat of transition to be 300 cal-
ories per mole and the heat of fusion to be 2.2 kilocalories
per mole.

Parkinson and Roberts (1957) determined the heat capa-
city of cerium in the temperature range of 1.5°K to 20°K and
obtained an anomaly in this interval.

Gonigberg et al. (1957) investigated the fcc to fcc
transition of cerium under a pressure of 7000 kilograms per
square centimeter. They found the heat of transition to be
880 ± 40 calories per mole at 13°C to 18°C.

Praseodymium

Cavallaro (1943) determined the heat of fusion of pra-
seodymium by a method of thermal analysis. He reported the
value of 3.1 kilocalories per mole.

Parkinson et al. (1951) investigated the heat capacity
from 2.5°K to 170°K. They listed the value of 6.50 calories
per degree per mole for the heat capacity at 170°K.

Stull and Sinke (1955) extrapolated the data of Park-
inson et al. (1951) to 300°K and gave a value of 6.46 calo-
ries per degree per mole. They estimated the heat of

Kelley (1949) gave the following equation for expressing the enthalpy of neodymium as a function of temperature:

$$H_T - H_{298.2} = 5.61T + 2.67 \times 10^{-3}T^2 - 1910, \qquad (5)$$

where H_T is the heat content (calories mole^{-1}) at some absolute temperature, T. This equation was reported as being valid within 2% over the temperature range 298°K to 900°K.

Parkinson et al. (1951) determined the heat capacity of neodymium from 2°K to 160°K. They gave the value of 6.84 for the molar heat capacity at 160°K.

Spedding and Miller (1951) employed a "drop" method with a Bunsen ice calorimeter to determine the heat capacity of neodymium from 0°C to 250°C. They found that the enthalpy (calories gram^{-1}) could be expressed as a function of temperature (°C) by the equation:

$$H_t - H_0 = .04491t + 2.445 \times 10^{-5}t^2 + 1.064 \times 10^{-7}t^3. \qquad (6)$$

Stull and Sinke (1955) estimated the heat of transition to be 340 calories per mole and the heat of fusion as 2.6 kilocalories per mole. They expressed the heat capacity as 7.21 calories per degree per mole at 300°K.

Johnson et al. (1956), by a comparison of the heats of vaporization and sublimation, estimated the heat of fusion of neodymium to be 3.5 kilocalories per mole.

Samarium

Stull and Sinke (1955) have estimated the heat capacity of samarium to be 6.50 calories per degree per mole at 300°K by a comparison of the data available for the neighboring elements. They also estimated the heat of transition to be 360 calories per mole and the heat of fusion to be 2.65 kilocalories per mole.

Roberts (1957) determined the heat capacity for samarium in the temperature range of 2°K to 20°K. They found an anomalous bump in the heat capacity.

Work has recently been completed in this Laboratory (Hill, 1957) on the low temperature heat capacity of samarium. The value found at 340°K is 7.35 calories per degree per mole.

THEORY AND METHOD

Theory

The thermodynamic definition of heat capacity is given by the following equations:

$$C_v = (\partial E/\partial T)_v \tag{7}$$

and

$$C_p = (\partial H/\partial T)_p, \tag{8}$$

where C_v is the heat capacity at constant volume, C_p is the heat capacity at constant pressure, E is the energy, H is the enthalpy, T is the temperature, v is the volume and p is the pressure. This notation will be used throughout this thesis. These two definitions can be related by some simple mathematical manipulations of thermodynamic equations. Utilizing the relationship for expressing the total differential of the energy in terms of the independent variables temperature and pressure:

$$dE = (\partial E/\partial T)_v dT + (\partial E/\partial v)_T dv \tag{9}$$

and partially differentiating dE with respect to T while holding p constant, we obtain:

$$(\partial E/\partial T)_p = (\partial E/\partial T)_v + (\partial E/\partial v)_T(\partial v/\partial T)_p. \tag{10}$$

We now use the equation relating enthalpy to energy:

$$dH = dE + pdv + vdp. \tag{11}$$

Taking the variation of dH with respect to T while again retaining p constant, we obtain:

$$(\partial H/\partial T)_p = (\partial E/\partial T)_p + p(\partial v/\partial T)_p. \qquad (12)$$

Substituting in the expression for $(\partial E/\partial T)_p$ from equation 10, we obtain:

$$(\partial H/\partial T)_p - (\partial E/\partial T)_v = \left[(\partial E/\partial v)_T + p\right](\partial v/\partial T)_p. \qquad (13)$$

The expression $(\partial E/\partial v)_T$ can be evaluated by differentiating the expression:

$$dE = TdS - pdv \qquad (14)$$

with respect to v while maintaining T constant to obtain:

$$(\partial E/\partial v)_T = T(\partial S/\partial v)_T - p, \qquad (15)$$

where S is the entropy. To evaluate $(\partial S/\partial v)_T$, we turn to the expression for the differential of Helmholtz free energy:

$$dA = - SdT - pdv \qquad (16)$$

and utilize the relationship:

$$\partial^2 A/\partial v \partial T = \partial^2 A/\partial T \partial v. \qquad (17)$$

Hence, we find:

$$(\partial S/\partial v)_T = (\partial p/\partial T)_v. \qquad (18)$$

By using the expression for total-differential of v in terms of the variables p and T, we obtain the relationship:

$$(\partial p/\partial T)_v = - (\partial v/\partial T)_p/(\partial v/\partial p)_T. \qquad (19)$$

Substituting our results from equations 15, 18, and 19 into equation 13 and using our definition equations 7 and 8, we obtain:

$$c_p - c_v = - T(\partial v/\partial T)_p^2/(\partial v/\partial p)_T \qquad (20)$$

or

$$C_p - C_v = \alpha^2 vT/\beta, \tag{21}$$

where the coefficient of thermal expansion α is equal to $(1/v)(\partial v/\partial T)_p$, the compressibility β is equal to $(-1/v) \cdot (\partial v/\partial p)_T$, v is the molal volume and T is the absolute temperature. This difference between C_p and C_v is often referred to as the dilatation term. It is C_p which is usually measured experimentally while C_v is the heat capacity usually employed in solid state theory.

The measured heat capacity at constant pressure can be looked upon as being the sum of several terms:

$$C_p = C_{v(1)} + C_{e(i)} + C_{e(o)} + \delta C, \tag{22}$$

where $C_{v(1)}$ is the lattice contribution to the heat capacity at constant volume, $C_{e(i)}$ is the 4f electronic contribution, $C_{e(o)}$ is the conduction electronic contribution and δC is the dilatation term.

The classical approach to the lattice contribution to the heat capacity treats the atoms as individual harmonic oscillators vibrating about their mean positions in the crystalline lattice. The mean energy of a one dimensional harmonic oscillator is equal to the sum of the kinetic and potential energies. From a kinetic theory treatment of particles, one finds that the average kinetic energy will be 1/2 kT and the total energy for one dimensional harmonic oscillator will be kT.

Utilizing Maxwell's Law which states that at the same temperature all molecules have the same average kinetic energy except near $0^\circ K$, the average energy of N harmonic oscillators in three dimensions may be seen to be:

$$\overline{E} = 3NkT = 3RT, \qquad (23)$$

where R is the gas constant and T is the absolute temperature.

From our definition of C_V, we find that:

$$C_V = (\partial\overline{E}/\partial T)_V = 3R = 6 \text{ calories degree}^{-1} \text{ mole}^{-1}. \qquad (24)$$

This value is the classical value of Dulong and Petit which they observed for many solids.

This is the limit for the lattice contribution to the heat capacity for solids at high temperatures. This classical approach was found to be in poor agreement with the fact that C_V approached zero as the temperature approaches absolute zero.

Einstein (1907) gave a qualitative explanation of the heat capacity versus temperature curve by utilizing Planck's hypothesis. He postulated that each atom's vibrations are like three perpendicular Planck oscillators. A Planck oscillator possesses discrete quantities of energy nh where n is an integer, h is Planck's constant and is the frequency. By using Boltzmann statistics to evaluate the mean energy for an oscillator and multiplying by N to obtain the mean energy per mole, he obtained the expression:

$$\bar{E} = 3Nh\nu/(e^{-h\nu/kT}-1). \tag{25}$$

By differentiating this expression with respect to T we obtain the heat capacity per mole:

$$C_v = \partial \bar{E}/\partial T = 3R(h\nu/kT)^2 e^{h\nu/kT}/(e^{h\nu/kT}-1)^2, \tag{26}$$

which agrees qualitatively with the C_v versus T curve. Since T is large at high temperatures, one can approximate $e^{h\nu/kT}$ equal to one and utilize the following expansion to obtain a first order approximation of the denominator:

$$e^{h\nu/kT} = 1 + h\nu/kT; \tag{27}$$

one finds that the Einstein function for C_v approaches the classical value of 3R.

Debye (1912) obtained a quantitative interpretation of the C_v versus temperature curve by assuming:

(1) that the atoms vibrated in a frequency spectrum from a minimum to a maximum frequency,

(2) that the solid could be treated as a continuous medium and

(3) that the velocity of propagation is independent of wave length.

He utilized the boundary condition that:

$$n(\lambda/2) = a, \tag{28}$$

where n is an integer, λ is the wave length and a is a dimension of the specimen. At the lower limit of the frequency, where n is equal to one, the energy involved with

this long a wave length is negligible and one need not consider the shape of the sample. The upper limit of the frequency spectrum is determined by assuming that the shortest half wave length will be approximately equal to the lattice spacing. There will be three standing waves set up in the solid, two transverse and one longitudinal. Debye obtained the following equation to express the lattice energy:

$$\bar{E} = 9Nh/\nu_m^3 \int_0^{\nu_m} \nu^3 d\nu/(e^{h\nu/kT}-1), \qquad (29)$$

where N is Avogadro's number, h is Planck's constant, ν_m is the maximum frequency of the spectrum, k is Boltzmann's constant and T is the absolute temperature. Introducing the variable θ (Debye temperature) $= h\nu_m/k$ and $x = h\nu/kT$ the equation simplified to:

$$\bar{E} = 9R(T/\theta)^3 \int_0^{x_m} x^3 dx/(e^x-1). \qquad (30)$$

At high temperatures when T is large and x is small we can use the approximation given by equation 27. Upon evaluating the energy at high temperatures, we find that it again approaches 3RT and thus the heat capacity at constant volume has the Dulong and Petit value of 3R. It can be shown that at very low temperatures that C_V varies as T^3 for the Debye function.

Born and Von Karman (1912, 1913) developed a more rigorous treatment of heat capacity than Debye utilizing both

Einstein and Debye functions. Blackman (1933, 1935, 1937a, 1937b) undertook the task of determining the distribution of frequencies for simple lattices.

The inner electronic contribution to the heat capacity is usually small at room temperature depending on the energy gap to the next J state. Europium and samarium may give quite large contributions because of their low level J states. The number of inner electrons in the next higher J states may become significant for some of the rare earths with 4f electrons so as to give an appreciable contribution to the heat capacity at $1000^\circ K$.

The outer electronic contribution is composed of the conduction or valence electronic contributions. A classical approach treats the conduction electrons as an ideal gas. The energy of an ideal gas depends on the average translational energy. Each translational degree of freedom contributes 1/2kt to the energy of an atom and there are three degrees of translational freedom for a gas. Thus, the energy of a gaseous atom would be 3/2kT or 3/2RT per mole. A conduction electron is treated kinetically in the same manner and we would thus expect the average energy for each conduction electron to be 3/2kT and the heat capacity to be 3/2k or approximately three calories per degree per mole per conduction electron.

Treating the conduction electrons from a quantum theory approach, we utilize Fermi-Dirac statistics and their distribution function (f) which can be written as:

$$f = 1/(e^{(E - E_F)/kT} + 1),\tag{31}$$

where E is the energy, E_F is the Fermi energy, k is Boltzmann's constant and T is the absolute temperature. The total energy per unit volume is given by Kittel (1956) as:

$$U = \int_0^\infty E\, f(E)g(E)dE,\tag{32}$$

where f(E) is the Fermi-Dirac distribution function and g(E) is the density of states. This expression can be solved to yield the equation:

$$U = U_0 + \pi^2(kT)^2 g\left[E_F(0)\right]/6\tag{33}$$

at low temperatures. In this expression $E_F(0)$ is the Fermi energy at $0^\circ K$. By differentiating this expression, we obtain:

$$C_V = (\partial U/\partial T)_V = \pi^2 k^2 Tg\left[E_F(0)\right]/3,\tag{34}$$

where $g\left[E_F(0)\right]$ can be expressed as:

$$g\left[E_F(0)\right] = 3N/2E_F(0) = 3N/2kT_F.\tag{35}$$

We may then express C_V as:

$$C_V = \pi^2 NkT/2T_F \text{ per unit volume}\tag{36}$$

or

$$C_V = \pi^2 zRT/2T_F = \gamma T \text{ per mole},\tag{37}$$

where z is the number of conduction electrons per atom.

Of these terms contributing to the heat capacity at high temperatures, the lattice contribution is by far the greatest. The γ for the conduction electronic contribution for the rare earths is about 1.6×10^{-3} and thus has second greatest importance. The inner electronic contribution will be of next greatest importance and the dilatation contribution will be of least importance for most of the rare earth metals.

Method

Methods for experimentally determining the high temperature heat content and heat capacity data can be categorized as follows:

 (1) adiabatic methods,

 (2) thermal analysis, and

 (3) "drop" methods.

The adiabatic method is used to measure the true heat capacity of a substance by adding a known amount of heat and observing the resulting temperature rise. Because of the difficulties of reducing the heat losses of the specimen at high temperatures to zero, the reproducibility of this method above $500^\circ C$ is poor. As high temperature techniques and instrumentation become more refined, high temperature adiabatic calorimeters may be employed more often.

(2) An electrical calibration of the calorimeter is not necessary as the calibration factor should be a constant for outgassed conductivity water and pure mercury.

(3) The precision of the calorimeter does not decrease with an increasing amount of heat liberated.

Some of the disadvantages of a Bunsen ice calorimeter are:

(1) All measurements are made relative to zero degree centigrade while most thermodynamic data are tabulated relative to 25°C.

(2) The volume of the calorimetric system must be maintained constant.

(3) A general disadvantage to both "drop" methods is that the substance, whose heat content is being measured, must reproducibily return to the same energy state at the temperature of the calorimeters. Thus, if a high temperature transition occurs in the substance, the high temperature allotropic modification must not be quenchable.

After considering the advantages as opposed to the disadvantages of a Bunsen ice calorimeter, this method was chosen in preference to a copper block type.

The calibration factor for a Bunsen ice calorimeter can be expressed by the equation:

The thermal analytical method employs a heating and cooling apparatus in which a material of known heat capacity is utilized to standardize the apparatus. By the interpolation of the temperature versus time curves, the heat capacity of another substance can be determined. This method is no better than an approximation using the techniques presently employed.

The "drop" methods determine the heat content of a sample between a furnace temperature and the temperature of a calorimeter. Two types of "drop" methods are currently employed. The difference between the two lies in the method for determining the heat liberated by the sample. The sample is dropped from a furnace at a constant temperature and in one method the heat is determined by measuring the temperature rise of a copper block into which the sample has been dropped; in the other method the heat liberated melts ice which is in equilibrium with water in a glass chamber and the resulting decrease in volume is determined by weighing the amount of mercury drawn into this chamber. The "drop" method was chosen for this work.

The Bunsen ice calorimeter has several advantages over the copper block type:

(1) An elaborate temperature measuring device is not necessary to determine the amount of heat liberated by the specimen.

(2) An electrical calibration of the calorimeter is not necessary as the calibration factor should be a constant for outgassed conductivity water and pure mercury.

(3) The precision of the calorimeter does not decrease with an increasing amount of heat liberated.

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After considering the advantages as opposed to the disadvantages of a Bunsen ice calorimeter, this method was chosen in preference to a copper block type.

The calibration factor for a Bunsen ice calorimeter can be expressed by the equation:

$$K = \Delta h_i / (v_i - v_w) d_m, \tag{38}$$

where K is the calibration factor in calories per gram of mercury intake, Δh_i is the heat of fusion of ice in calories per gram, v_i is the specific volume of ice, v_w is the specific volume of water and d_m is the density of mercury.

Ginnings and Corruccini (1947a) of the National Bureau of Standards have electrically determined this factor to be 64.631 $\pm$ .014 calories per gram of mercury intake.

A high temperature calorimetric standard should possess the following characteristics:

(1) It should not exhibit any transformation up to approximately 1500°C.

(2) It should be available commercially in high purity.

(3) It should have a high heat capacity per unit volume.

(4) It should be chemically stable in air, non-hygroscopic and non-volatile.

Ginnings and Furukawa (1953) recommended α- Al_2O_3 (corundum) to fulfill these requirements and it is now accepted as the calorimetric standard above room temperature.

The reliability of the method has been discussed by Ginnings and Corruccini (1947b) in great detail. They state, after a consideration of all the errors of the method, that the error in the heat content does not exceed 0.2%. To

support this statement, they determined the enthalpy of water at 254°C and found it to agree with the accepted value within 0.04%.

MATERIALS

The α - Al$_2$O$_3$ (corundum) was purchased from Linde Air Products as a fused cylindrical rod six inches long and 1/2 inch in diameter. A one-inch specimen was used in this study. The platinum crucibles were purchased from the American Platinum Company in the form of cylindrical crucibles 1 1/4 inches long with an outside diameter of 5/8 inch and a wall thickness of 0.010 inch. The platinum used for a lid and bail wire was also purchased from the American Platinum Company and formed to the desired shape at the Ames Laboratory.

The pure rare earths were prepared from the ore utilizing ion-exchange techniques. These techniques were described in great detail by Spedding et al. (1950, 1951, 1954) and Spedding and Powell (1954).

Cerium, praseodymium and neodymium were prepared by the metalothermic reduction of the anhydrous fluorides with calcium as described by Spedding and Daane (1954, 1956). The anhydrous fluorides were prepared by heating an intimate mixture of their respective oxides with ammonium bifluoride and after the reaction is completed, distilling off the excess ammonium bifluoride. The cerium, praseodymium and neodymium were heated in a tantalum crucible above their

melting points to distill the excess calcium from the rare earth metals.

Samarium was prepared by the procedure described by Daane et al. (1953). Samarium oxide was heated with lanthanum metal in a vacuum and as the samarium is much more volatile than lanthanum, it distilled and condensed on a cold finger where it was collected.

Tantalum crucibles which fitted snugly inside the drawn platinum crucibles were used to contain the rare earth metals. These crucibles were fabricated from 0.005-inch sheet tantalum purchased from the Fansteel Metallurgical Corporation. The dimensions of these cylindrical crucibles were 3/5-inch inside diameter and 1 1/8 inches long. After fabricating, these crucibles were heated to 1800°C in an atmosphere of hydrogen and then heated to 2000°C in a vacuum to relieve welding effects. The crucibles were then weighed and small pieces of rare earth metal introduced into them. They were then heated about 200°C above the melting point of the rare earth metal that they contained and held at this temperature for 30 minutes to expel any residual calcium which might have remained after casting. In the cases of cerium, praseodymium and neodymium this casting process took place in a vacuum whereas with samarium, because of its high vapor pressure, the casting was carried out under one atmosphere of helium. After enough rare earth metal had been

added so that the meniscus of the metal was about 1/4 inch below the top of the crucible, it was weighed and the weight of rare earth metal computed from the difference in weight of the filled and empty crucible.

A lid was formed by drawing 0.005-inch tantalum sheet into a cuplet which fitted into the crucible snugly. The lid was welded in place in a helium atmosphere using a tantalum electrode in a welder developed in this Laboratory. The crucible was held in a brass block while welding so as to keep the rare earth metal cool. Weighing, after welding was completed, indicated that the sample had lost no appreciable weight by vaporization of either the rare earth or tantalum.

This sample was then placed within a weighed platinum jacket which was welded shut in an atmosphere of helium in the same manner in which the tantalum vessel was closed except that a spectrographically pure graphite electrode was employed. A bail fashioned from #18 B and S gauge platinum wire was spot-welded to the outside of the platinum crucible so that it could be suspended from a #26 B and S gauge platinum(13% rhodium) wire within the center of a resistance furnace. In the sealing operation, additional amounts of tantalum and platinum were added such that the weights of these two metals in the final sample were the same as in the

empty container whose heat content had been previously measured as a blank.

The corundum sample was sealed under a helium pressure of one atmosphere by welding the platinum container in a procedure similar to that outlined above.

Spectrographic analyses performed on each of the rare earths gave the results shown in Table 1. It should be noted that only a qualitative analytical method was available for the corundum but other analyses of this same material have indicated the purity to be greater than 99.9%.

The weight of α- Al_2O_3 (corundum) used to standardize the apparatus was 12.3136 grams. The weights of the rare earth metals were:

 (1) cerium - 21.9943 grams

 (2) praseodymium - 21.3512 grams

 (3) neodymium - 21.1556 grams

 (4) samarium - 22.5138 grams

The weight of tantalum used in the blank and each sample was 4.7584 grams while the weight of platinum in each case was 13.3152 grams.

Table 1. Spectrographic analysis of samples

Sample	Impurities

(Quantitative analyses)[a]

	Ca	La	Si				
cerium	±0.05%	±0.01%	±0.02%				

	Ca	Ce	Fe	La	Nd	Si	Ta
praseodymium	±0.05%	±0.1%	±0.01%	±0.1%	±0.1%	±0.02%	±0.1%

	Ca	Fe	Pr	Sm	Si	Ta	
neodymium	±0.1%	±0.01%	±0.04%	±0.03%	±0.02%	±0.2%	

	Ca	Eu	Fe	La	Mg	Si	
samarium	±0.05%	±0.2%	~0.01%	±0.01%	±0.01%	±0.01%	

(Qualitative analyses)[b]

	Fe	Mg	Si
corundum	very weak	very weak	weak

[a]The numbers with the symbol ± represent the lower limit of detection of the spectrographic method.

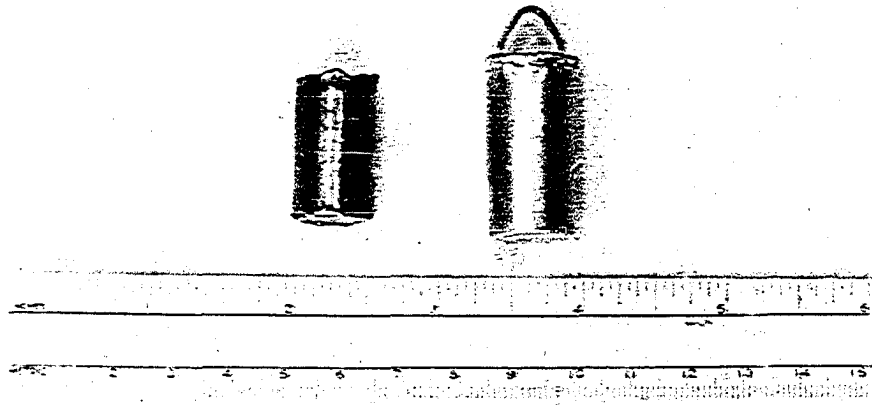[b]The relative intensity of the impurity lines are given.

Figure 1. A sample sealed in a tantalum crucible and a
           sealed platinum jacket

APPARATUS AND PROCEDURE

Apparatus

The Bunsen ice calorimeter employed in this investigation is shown in Figure 2 and is similar to the one used by Furukawa et al. (1956) with some modifications. In this figure: A is a 1 1/16-inch inside-diameter Monel tube with a wall thickness of 0.010 inch except for a three-inch section at F which had a wall thickness of 0.031 inch. This thin-walled Monel tube decreased the conduction of heat from the room to the calorimeter proper. The three-inch section required the additional thickness because the support, to suspend the calorimeter in the constant-temperature bath, was attached at this position. B is a 1/4-inch diameter stainless-steel tube which was connected to a Welch-1400 mechanical vacuum pump to provide a vacuum between the two glass chambers and insulate the calorimeter proper from local temperature variations in the constant-temperature ice bath. C is a 1/4-inch stainless-steel tube which led from the mercury pool in the bottom of the calorimeter to the mercury-delivery apparatus. This tube was coiled and situated on the upper brass head to provide cooling. This cooling coil assembly allowed for the cooling of mercury to $0^{\circ}C$ before entering the calorimeter proper. The

end of the stainless-steel tube was tapered in a one to ten
ratio and fitted a 7/25 glass standard taper at the point C.
This connection was sealed utilizing Apiezon-hard sealing
wax which allows occasional cleaning of the glass capillary
and delivery tube. D is a 1/8-inch Super-nickel tube which
led from the bottom of the tapered copper well to the out-
side of the constant-temperature bath. Argon was passed
through coiling coils placed below the mercury cooling coils
on the top of the upper brass head. This allowed the cool-
ing of the gas to $0^{\circ}C$ before it entered the bottom of the
tapered copper well. This gas flowed at the rate of six
milliliters per minute and prevented water vapor from con-
densing in the calorimeter well. E is a 3/5 millimeter
glass capillary. By closing the teflon stopcock, which was
located between the capillary and the beaker of mercury, one
was able to determine the heat leak by observing with a
cathetometer the position of the meniscus of the mercury in
the calibrated capillary at time intervals. The capillary
was calibrated "in situ" with the cathetometer which could
be read to $\pm$ 0.05 millimeter. This calibration "in situ"
allowed for the compressibility of the calorimetric system.
F is a split plexi-glass cylindrical support whose inside
diameter fitted snugly around the thick section of the cen-
tral Monel tube. Its function was to thermally insulate
the calorimeter tube from the metal support. G is a metal

support which suspended the calorimeter in the constant-temperature bath. Four pairs of screws served to attach the calorimeter to the metal support. The three stainless-steel arms which extended from the center attachment to the outside of the barrel have screws through their ends. These screws seated in metal tabs welded to the outside of the barrel and served to level the calorimeter. H is the gate mechanism which prevented radiation from the furnace from entering the calorimeter. The upper and lower ends of the gate shaft were seated in bearings to permit easy turning of the gate. The gate is a 1/16-inch thick, chromium-plated, copper disk with a section in the shape of 1/2 of a lemniscate cut out of it. This shape permitted the sweeping of the dropping wire to one wall of the calorimeter after the sample had been dropped from the furnace. The halves of the gate housing were separated by an "O" ring and were held together by small screws which passed through insulators located on the top half of the housing. This aided in insulating the two halves from one another. I is a 1/4-inch stainless-steel tube which facilitated the introduction of outgassed conductivity water and mercury into the inner glass chamber. J is the collar seal for obtaining a vacuum seal between the outer glass flask and the metal head. The outer flask had a ground glass flange on the open end. The width of the ground glass portion was

1/2 of an inch with the glass flange being 1/4 of an inch thick. This ground glass flange seated on a Neopreme gasket which was seated in a groove in the brass head. An "O" ring was fitted on the outside of the glass flange and was compressed by a brass collar which screwed on the metal head. A vacuum was drawn between the glass flasks and the brass collar was screwed tightly in place. K is a glass to metal Kovar seal which was soft soldered to the inner brass head. L is a tapered, silver-plated, 0.010-inch wall thickness, copper well fitted on the outside with 18 copper vanes spaced 1/4 of an inch apart. This assembly facilitated the rate of heat dissipation by the sample to the calorimeter. M is outgassed conductivity water while N is the ice mantle frozen about the calorimeter well. O is the mercury located in the bottom of the chamber, the mercury delivery tube and the beaker. P are the glass flasks which were four and five inches in diameter. Q is a metal screen which prevented ice, that was introduced below it, from floating to the top of the constant temperature bath. R is a two-inch diameter copper tube that was used to introduce ice below the metal screen. S is the constant-temperature bath made up of ice and water and T is a 30-gallon stainless-steel barrel which contained the bath. U is a two-inch layer of wool felt. V is a double-walled plywood box which contained a four-inch layer
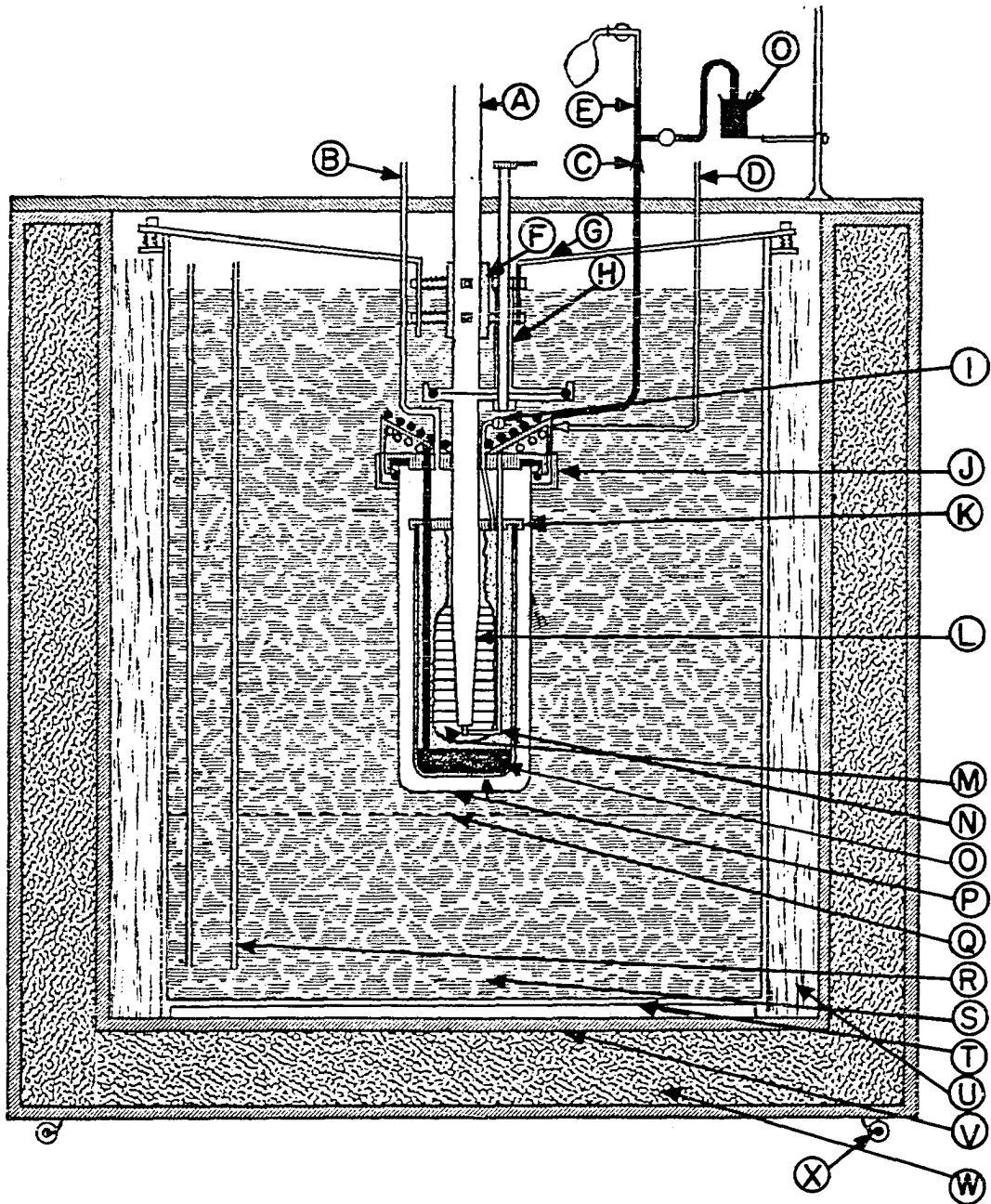
Figure 2.   A Bunsen ice calorimeter
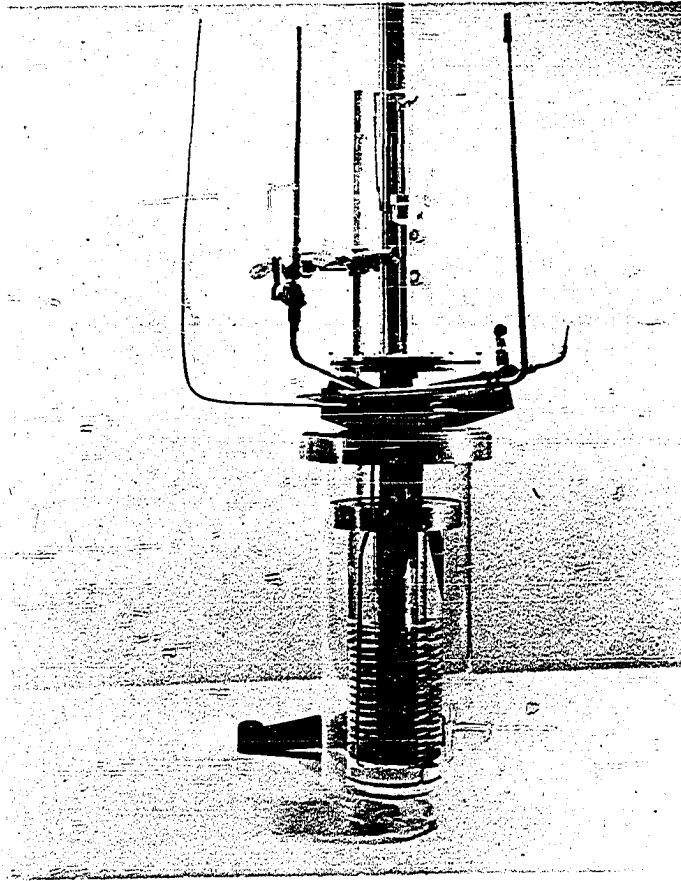
Figure 3.   The Bunsen ice calorimeter employed before the
             inner glass to metal seal was changed to a
             Kovar seal

of Dicalite (W) for insulation. X are casters which permitted the moving of the apparatus.

The furnace and dropping mechanism are shown in Figure 4. The dropping mechanism is similar to the one described by Southard (1941) while the furnace was a modification of that described by Spedding and Miller (1951). A in Figure 4 represents a direct current solenoid which suspended the soft iron piston (B) prior to dropping the sample from the furnace into the calorimeter. The dropping wire was connected to the bottom of this hollow soft iron piston by means of a set screw. The weight of piston-sample assembly was maintained essentially constant in order to reproduce the same time for dropping for both the empty capsule and the sample. This was accomplished by removing lead granules from inside the soft iron piston when dropping the sample. C is a string which held the piston in an "up" position and raised it after being dropped. D refers to an one-inch inside diameter brass tube which was 47 inches long. The bottom of the tube was closed except for a small hole through which the dropping wire passed. The tube was slit down one side to six inches from the bottom and hence allowed the snugly-fitted iron piston to fall quite freely to within six inches of the bottom where it was air-cushioned and thus allowed the sample to be gently introduced into the calorimeter. F are Transite disks closing the ends of the furnace.

G is #18 B and S Gauge platinum(13% rhodium) wire which
served as the main furnace windings. H is #36 B and S
gauge platinum wire which functioned as the sensing element
for a temperature controller. This temperature control unit
used the resistance of the sensing element as one arm of an
adjustable Wheatstone bridge which triggered either the addi-
tion or subtraction of furnace power depending upon the need.
The controller was described by Svec et al. (1955) and dif-
fered only in that the voltage output to the furnace was
varied to compensate for the temperature coefficient of re-
sistance of the windings of the furnace. The authors con-
tended that the temperature variation was no greater than
$\pm$ 0.1^{o}C in the range of 100°C to 700°C. I is a #18 B and S
gauge platinum(13% rhodium) wire which served as auxiliary
end windings that decreased the thermal gradient within the
furnace. The power to these windings was supplied by a five
kilowatt Stabline voltage regulator and was varied for each
temperature with a variable transformer. J is magnesium
oxide insulation; the plug in the top of the furnace was
also magnesium oxide. K is a #26 B and S guage platinum
(10% rhodium)-platinum thermocouple whose hot junction was
located about three inches above the center of the furnace.
Another platinum(10% rhodium)-platinum thermocouple was
located with its hot junction at the center of a cylindrical
platinum shell (O) suspended in the center of the furnace.

L is the aluminum oxide center core of the furnace on which the heating element was wound; aluminum oxide cement held the windings in place. M is Dicalite insulation while N is a dead air space which aided in insulating the furnace proper from the room. O is a 0.020-inch thick platinum cylinder three inches high, situated in the center of the furnace, which served to minimize any residual thermal gradients in the vicinity of the sample. P are two platinum disks which helped to prevent the radiation of heat by the sample out of the calorimeter immediately after it had been dropped from the furnace. Q is the sample. R is a steel ring which fitted up against the Transite and had three indentations into which the heads of leveling screws (S) fitted; this kept the furnace in a vertical position. T is the furnace support through which the screws passed. This support led to a swinging mechanism which rotated 180 degrees quite freely and was fastened to the wall. W is a one-inch diameter brass tube that aligned the furnace directly over the calorimeter. A Synthane tube, not shown, fitted snugly on the outside of W and the upper portion of the calorimeter tube and served to prevent heat conduction from the furnace to the calorimeter when the two were aligned. X is the cold junction at 0°C for the thermocouples.

The copper wires which led out of the cold junction were attached to a potentiometer with which the voltage generated by the thermocouples was measured.

Figure 4.   The high temperature resistance furnace and
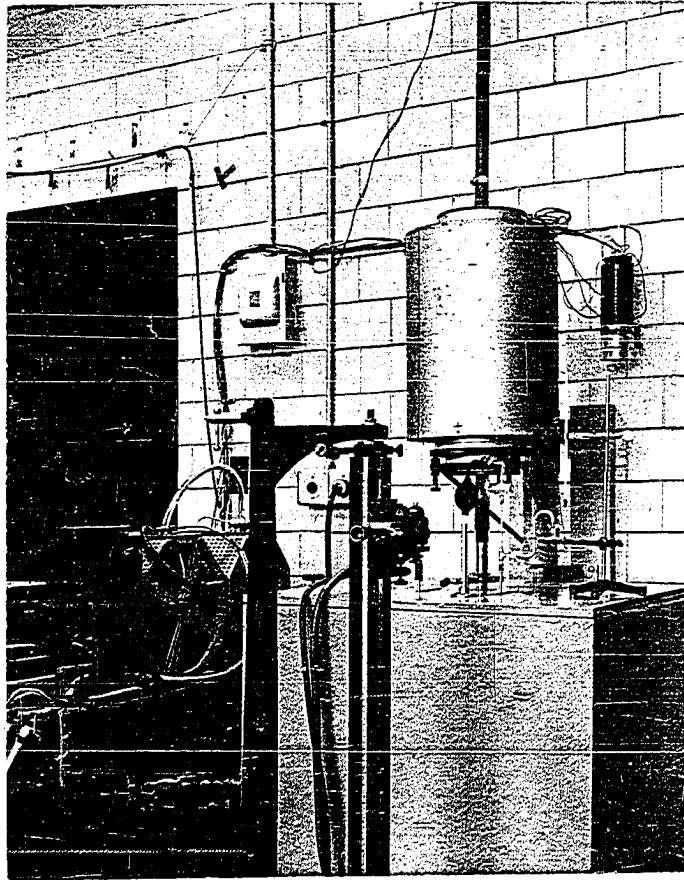   dropping mechanism
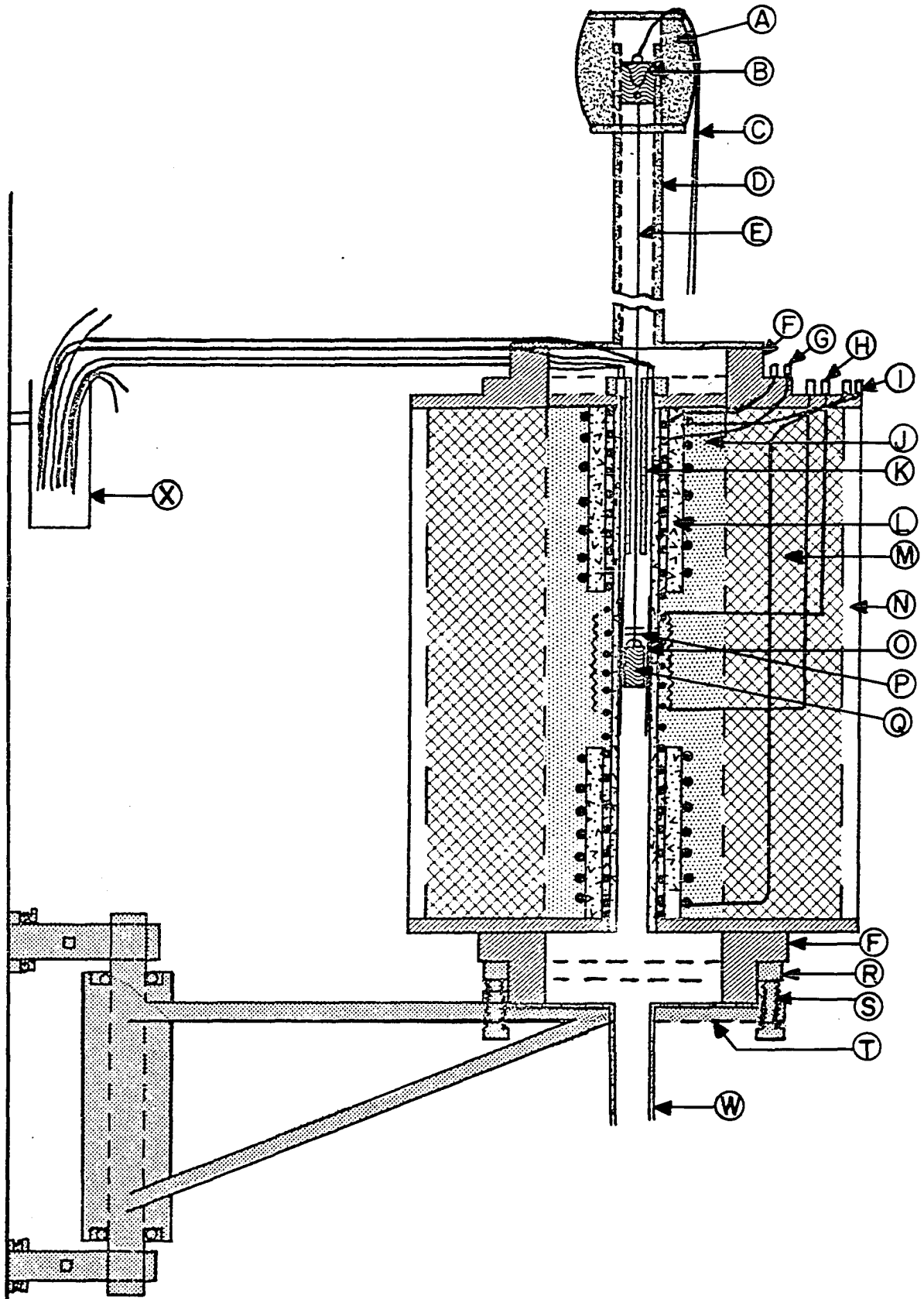
Figure 5. The high temperature furnace and calorimeter in operation

Procedure

After the calorimeter was assembled, the inner glass chamber was flushed with distilled water for a day to remove any soluble impurities and was then rinsed several times with conductivity water. The mercury used in the calorimeter was triply-distilled mercury which had been air distilled and filtered to remove any base-metal impurities. The mercury was poured into a flask and the flask was evacuated to remove any occluded air bubbles.

Conductivity water was obtained from a still operated in the Ames Laboratory. A four-liter suction flask, with one arm of the double end of a two-way stopcock attached to its bottom, was filled with conductivity water. The single end of the two-way stopcock terminated with a ball joint which was sealed with Apiezon-W wax to the oblique-angled tube which had an outer 7/25 standard-taper at its other end. This standard-taper joint was sealed with Apiezon-W wax to the 1/4-inch mercury tube of the calorimeter. The conductivity water was outgassed by evacuating the space above the water with a trapped mechanical vacuum pump. The calorimeter was evacuated through the auxiliary valve (I) and the open arm of the two-way stopcock. After the water had been thoroughly outgassed, the two-way stopcock was turned open to the four-liter suction flask and the calorimeter filled

with conductivity water. The ball joint was then opened and
a funnel with a ball joint at its lower end was attached to
the top of the oblique tube. The mercury was filtered into
this funnel and passed through the water to the top of the
cooling coils. This forced the water in the upper section
of the delivery tube up into the funnel and this water,
which could have dissolved air during its short exposure,
was not used. To form a pool of mercury in the bottom of
the inner glass flask, the auxiliary valve (I) was opened
for short intervals as the mercury entered the calorimeter
chamber until the level of the mercury pool at the bottom of
the chamber was about 1/2 of an inch higher than the end of
the delivery tube.

The oblique tube was removed at the standard-taper and
the glass mercury-accounting assembly sealed to the taper on
the stainless-steel tube with Apiezon wax. The space be-
tween the glass flasks was evacuated and the calorimeter was
allowed to cool in a constant temperature bath to $0^{\circ}C$. An
ice mantle was frozen about the center well by a stream of
helium which had passed through a copper cooling coil im-
mersed in liquid nitrogen which was in a four-quart dewar
flask. The outlet from the coil was attached to a glass
tube which extended to within 1/4 of an inch of the bottom
of the calorimeter well and was centered within the well by
means of two rubber stoppers which fitted about it. The

rate of freezing was controlled by adjusting the rate of flow
of helium. This open-end glass tube directed the flow of
helium to the bottom of the well and localized most of the
freezing in that vicinity. The shape of the mantle was ob-
served through a glass periscope designed for this purpose.
After the lower section of the well was covered with ice,
the open-end glass tube was removed and a copper tube, with
horizontal jets situated near its bottom, was used. By ob-
serving the shape of the mantle and adjusting the height of
the inserted tube, an ice mantle of the desired shape was
frozen.

After the mantle was frozen, water was removed from the
constant-temperature bath and a small amount of alcohol was
added. The constant-temperature bath was stirred well and
more ice added. The heat leak of the calorimeter was deter-
mined and if quite large, more alcohol was added to the bath.
By the addition of alcohol, the heat leak could be adjusted
to a very low value. If too much alcohol was added initially,
some solution was withdrawn and distilled water added.

The enthalpy as a function of temperature was deter-
mined for an empty platinum crucible which was later used to
contain the $\alpha-$ Al_2O_3. A platinum crucible containing a
snugly-fitted tantalum crucible was used for the blank in
the case of the rare earths. The weights of platinum and
tantalum used were slightly greater than the empty crucible

so that a few tenths of a gram of these metals could be added instead of subtracted when the rare earth samples were prepared.

A #26 B and S gauge platinum(13% rhodium) wire was attached to the soft iron piston and the other end extended through the furnace with the piston in the "down" position. A weight was fastened to the other end of the wire and a current passed through the wire to heat it and thus straighten it. The length of wire was measured with a cathetometer and then cut to a specified length. The two radiation shields were placed on the wire and it was fastened to the bail of the sample. The radiation shields were fixed in a horizontal position directly over the crucible. The position of the bottom of the sample was such that with the piston down, the sample was just resting in the bottom of the calorimeter. This distance also coincided with the sample being in the center of the furnace when the piston was in an "up" position. The sample's position in the furnace was adjustable by varying the height of the solenoid.

The temperature of the sample was determined with a platinum(10% rhodium)-platinum thermocouple whose hot junction was 1/4 of an inch from the center of the sample. At the end of each day, this thermocouple was standardized relative to an inserted thermocouple whose hot junction was located within a dummy platinum capsule put in the furnace.

This standardizing thermocouple was checked each day with the freezing points of certified National Bureau of Standards samples.

The ice bath about the calorimeter was packed each morning and about two milliliters of methanol added. This packing was sufficient to maintain a heat leak of less than 1/2 of a calorie per hour for 16 hours. After packing the calorimeter was leveled with a plumb bob.

The circuit to the solenoid was closed and the soft iron piston raised until it was suspended in the center of the solenoid by its magnetic field. The sample was then in the center of the furnace so a string was fastened to the piston and the circuit to the solenoid opened. The furnace was swung over the calorimeter and the synthane coupling used to align the calorimeter and the furnace.

The stopcock, situated on the mercury accounting assembly, was closed and thus required any volume change in the calorimeter to be observable in the capillary. The heat leak was determined by observing the height of mercury in a calibrated capillary at time intervals. The beaker of mercury was weighed noting the position of the mercury meniscus and the time. The beaker of mercury was introduced to the accounting system by forcing a droplet of mercury on the delivery tip; this prevented air bubbles from entering the mercury delivery tube. A few minutes prior to dropping the

circuit to the solenoid was closed and the string detached.
The radiation gate was opened for ten seconds and the cir-
cuit to the solenoid opened, releasing the piston and sample.
The time for the sample to come to equilibrium within the
calorimeter was about 40 minutes. By dropping the sample
after being suspended in the furnace at the same temperature
for various times, it was found that the thermal equilibrium
was attained in the furnace in 60 minutes. The synthetic
sapphire required about two and one-half hours in the fur-
nace and calorimeter to reach equilibrium. After the sample
came to equilibrium in the calorimeter, the height of the
mercury meniscus was adjusted to approximately the value at
which the mercury was previously weighed and the mercury was
reweighed. This weight was corrected for any difference in
the heights of the mercury meniscus. The "after" heat leak
was determined as outlined above for the "before" heat leak.
The intake of mercury for the sample could be expressed by
the equation:

$$\Delta W = \Delta W_t + k (R_1 - R_2) - t_1 r_1 - t_2 r_2, \qquad (39)$$

where ΔW is the intake of mercury due to the sample only,
ΔW_t is total difference in the mercury weighed, k is the
calibration factor of the capillary in milligrams per milli-
meter, R_1 and R_2 are the heights of the mercury meniscus at
the first and second weighings of the mercury, t_1 is the
time interval between recording R_1 and dropping the specimen

and t_2 is the time interval between the dropping time and recording R_2, and r_1 and r_2 are the rates of mercury intake before and after dropping, respectively. By subtracting the mercury intake for the blank from that of the sample at the same temperature and multiplying this difference by 64.631, we determined the enthalpy for the rare earth metal or α- Al_2O_3 at a given temperature.

RESULTS

Aluminum Oxide

Aluminum oxide, n-heptane, benzoic acid, diphenyl ether
and water were recommended by the U. S. Calorimetry Confer-
ence in 1949 as Standards for an intercomparison of calorim-
eters. Aluminum oxide was chosen as the high temperature
calorimetric standard for reasons previously outlined. Gin-
nings and Furukawa (1953) tabulated smoothed values of en-
thalpy and heat capacity for these materials. Furukawa
et al. (1956), Walker et al. (1956), Shomate and Cohen (1955),
Oriani and Murphy (1954), Egan et al. (1950), Ginnings and
Corruccini (1947b) and Shomate and Naylor (1945) have been
the more recent investigators who have determined the high
temperature thermodynamic function of α- Al_2O_3. The in-
vestigations at the National Bureau of Standards by Gin-
nings and Corruccini (1947b) and Furukawa et al. (1956)
agreed within experimental error with one another. Since
the work by this Laboratory for determining the high tem-
perature heat content of aluminum oxide was completed before
the latter paper was available, the comparison was made with
work presented in 1947.

After an evaluation of the errors in the Bunsen "drop"
method, Ginnings and Corruccini (1947b) stated that their

enthalpy was within 0.2% of the true value. The temperature range which they investigated was from $0°C$ to $900°C$.

We have determined the heat content of α- Al_2O_3 from $0°C$ to $1100°C$. The heat content of an empty platinum capsule was determined over this temperature range at 100-degree intervals. This capsule was used to contain the α- Al_2O_3 rod whose heat content was then determined at 100-degree intervals. The heat content of the empty capsule was interpolated to each of the temperatures at which the enthalpy of the sample was measured. By substracting the heat content of the capsule from that of the capsule plus α- Al_2O_3, the enthalpy of the corundum was determined.

Figure 6 shows a plot of the enthalpy (calories mole^{-1}) versus temperature ($°C$) while Figure 7 gives a comparison of the mean specific heat (calories degree^{-1} gram^{-1}) with the data of the National Bureau of Standards up to $900°C$. The data of this study are tabulated up to $1100°C$ where the highest enthalpy value was determined. Table 2 tabulates the heat content at various temperatures and compares the data with those determined by the National Bureau of Standards (Ginnings and Corruccini, 1947b). The reproducibility, listed in the table, was the result of carrying out at least three drops at each temperature and computing the deviation of these points from the mean value of the enthalpy listed. The lower reproducibility at $100°C$ was due to the uncer-
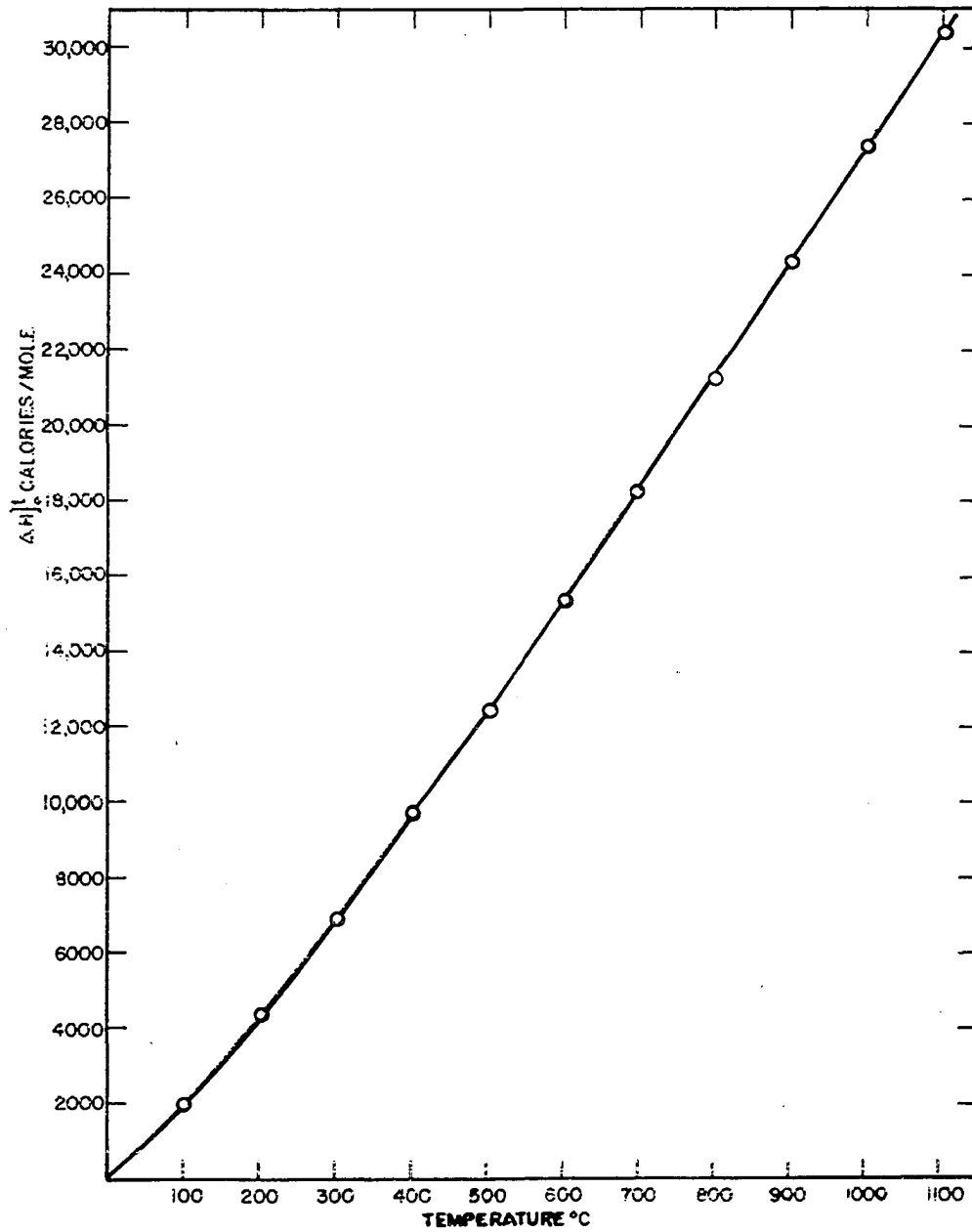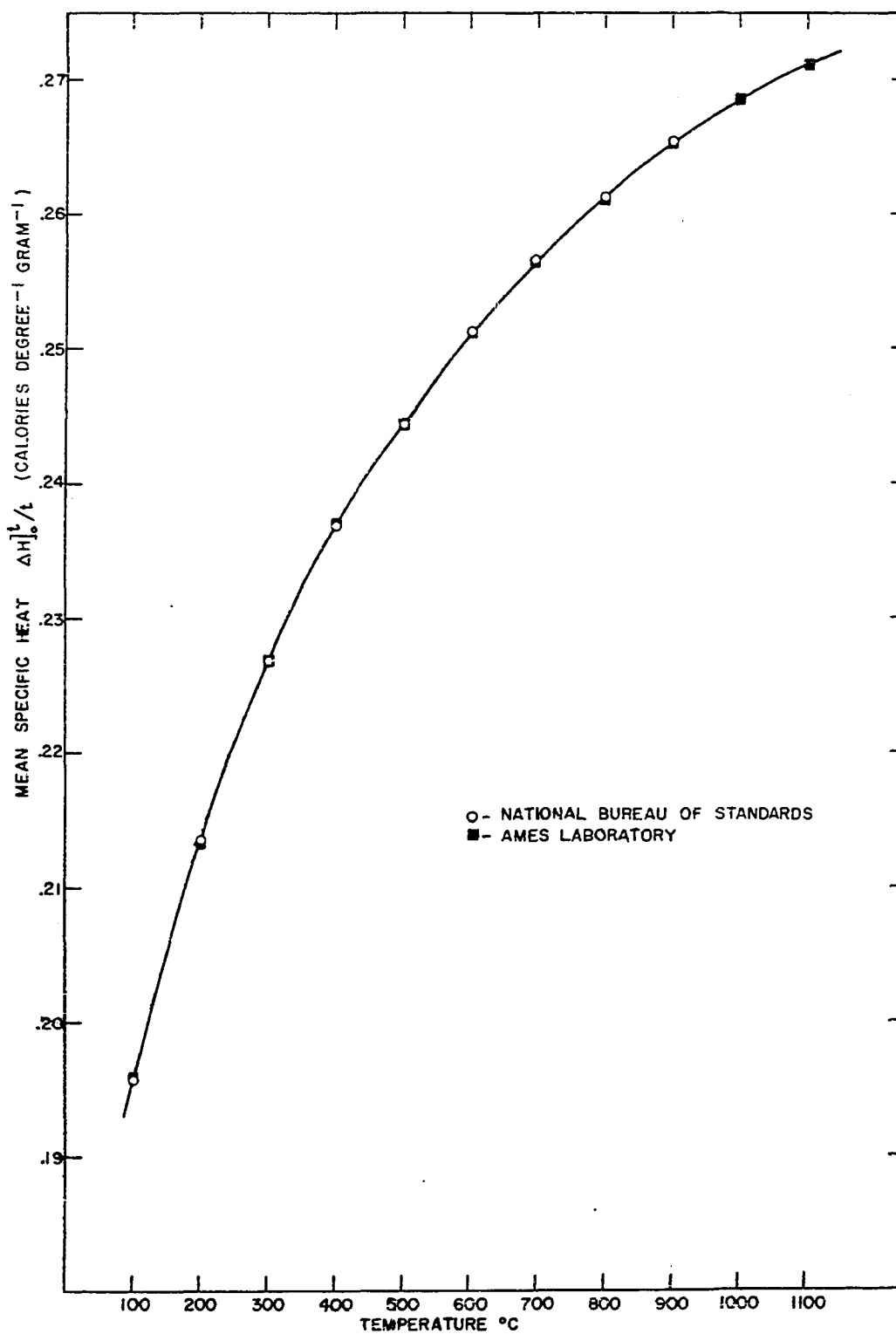
Figure 6. Enthalpy versus temperature for α- Al_2O_3

Figure 7. A comparison of the mean specific heat versus
temperature for α- Al_2O_3

Table 2.   Heat content measurements of α- Al_2O_3

Furn. temp.	Meas. heat of sample (cals. gms.$^{-1}$)	Reproduc- ibility (%)	N.B.S. heat of sample (cals. gms.$^{-1}$)	Deviation of meas. from N.B.S. (%)
100.5	19.70	.21	19.69	+.05
201.0	42.85	.07	42.92	-.16
301.5	68.41	.06	68.40	+.01
402.1	95.29	.11	95.25	+.04
500.9	122.42	.08	122.43	-.01
600.6	150.75	.06	150.80	-.03
698.2	178.94	.03	179.03	-.05
800.0	208.78	.06	208.97	-.10
901.6	239.13	.03	239.23	-.04
1001.5	268.77	.10		
1102.0	298.72	.07		

tainity in the temperature where an error of $0.1^\circ C$ would introduce an error of 0.1% in the enthalpy. The maximum deviation of the data from those of the National Bureau of Standards was at $201^\circ C$. This deviation of 0.16% was within the 0.2% listed as the error in the method. The agreement between the two sets of data was considered sufficient to standardize the apparatus.

Cerium

The enthalpy of cerium was determined from $0^\circ C$ to $1100^\circ C$ at 100-degree intervals except near the transition temperature and melting point where more closely spaced observations were made. The heat content of a platinum capsule containing a snugly-fitted tantalum crucible was determined at 100-degree intervals from $0^\circ C$ to $1100^\circ C$. The weight of platinum and tantalum then used to contain the cerium was adjusted to the weight of these metals employed in the blank determination. For temperatures which did not correspond closely to the temperature at which the enthalpy was determined for the blank, the heat content of the blank was determined by an evaluation of an empirical quadratic equation. The coefficients of this equation were determined by the enthalpy and temperature values of the blank near the temperature in question. The enthalpy of the blank was subtracted from that of the blank plus cerium to determine the heat content of the cerium.

Figure 8 shows a plot of the enthalpy (calories mole^{-1}) versus temperature from $0^\circ C$ to $1100^\circ C$. The enthalpy exhibits large vertical breaks at the transition and melting points. Figure 9 illustrates the behavior of the derived heat capacity (calories degree^{-1} mole^{-1}) over this temperature range. Table 3 lists the measured heat content of

cerium and the temperature at which the value was determined. The third column in Table 3 gives the reproducibility of the measured value obtained in the manner outlined for α- Al_2O_3 and column five tabulates the deviation of values calculated with an empirical equation from the experimental ones. Table 4 lists the calculated thermodynamic functions of cerium from 273.2°K to 1373°K at 50-degree intervals. The value of $S^O - S_O^O$ at 273.2°K was obtained from the work of Parkinson et al. (1951).

A least-squares treatment of the data below the transition temperature showed that the data could be satisfactorily fitted by the three parameter cubic equation:

$$\Delta H]_O^t = 6.366t + 1.474 \times 10^{-3}t^2 + 3.954 \times 10^{-7}t^3, \tag{40}$$

where $\Delta H]_O^t$ is the enthalpy (calories mole^{-1}) and t is the temperature (°C). This equation is valid from 0°C to 730°C and has an average deviation of the calculated from the experimental points of 0.14%. By differentiating this equation with respect to temperature, we found the following equation for expressing the heat capacity (calories degree^{-1} mole^{-1}) as a function of temperature (°C):

$$C_p = 6.366 + 2.948 \times 10^{-3}t + 1.186 \times 10^{-6}t^2. \tag{41}$$

The entropy can be evaluated utilizing the expression:

$$\Delta S = \int_O^t C_p dt/(t + 273.2) \tag{42}$$

and upon substitution of equation 41 and integration, this gave

the equation:

$$\Delta S]_0^t = 13.01 \ \log(t + 273.2)/273.2 + 2.62 \times 10^{-3}t$$
$$+ \ 5.932 \times 10^{-7}t^2, \tag{43}$$

where $\Delta S]_0^t$ is the entropy (calories degree^{-1} mole^{-1}) and t is the temperature ($^\circ$C). The free energy function was evaluated by the expression:

$$- (F^\circ - H_{273.2}^\circ)/T = S^\circ - S_0^\circ - (H^\circ - H_{273.2}^\circ)/T, \tag{44}$$

where T is the temperature ($^\circ$K) and the expression on the left is in calories degree^{-1} mole^{-1}.

Between the transition temperature and the melting point, the heat content relative to 0°C can be expressed by the equation:

$$\Delta H_0^t = 9.047t - 318, \tag{45}$$

where $\Delta H]_0^t$ is the enthalpy (calories degree^{-1} mole^{-1}) and t is the temperature ($^\circ$C). This equation is valid from 730°C to 804°C with an average deviation of the calculated from the measured values of 0.02%. The heat capacity has the constant value of 9.05 calories per degree per mole over this temperature range. The change in entropy (calories degree^{-1} mole^{-1}) in this temperature interval is given by the equation:

$$\Delta S]_{730}^t = 20.84 \ \log(t + 273.2)/1003.2, \tag{46}$$

The enthalpy (calories mole^{-1}) of liquid cerium from 804°C to 1100°C can be expressed as a function of temperature ($^\circ$C) by the equation:

$$\Delta H]_o^t = 9.345t + 680, \tag{47}$$

with an average deviation from the experimental points of
0.04%. Over this same temperature interval, the heat ca-
pacity exhibits the constant value of 9.35 calories per de-
gree per mole while the entropy (calories degree^{-1} mole^{-1})
can be expressed as:

$$\Delta S]_{804}^t = 21.52 \log(t + 273.2)/1077.2. \tag{48}$$

The transition temperature of 730°C utilized in these
calculations was reported by Spedding et al. (1957a) who
measured the temperature coefficient of resistivity of the
metal while Spedding and Daane (1956) employed thermal anal-
ysis to determine the melting point of cerium, 804°C. The
heat of transition was determined by evaluating equations 40
from equation 45. Similarly, the heat of fusion was evalu-
ated by subtracting the enthalpy of equation 45 from equa-
tion 47 which were calculated at 804°C, the melting point.
The errors in the heats of transition and fusion were cal-
culated from the average deviation of the calculated from
the measured enthalpies. The heat of transition was found
to be 700 calories per mole and the heat of fusion to be
1238 calories per mole with uncertainties of 1.2% and 0.3%,
respectively. The entropies of transition and fusion were
calculated by dividing the heats of transition and fusion by
their respective absolute temperatures and were found to be
0.70 and 1.15 calories per degree per mole.
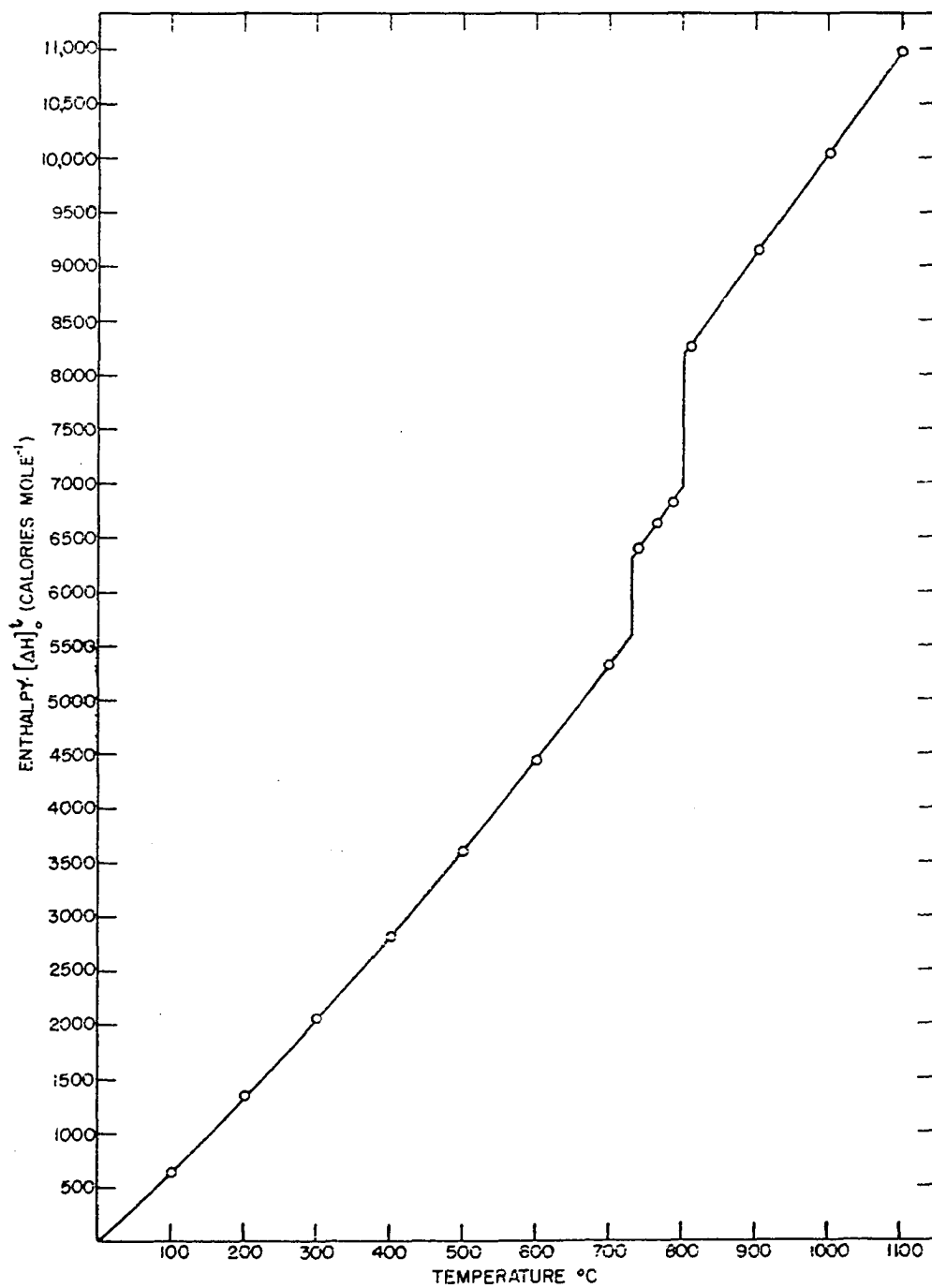
Figure 8.   Enthalpy versus temperature for cerium
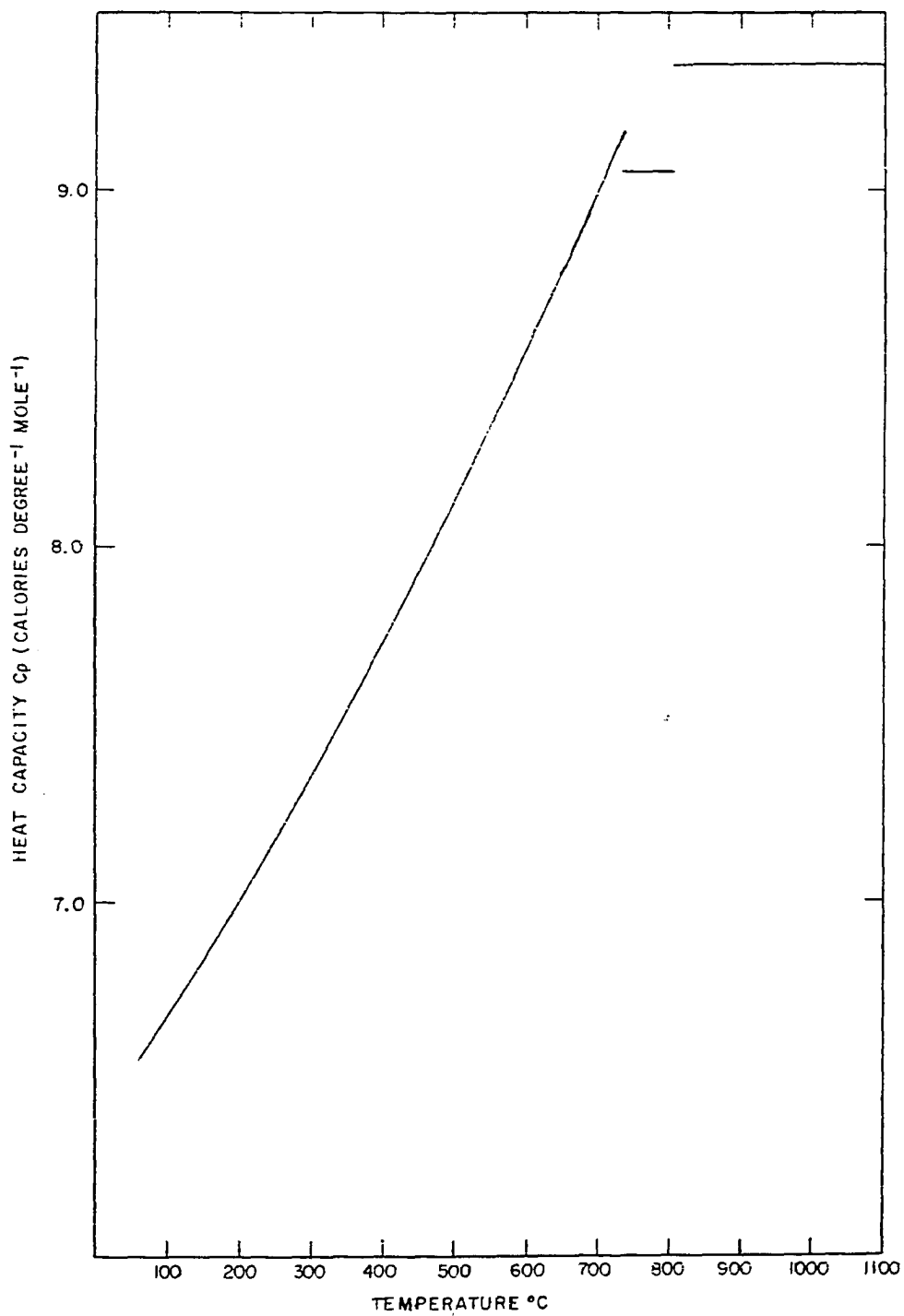
Figure 9.   Heat capacity versus temperature for cerium

Table 3.   Heat content measurements of cerium

Furn. temp. (°C)	Meas. heat of sample (cals. mole^{-1})	Reproducibility (%)	Calculated heat of sample (cals. mole^{-1})	Deviation of calculated from observed (%)
100.3	652.4	.20	653.7	+.20
202.1	1348	.10	1350	+.13
300.5	2061	.07	2057	−.19
400.3	2808	.04	2810	+.09
500.7	3600	.07	3607	+.18
600.7	4446	.05	4442	−.11
701.3	5323	.03	5326	+.05
743.0	6403	.02	6404	+.02
767.0	6622	.05	6621	−.02
789.7	6825	.04	6826	+.02
811.4	8266	.03	8257	−.11
905.7	9141	.04	9141	+.00
1002.2	10,043	.13	10,045	+.02
1100.8	10,970	.06	10,973	+.03

Table 4.   Thermodynamic functions of cerium (calories degree^{-1} mole^{-1})

$T^{\circ}K$	$C_p^{\,o}$	$S^o - S_o^o$	$\dfrac{H^o - H^o_{273.2}}{T}$	$-\dfrac{F^o - H^o_{273.2}}{T}$
273.2	6.37	16.14	0	16.14
323.2	6.52	17.22	.996	16.22
373.2	6.67	18.17	1.746	16.42
423.2	6.84	19.01	2.338	16.67
473.2	7.01	19.78	2.822	16.96
523.2	7.18	20.51	3.230	17.28
573.2	7.36	21.17	3.582	17.59
623.2	7.55	21.79	3.892	17.90
673.2	7.74	22.38	4.170	18.21
723.2	7.94	22.94	4.424	18.52
773.2	8.14	23.48	4.657	18.82
823.2	8.35	23.99	4.875	19.11
873.2	8.57	24.49	5.080	19.41
923.2	8.79	24.98	5.274	19.71
973.2	9.01	25.45	5.460	19.99
1003.2	9.15	25.73	5.568	20.16
1003.2	9.05	26.43	6.266	20.16
1048.2	9.05	26.83	6.385	20.44
1077.2	9.05	27.07	6.457	20.61
1077.2	9.35	28.22	7.606	20.61

Table 4. (Continued)

$T^{\circ}K$	C_p°	$S^{\circ} - S_o^{\circ}$	$\dfrac{H^{\circ} - H^{\circ}_{273.2}}{T}$	$-\dfrac{F^{\circ} - H^{\circ}_{273.2}}{T}$
1123.2	9.35	28.61	7.678	20.93
1173.2	9.35	29.02	7.749	21.27
1223.2	9.35	29.41	7.814	21.60
1273.2	9.35	29.78	7.875	21.90
1323.2	9.35	30.14	7.931	22.21
1373.2	9.35	30.49	7.983	22.51

Praseodymium

The heat content of praseodymium was determined from $0^{\circ}C$ to $875^{\circ}C$ at 100-degree intervals with more closely spaced measurements near the transition at $800^{\circ}C$. The praseodymium leaked through the crucible at a temperature near the melting point, destroying the sample. The metal had been melted in the tantalum crucible during the preparation of the sample without any leakage. A simple explanation of the failure of the tantalum crucible was not obvious and this difficulty was not encountered with the other rare earth metals studied. The heat content of the container was accounted for in the manner outlined for cerium.

Figure 10 illustrates a plot of enthalpy (calories mole^{-1}) versus temperature from 0°C to 876°C with a vertical break in the curve occuring at the transition temperature. Figure 11 represents the curve of heat capacity (calories degree^{-1} mole^{-1}) as a function of temperature from 0°C to the transition temperature, 798°C. Table 5 lists the measured and calculated heat contents at various temperatures with the corresponding reproducibilities and deviations. Table 6 gives the calculated thermodynamic functions for praseodymium at 50-degree intervals up to 798°C. The value of S° − S$_0^o$ at 273.2°K was obtained from the work of Parkinson et al. (1951).

A least-squares treatment of the enthalpy (calories mole^{-1}) and temperature for a three parameter equation gave:

$$\Delta H\big]_0^t = 6.592t + 5.104\text{x}10^{-4}t^2 + 1.543\text{x}10^{-6}t^3, \qquad (49)$$

which fits the experimental points from 0°C to 798°C with an average deviation of 0.26% between the measured and calculated points. The heat capacity (calories degree^{-1} mole^{-1}) can be represented as a function of temperature (°C) over the same temperature interval by the equation:

$$C_p = 6.592 + 1.021\text{x}10^{-3}t + 4.628\text{x}10^{-6}t^2, \qquad (50)$$

The change in entropy (calories degree^{-1} mole^{-1}) as a function of temperature from 0°C to 798°C can be calculated from the expression:

$$\Delta S]_0^t = 15.334 \, \log(t + 273.2)/273.2 - 243 \times 10^{-4} t$$
$$+ 2.314 \times 10^{-6} t^2. \tag{51}$$

Since only two experimental points were measured above the transition temperature, the thermodynamic functions were not calculated in this temperature region. By a comparison of the temperature interval between the transition temperature and the melting point for the other rare earths studied, it was assumed that the enthalpy would vary linearly with temperature and an empirical linear equation was calculated from the two measured points. This equation was used to evaluate the higher value of the enthalpy and equation 49 was used to compute the lower value at the transition temperature. Since the "drops" below the transition were carried out at 793.3°C, the value of 798°C as determined by Spedding and Daane (1956), utilizing thermal analysis, was used as the transition temperature. The error in the heat of transition was evaluated utilizing the average deviation of the calculated from the measured values below the transition point. The heat of transition was computed to be 722 calories per mole with an error of 3.8% at 798°C while the entropy of transition was calculated as 0.67 calories per degree per mole.
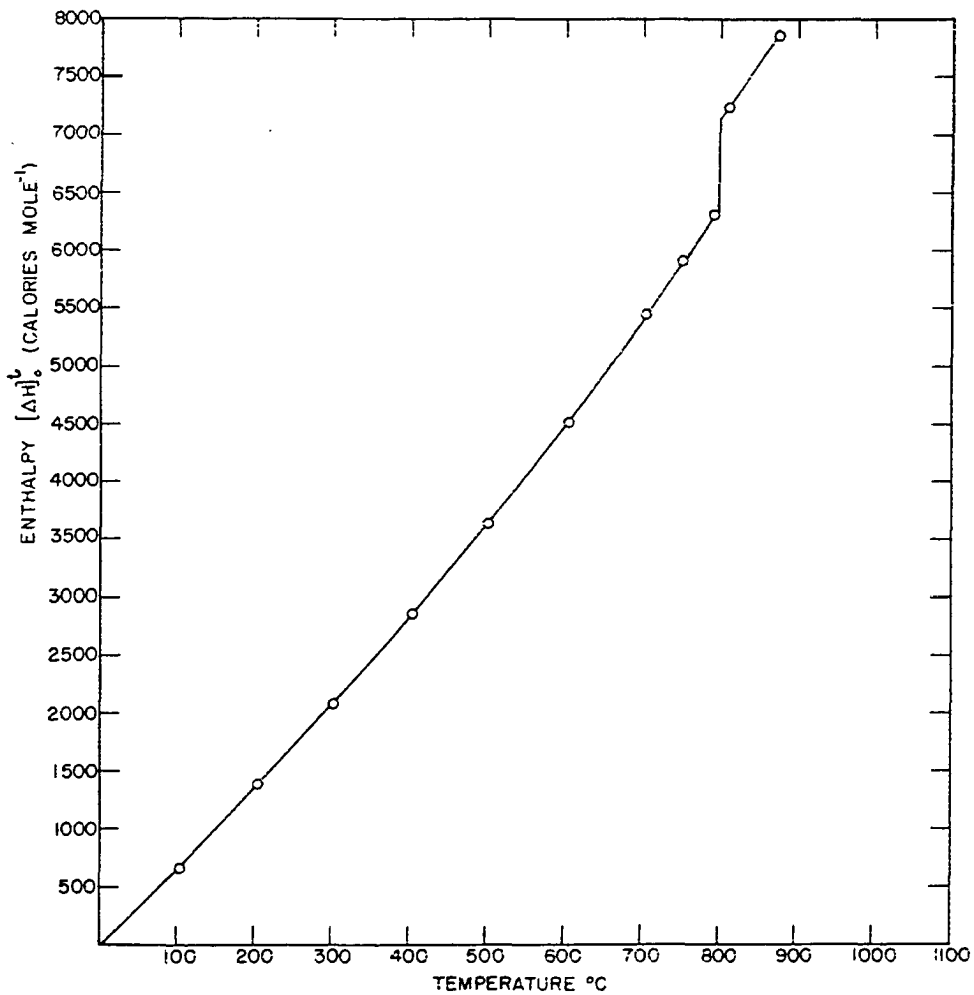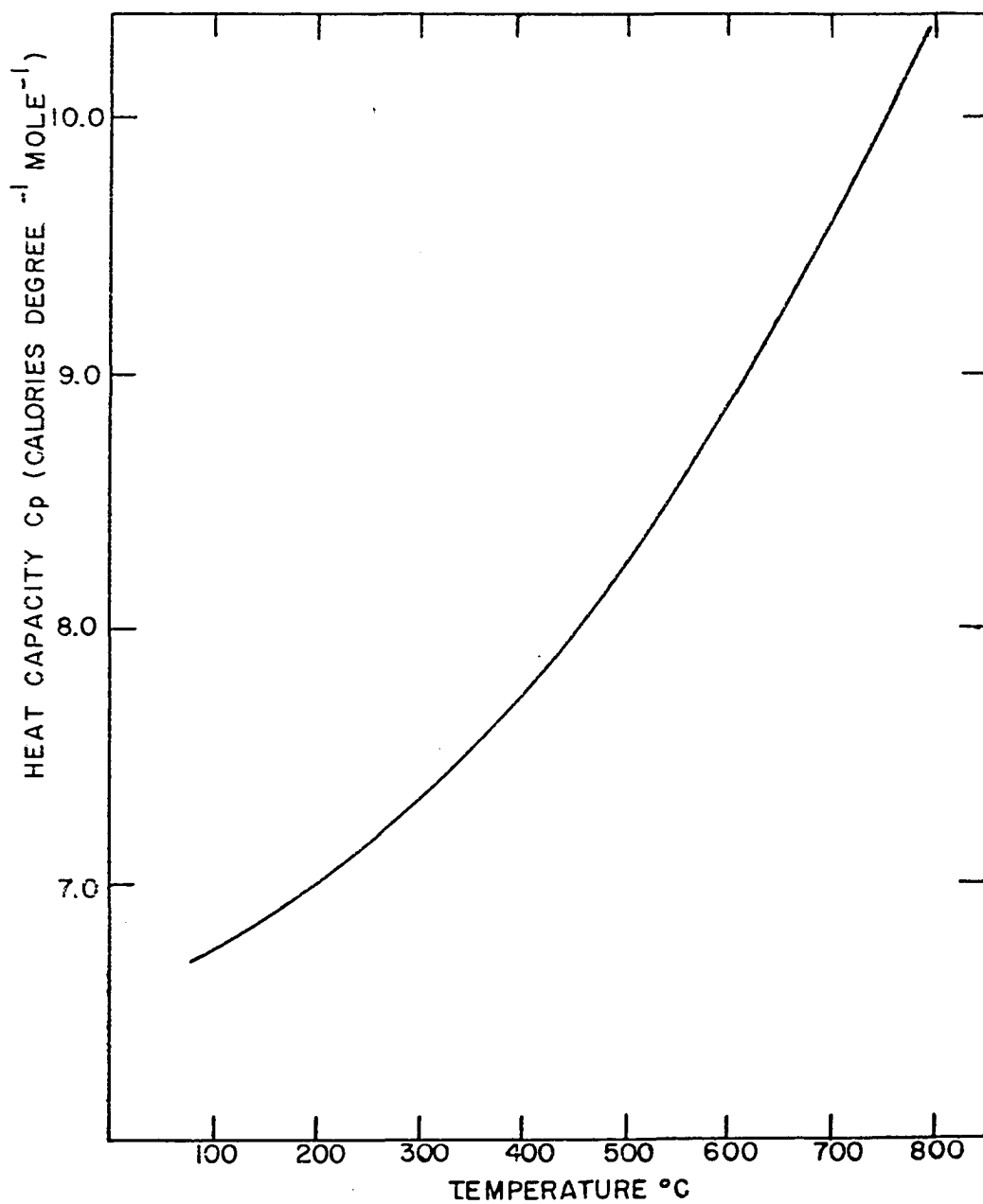
Figure 10. Enthalpy versus temperature for praseodymium

Figure 11. Heat capacity versus temperature for praseodymium

Table 5. Heat content measurements of praseodymium

Furn. temp. (°C)	Meas. heat of sample (cals. mole⁻¹)	Reproduc-ibility (%)	Calculated heat of sample (cals. mole⁻¹)	Deviation of calculated from observed (%)
100.5	660.2	.20	668.7	+1.29
202.3	1364	.13	1367	+ .21
302.4	2085	.09	2083	− .09
401.8	2837	.04	2831	− .22
503.7	3645	.06	3647	+ .06
605.0	4505	.04	4517	+ .25
705.4	5439	.05	5445	+.12
753.4	5906	.03	5914	+.12
793.3	6321	.05	6321	.00
813.4	7239	.08		
876.6	7839	.10		

Neodymium

The heat content of neodymium was determined from 0°C to 1100°C as a function of temperature. The weights of platinum and tantalum containers were the same as employed in the blank experiment. Figure 12 gives the behavior of the enthalpy (calories mole⁻¹) from 0°C to 1100°C. It should be

Table 6. Thermodynamic functions of praseodymium (calories degree^{-1} mole^{-1})

$T^\circ K$	$C_p{}^\circ$	$S^\circ - S_0^\circ$	$\dfrac{H^\circ - H^\circ{}_{273.2}}{T}$	$- \dfrac{F^\circ - H^\circ{}_{273.2}}{T}$
273.2	6.59	17.03	0	17.03
323.2	6.65	18.15	1.024	17.13
373.2	6.74	19.11	1.784	17.33
423.2	6.84	19.95	2.377	17.57
473.2	6.98	20.73	2.855	17.87
523.2	7.14	21.44	3.257	18.18
573.2	7.32	22.10	3.604	18.50
623.2	7.52	22.71	3.909	18.80
673.2	7.74	23.31	4.186	19.13
723.2	7.99	23.87	4.400	19.47
773.2	8.26	24.42	4.679	19.74
823.2	8.55	24.95	4.906	20.04
873.2	8.87	25.45	5.123	20.33
923.2	9.21	25.97	5.336	20.63
973.2	9.57	26.45	5.544	20.91
1023.2	9.96	26.94	5.752	21.19
1071.2	10.35	27.41	5.949	21.46
1071.2		28.08	6.623	21.46

noted that the enthalpy value at 985°C, while the last measurement in the solid region, was 35 degrees below the melting point. This was because the enthalpy determinations between 985°C and 1020°C were above the linear curve generated by the first two measurements in this transition range. Hence, some type of anomalous behavior was detected just below the melting point and may have been due to a premelting phenomenon. Figure 13 illustrates the temperature dependence of the heat capacity (calories degree^{-1} mole^{-1}) from 0°C to 1100°C. Table 7 lists the measured and calculated heat contents with their respective reproducibilities and deviations. A tabulation of the thermodynamic functions from 0°C to 1100°C at 50-degree intervals is given in Table 8. The value of $S° - S_0°$ at 273.2°K was obtained from the data of Parkinson et al. (1951).

The method of least squares was employed to fit three empirical equations to the data in the three temperature ranges. The data from 0°C to 862°C could be fitted with the three parameter equation:

$$\Delta H]_0^t = 6.518t + 1.239 \times 10^{-3}t^2 + 1.085 \times 10^{-6}t^3, \quad (52)$$

where $\Delta H]_0^t$ is the enthalpy (calories mole^{-1}) and t is the temperature (°C). The average deviation of the calculated from the measured values is 0.2%. By differentiating this equation with respect to temperature, the heat capacity as a function of temperature (°C) was found to be:

$$C_p = 6.518 + 2.477 \times 10^{-3} t + 3.256 \times 10^{-6} t^2. \qquad (53)$$

The entropy (calories degree^{-1} mole^{-1}) relative to 0°C over this temperature range is represented by the expression:

$$\Delta S]_0^t = 14.012 \log(t + 273.2)/273.2 + 1.588 \times 10^{-3} t$$
$$+ 1.623 \times 10^{-6} t^2. \qquad (54)$$

The heat content (calories mole^{-1}) varies linearly with temperature from 862°C to 1024°C and can be expressed as:

$$\Delta H]_0^t = 10.654t - 1238, \qquad (55)$$

with an average deviation of 0.003% while the heat capacity exhibits the constant value of 10.65 calories per degree per mole. The entropy (calories degree^{-1} mole^{-1}) relative to 862°C can be calculated from the equation:

$$\Delta S]_{862}^t = 24.54 \log(t + 2732)/1135.2. \qquad (56)$$

In the liquid range from 1024°C to 1100°C, the enthalpy is expressed by:

$$\Delta H]_0^t = 11.661t - 564, \qquad (57)$$

with an average deviation of 0.17% from the observed values. The heat capacity has the value of 11.66 calories per degree per mole while the entropy (calories degree^{-1} mole^{-1}) calculated from this value can be expressed with the equation:

$$\Delta S]_{1024}^t = 26.86 \log(t + 273.2)/1297, \qquad (58)$$

Through studies of the coefficient of resistivity, Spedding, et al. (1957a) determined the transition temperature to be 862°C while Spedding and Daane (1956), utilizing thermal analysis, found 1024°C to be the melting point of
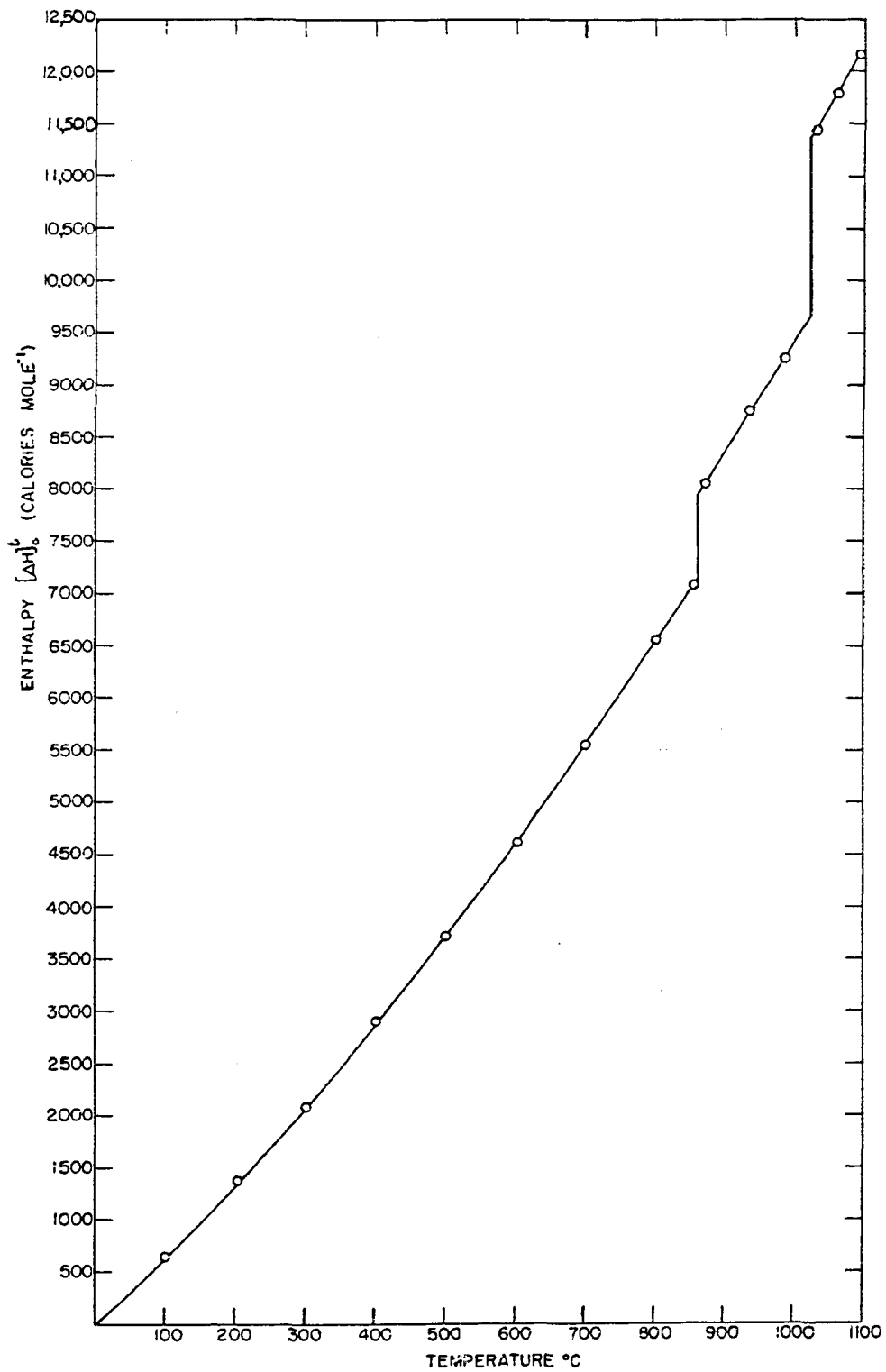
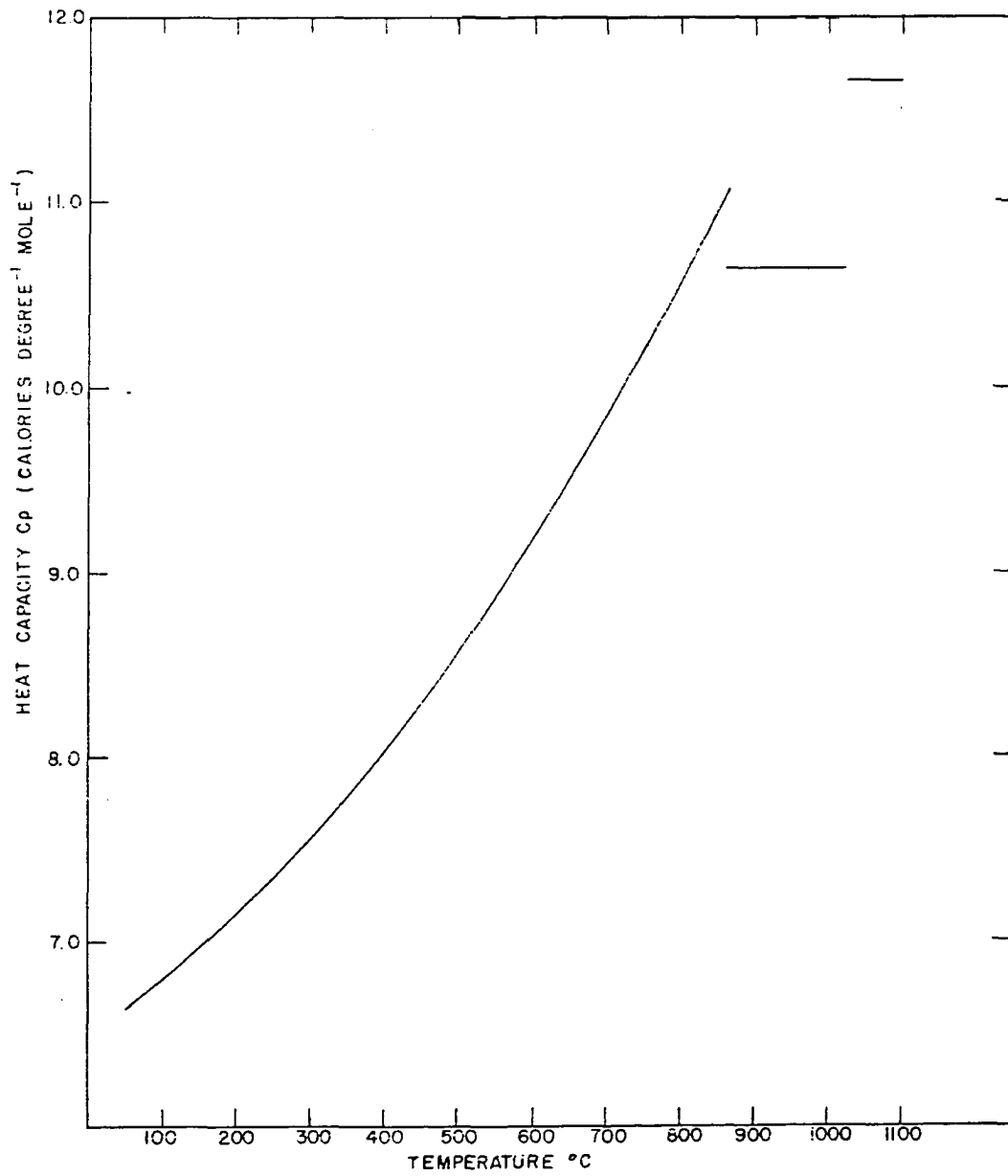Figure 12.   Enthalpy versus temperature for neodymium

Figure 13. Heat capacity versus temperature for neodymium

Table 7. Heat content measurements of neodymium

Furn. temp. (^oC)	Meas. heat of sample (cals. mole^{-1})	Reproducibility (%)	Calculated heat of sample (cals. mole^{-1})	Deviation of calculated from observed (%)
99.3	657.0	.25	660.6	+.55
202.3	1382	.10	1378	-.25
300.5	2097	.06	2100	+.13
400.6	2876	.01	2880	+.12
501.4	3709	.13	3716	+.21
602.6	4608	.09	4615	+.16
701.0	5545	.03	5551	+.11
801.2	6572	.05	6575	+.05
851.8	7105	.09	7121	+.23
872.5	8058	.08	8058	+.00
938.9	8764	.05	8765	+.01
984.8	9254	.08	9254	+.00
1030.2	11,432	.06	11,449	+.15
1059.9	11,822	.08	11,795	-.23
1093.7	12,174	.08	12,189	+.13

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Table 8. Thermodynamic functions of neodymium (calories degree^{-1} mole^{-1})

T$^{\circ}$K	C_p°	$S^{\circ} - S_0^{\circ}$	$\dfrac{H^{\circ} - H^{\circ}_{273.2}}{T}$	$-\dfrac{F^{\circ} - H^{\circ}_{273.2}}{T}$
273.2	6.52	17.07	0	17.07
323.2	6.64	18.18	1.018	17.16
373.2	6.80	19.15	1.783	17.37
423.2	6.96	20.01	2.384	17.63
473.2	7.15	20.80	2.880	17.92
523.2	7.34	21.52	3.293	18.23
573.2	7.55	22.21	3.655	18.55
623.2	7.79	22.85	3.979	18.87
673.2	8.03	23.46	4.269	19.19
723.2	8.29	24.03	4.540	19.49
773.2	8.57	24.60	4.792	19.81
823.2	8.86	25.14	5.030	20.11
873.2	9.18	25.68	5.258	20.42
923.2	9.51	26.20	5.479	20.72
973.2	9.85	26.71	5.695	21.01
1023.2	10.21	27.22	5.906	21.31
1073.2	10.58	27.71	6.115	21.59
1135.2	11.08	28.32	6.372	21.95
1135.2	10.65	28.95	7.000	21.95
1173.2	10.65	29.30	7.119	22.18

Table 8. (Continued)

$T^{\circ}K$	$C_p{}^{\circ}$	$S^{\circ} - S_0^{\circ}$	$\dfrac{H^{\circ} - H^{\circ}{}_{273.2}}{T}$	$-\dfrac{F^{\circ} - H^{\circ}{}_{273.2}}{T}$
1223.2	10.65	29.75	7.263	22.49
1273.2	10.65	30.17	7.397	22.77
1297.2	10.65	30.37	7.457	22.91
1297.2	11.66	31.68	8.770	22.91
1323.2	11.66	31.91	8.826	23.08
1373.2	11.66	32.34	8.932	23.41

neodymium. Evaluating equations 52 and 55 at $862^{\circ}C$ and subtracting the value found for equation 52 from the value of equation 55, the heat of transition was found to be 713 calories per mole with an error of 2%. The heat of fusion was calculated by evaluating equations 55 and 57 at $1024^{\circ}C$ and subtracting the value of 55 from equation 57. The value calculated was 1705 calories per mole with an error of 1.1%. The errors for these values were computed in the same manner as the errors for the heats of transition and fusion of cerium. The entropies of transition and fusion are 0.63 and 1.31 calories per degree per mole, respectively.

Samarium

The heat content of samarium was determined at 100-
degree intervals from 0°C to 1125°C. The enthalpy and the
heat capacity were found to be somewhat greater than those
determined for the other rare earth metals studied. The
heats of transition and fusion were also greater.

Figure 14 gives a curve of the enthalpy (calories
mole^{-1}) versus temperature from 0°C to 1125°C with discon-
tinuities occuring at the transition and melting points.
Figure 15 illustrates the behavior of the heat capacity
(calories degree^{-1} mole^{-1}) as a function of temperature
(°C). It should be noted that the shape of the curve is
quite different from those obtained for the other rare
earths. Table 9 gives experimental and calculated heat
contents with their corresponding reproducibilities and
deviations. Table 10 lists the calculated thermodynamic
functions at 50-degree intervals where the $S^o - S_o^o$ value
at 273.2°C was obtained from the data of Hill (1957).

The least-squares method was applied to the data in
the three temperature regions and the data fitted to three
empirical equations. From 0°C to 917°C the enthalpy (cal-
ories mole^{-1}) can be expressed as a function of temperature
by the equation:

$$\Delta H]_0^t = 11.804t + 4.776 \times 10^{-4} t^2$$

$$- 3.477 \times 10^3 \log(t + 273.2)/273.2 \quad (59)$$

with an average deviation of 0.4%. The heat capacity (calories degree^{-1} mole^{-1}) was obtained by differentiating equation 59 with respect to temperature ($^\circ$C) to yield:

$$C_p = 11.80 + 9.553 \times 10^{-4} t - (1.510 \times 10^3)/(t + 273.2). \quad (60)$$

The entropy (calories degree^{-1} mole^{-1}) as a function of temperature ($^\circ$C) was derivable from the heat capacity equation and gave the result:

$$\Delta S]_0^t = 26.584 \log(t + 273.2)/273.2 + 9.553 \times 10^{-4} t$$

$$+ 1.510 \times 10^3/(t + 273.2) - 5.53. \quad (61)$$

The heat content (calories mole^{-1}) between 917°C and 1072°C varies linearly with temperature and can be expressed as:

$$\Delta H]_0^t = 11.216t - 538, \quad (62)$$

with an average deviation of 0.06%. The heat capacity has the constant value of 11.22 calories per degree per mole in this temperature interval while the entropy (calories degree^{-1} mole^{-1}) relative to 917°C can be computed from the relation:

$$\Delta S]_{917}^t = 25.83 \log(t + 273.2)/1190. \quad (63)$$

The enthalpy (calories mole^{-1}) of the liquid from 1072°C to 1125°C can also be fitted with a two parameter equation:

$$\Delta H]_0^t = 14.041t - 1505, \quad (64)$$

with an average deviation of 0.09% while the heat capacity

is constant at 14.04 calories per degree per mole. The en-
tropy (calories degree^{-1} mole^{-1}) relative to 1072°C can be
expressed by the equation:

$$\Delta S]^{t}_{1072} = 32.34 \; \log(t + 273.2)/1345. \qquad (65)$$

Spedding and Daane (1956), by means of thermal analysis,
determined the transition temperature to be 917°C and the
melting point to be 1052°C; the samarium used in this deter-
mination contained 0.2% europium.

By carrying out successive "drops" at five-degree tem-
perature intervals above the reported melting point, the
melting point of samarium was found to be 1072 $\pm$ 5°C. This
value was used as the melting point for computing the heat
of fusion. Equations 59 and 62 were evaluated at 917°C and
the value for the heat of transition, obtained by subtract-
ing the enthalpy of equation 59 from equation 62, is 744
calories per mole with an error of 5%. The enthalpies from
equations 62 and 64 at 1072°C were subtracted and the value
of 2061 calories per mole with an error of 0.7% was found
for the heat of fusion. The entropies of transition and
fusion were calculated to be 0.63 and 1.53 calories per de-
gree per mole, respectively.

Figure 16 gives a comparison of the heat capacities
(calories degree^{-1} mole^{-1}) for cerium, praseodymium, neodym-
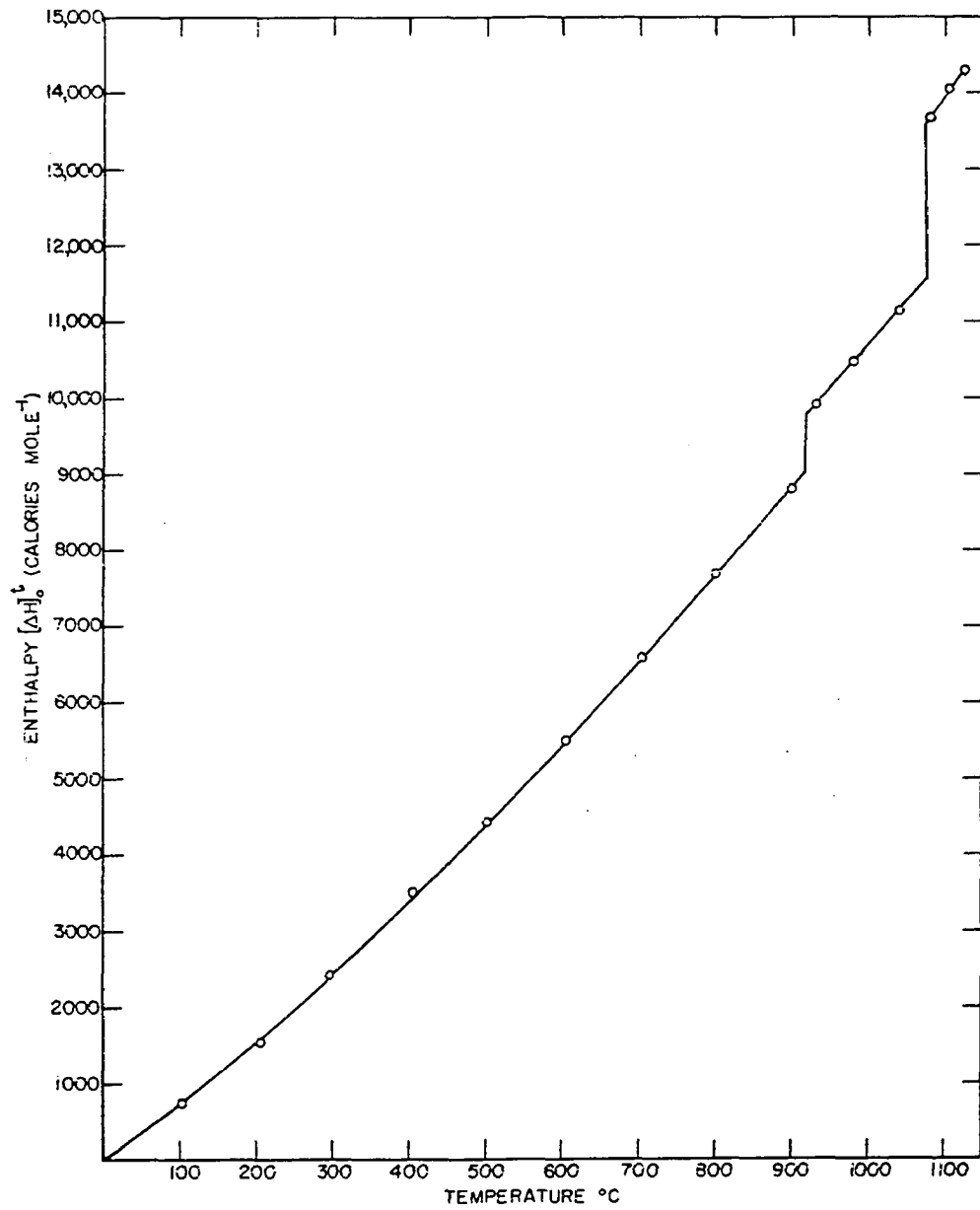ium and samarium from 0°C to their respective transition
temperatures.

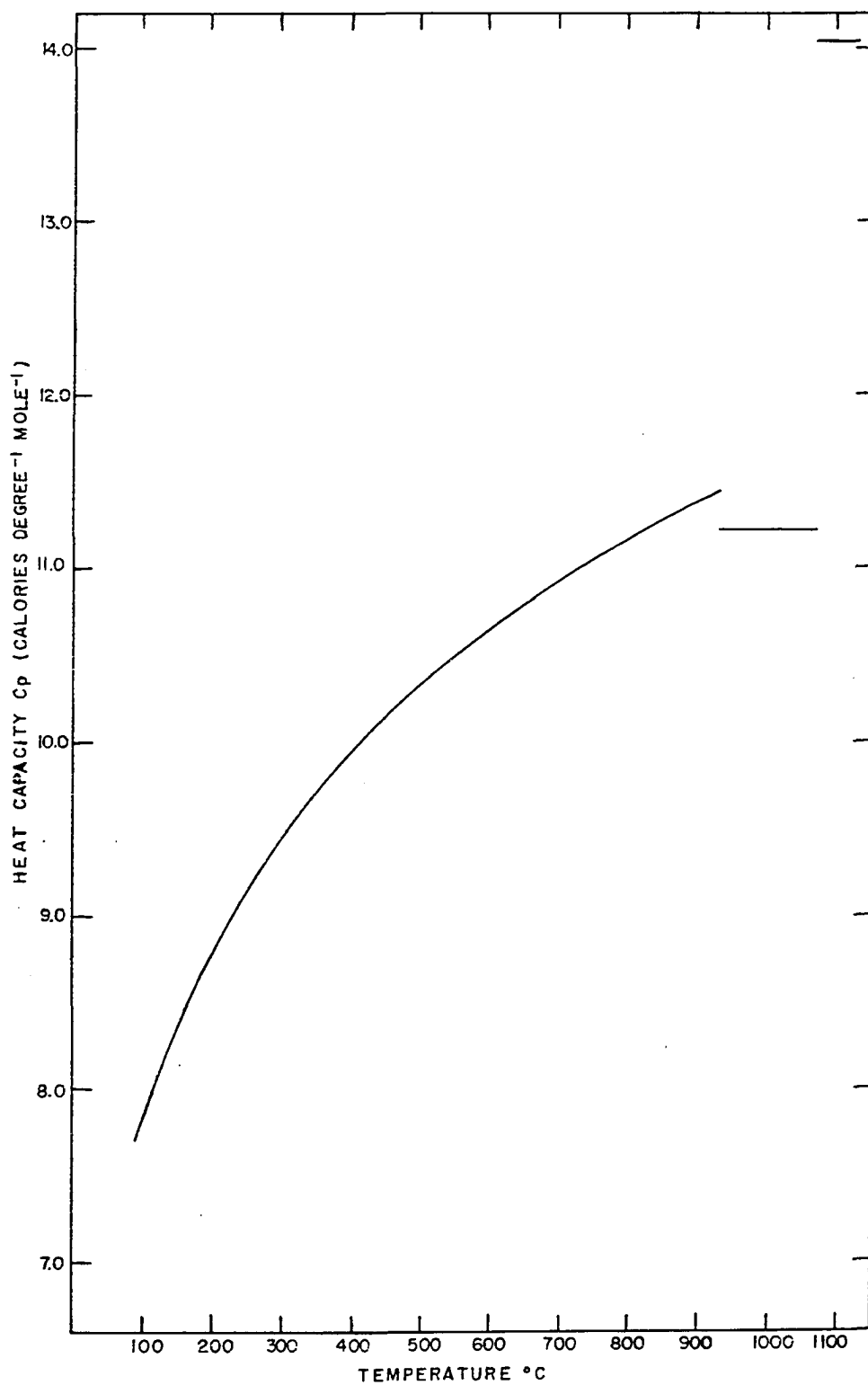Figure 14. Enthalpy versus temperature for samarium

Figure 15. Heat capacity versus temperature for samarium

Table 9.   Heat content measurements of samarium

Furn. temp. (^{o}C)	Meas. heat of sample (cals. mole^{-1})	Reproducibility (%)	Calculated heat of sample (cals. mole^{-1})	Deviation of calculated from observed (%)
101.4	726.0	.23	725.1	-.18
200.6	1540	.05	1554	+.89
293.7	2412	.10	2406	-.27
400.6	3483	.12	3442	-1.16
501.2	4439	.05	4462	+.53
601.0	5493	.06	5510	+.32
700.7	6593	.09	6587	-.09
799.4	7674	.05	7676	+.02
899.8	8797	.04	8807	+.12
928.2	9878	.11	9873	-.05
976.9	10,411	.07	10,419	+.08
1038.0	11,109	.05	11,105	-.04
1078.9	13,636	.04	13,644	+.06
1103.7	14,013	.09	13,993	-.14
1124.7	14,277	.04	14,287	+.07

Table 10. Thermodynamic functions of samarium (calories degree^{-1} mole^{-1})

T$^\circ$K	$C_p{}^\circ$	$S^\circ - S_0^\circ$	$\dfrac{H^\circ - H^\circ{}_{273.2}}{T}$	$-\dfrac{F^\circ - H^\circ{}_{273.2}}{T}$
273.2	6.27	16.35	0	16.35
323.2	7.18	17.48	1.168	16.31
373.2	7.84	18.56	1.914	16.65
423.2	8.37	19.58	2.647	16.93
473.2	8.80	20.54	3.276	17.26
523.2	9.15	21.45	3.823	17.63
573.2	9.45	22.30	4.300	18.00
623.2	9.71	23.09	4.726	18.36
673.2	9.94	23.35	5.104	18.75
723.2	10.14	24.58	5.447	19.13
773.2	10.33	25.26	5.755	19.50
823.2	10.50	25.91	6.037	19.87
873.2	10.64	26.53	6.298	20.23
923.2	10.78	27.14	6.538	20.60
973.2	10.92	27.71	6.759	20.95
1023.2	11.04	28.27	6.966	21.30
1073.2	11.15	28.79	7.159	21.63
1123.2	11.27	29.29	7.339	21.95
1173.2	11.37	29.80	7.509	22.29
1190.2	11.41	29.96	7.564	22.40

Table 10. (Continued)

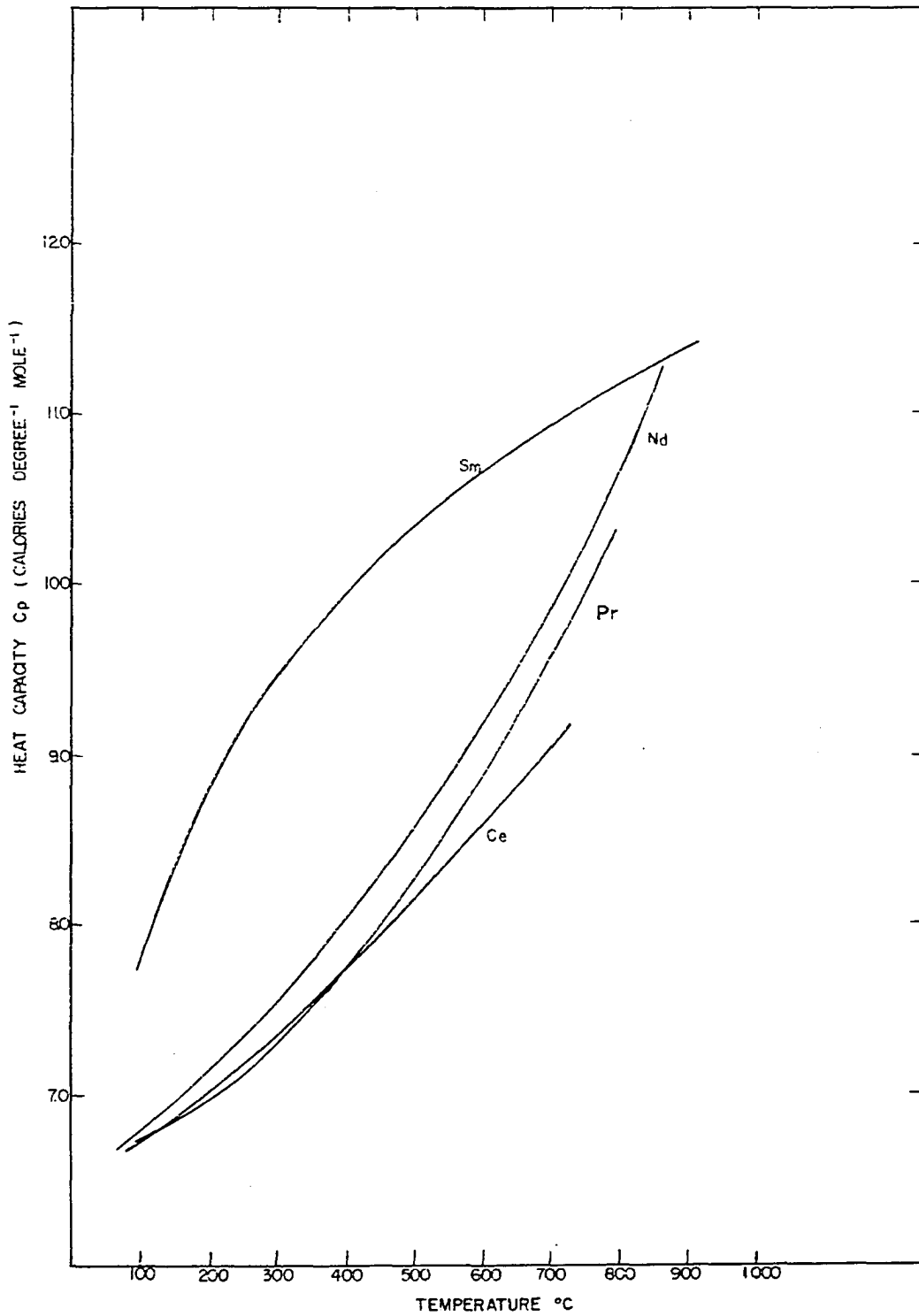| $T^{\circ}K$	C_p°	$S^{\circ} - S_{\circ}^{\circ}$	$\dfrac{H^{\circ} - H^{\circ}_{273.2}}{T}$	$-\dfrac{F^{\circ} - H^{\circ}_{273.2}}{T}$
1190.2	11.22	30.59	8.189	22.40
1223.2	11.22	30.90	8.271	22.63
1273.2	11.22	31.35	8.387	22.96
1323.2	11.22	31.78	8.494	23.29
1345.2	11.22	31.96	8.540	23.42
1345.2	14.04	33.49	10.072	23.42
1373.2	14.04	33.77	10.151	23.62
1398.0	14.04	34.03	10.222	23.81

Figure 16. A comparison of the heat capacities for the rare
earth metals studied

DISCUSSION

The agreement between the mean specific heat of
α- Al_2O_3 tabulated by the National Bureau of Standards and
this work indicated that the apparatus was functioning prop-
erly. Ginnings and Corruccini (1947b) examined the errors
of this method, including temperature, measured heat dissi-
pation, time of drop and loss of heat during dropping and
claimed 0.2% accuracy in the enthalpy.

The standard deviation of the heat contents of the con-
tainer plus sample and the blank were computed from at least
three drops at each temperature. The standard deviations of
the sample were calculated from the standard deviations of
the sample plus container and the blank. The reproducibili-
ties were obtained by dividing the standard deviation of the
sample at a specified temperature by its enthalpy. The
equations which were given to fit the data were obtained by
utilizing a least-squares treatment on several three param-
eter equations below the transition temperature and choosing
the equation which best fitted the data. Between the transi-
tion temperature and the melting point and in the liquid
range studied, linear equations with two parameters were
needed to fit the data properly. Below $100^{\circ}C$ the equation
does not necessarily fit the true enthalpy curve as the
shape of the curve in this region is determined by points at

higher temperatures. The deviations of the calculated from the observed results were obtained by evaluating the empirical equation at the temperature of the measured value and dividing the difference by the measured enthalpy.

The heats of transition and fusion were obtained by evaluating the enthalpy equations which defined the shapes of the curves above and below the respective temperatures and subtracting the smaller from the larger value. The errors in these heats were computed from the average deviations of the calculated from the measured values of the two equations employed.

Jaeger et al. (1936, 1938b) gave an equation for expressing the heat capacity of cerium as a function of temperature from 380° to 480°C. The value of C_p at 400°C calculated from their equation is 7.43 calories per degree per mole compared with 7.74 determined in this investigation. They reported the melting point of their cerium sample to be 635°C while the presently accepted melting point of cerium is 804°C. The value of 8.44 calories per degree per mole for the heat capacity at 400°C was calculated from Kelley's (1949) equation. His equation was obtained by fitting the experimental data of Hillebrand (1876) and Jaeger et al. (1936, 1938b) with an empirical equation. Parkinson et al. (1951) reported the heat capacity at 170°K equal to 6.90 calories per degree per mole. The metal which

was employed in their determinations was prepared by the metalothermic reduction of the anhydrous chloride in a ceramic crucible and may have a high oxygen content because of this. Cavallaro (1943) determined the heat of fusion of cerium to be 5.5 kilocalories per mole while Kojama and Kikuchi (1953) estimated it to be 3.1 kilocalories per mole. Brewer (1950) and Stull and Sinke (1955) estimated the heat of fusion to be 2.2 kilocalories per mole, but both assigned too low of a value to the heat of transition. The heats of transition and fusion were experimentally determined to be 700 and 1240 calories per mole, respectively.

Parkinson et al. (1951) reported the heat capacity of praseodymium to be 6.50 calories per degree per mole at $170^\circ K$; their metal was prepared in the manner described for cerium. Stull and Sinke (1955) estimated the heat capacity of praseodymium to be 7.7 calories per degree per mole at $400^\circ C$; the value of 7.74 experimentally determined in this work agrees quite well with their estimate. However, their estimate of 320 calories per mole for the heat of transition is considerable lower than the experimental value of 722 calories per mole.

Jaeger et al. (1938a, 1938b) determined the heat capacity of neodymium and gave equations to express C_p as a function of temperature in two temperature regions. Evaluating the appropriate equation at $400^\circ C$, the value of 10.45 calo-

ries per degree per mole was obtained. Although their sample
was initially quite pure, they found that it alloyed with
their platinum container during their determinations. Since
the equation for the heat capacity of neodymium of Spedding
and Miller (1951) was fitted to the data of Jaeger et al.
(1938a, 1938b), it was not evaluated. Kelley (1949) fitted
most of the data of Jaeger et al. (1938a, 1938b) to a single
empirical equation; his equation gives the value of 9.2 cal-
ories per degree per mole for the heat capacity of neodymium
at 400°C. This investigation showed the heat capacity equal
to 8.03 calories per degree per mole at 400°C. Parkinson
et al. (1951) reported the heat capacity at 170°K to be 6.84
calories per degree per mole; their neodymium was also pre-
pared by a metalothermic reduction in a ceramic crucible.
Stull and Sinke (1955) estimated the heats of transition and
fusion to be 340 and 2600 calories per mole, respectively;
the values 713 and 1705 calories per mole were experimentally
determined in this study.

Hill (1957) experimentally determined the heat capacity
of samarium to be 7.35 calories per degree per mole at 340°K
while the value of 7.42 calories per degree per mole found
in this investigation agrees quite well. Both of these val-
ues are much higher than the estimate by Stull and Sinke
(1955) of 6.61 calories per degree per mole at 340°K. They
estimated the heats of transition and fusion to be 360 and

2650 calories per mole whereas the values of 744 and 2061 were experimentally determined.

A qualitative treatment of the contributions to the heat capacity can be looked upon as the addition of various effects as given in equation 22. The addition of these contributions should be equal to the measured heat capacity. An illustration of how well the total measured heat capacity can be accounted for may be seen by evaluating the contributions at some temperature which, for convenience, shall be chosen as 1000°K.

The lattice contributions to the heat capacity at 1000°K should be equal to the upper limit of Debye's equation for the heat capacity, 3R. This treats the atoms as harmonic oscillators and deviations due to anharmonicity would give a departure from this constant value.

The contribution of the 4f electrons by promotion to the next higher energy state within the multiplet can be approximated. The metals are looked upon as being trivalent ions which of course is not strictly true. The ground states of the trivalent species following Hund's rules are:

(1)   cerium $^3F_{5/2}$

(2)   praseodymium $^3H_4$

(3)   neodymium $^4I_{9/2}$

(4)   samarium $^6H_{5/2}$

The higher states of the multiplet in each are denoted by unit increments of J from $J_{min} = L - S$ to $J_{max} = L + S$. Cerium has one J state above the ground state, praseodymium has two, neodymium has three and samarium has five. Van Vleck (1932) has calculated the first energy gap for samarium and europium to explain their magnetic susceptibilities at room temperature. He computed the "over-all" width of the multiplet by means of the hydrogenic formula:

$$1/c \, \Delta \nu = 5.82(2L + 1)(Z - \sigma)^4 cm^{-1}/n^3 \ell (\ell +1)(2\ell +1) \quad (66)$$

where $1/c \, \Delta \nu$ is the total width of the multiplet, L is the total angular momentum of the 4f electrons, Z is the atomic number, σ is the screening constant from x-ray data, taken as 34 to account for the observed magnetic susceptibilities, n is the principle quantum number of the group in question and ℓ is the azimuthal quantum number indicating the greatest angular momentum of a single electron in the incomplete orbital. The energy of a J level within the multiplet can be expressed as:

$$W_J = 1/2 AJ(J + 1) + constant, \quad (67)$$

with the appropriate value of A. Hence the total width of the multiplet is proportional to:

$$1/2 \left[J_{max}(J_{max} + 1) - J_{min}(J_{min}+1) \right] , \quad (68)$$

and the energy difference between successive intervals may be seen to be proportional to $J_{min} + x$ where x is the number of intervals above the ground state of the state in question.

The height of each state above the ground state can be calculated by the ratio of proportions of the energy gap to the total width. Multiplying this ratio by the total width of the multiplet gives the energy differences between states. By employing the Boltzman distribution law and computing the average energy in terms of the partition function (f), the heat capacity for crystals can be expressed by:

$$C_{e_{(i)}} = (R/T^2) \partial^2 \ln f / \partial (1/T)^2, \qquad (69)$$

where $C_{e_{(i)}}$ is expressed as calories per degree per mole when R is expressed in calories per degree and T is the absolute temperature. The partition function (f) can be expressed by the equation:

$$f = \sum_i g_i e^{-\epsilon i/kt}, \qquad (70)$$

where g_i is the statisical weight factor of the state equal to 2J + 1 in our case, ϵ_i is the sum of the ground state energy plus the energy level in question, k is Boltzman's constant and T is the absolute temperature. Calculations indicated that this contribution at room temperature is negligible for cerium, praseodymium and neodymium but is equal to about 0.6 calories per degree per mole for samarium. At 1000°K the inner electronic contributions to the heat capacity calculated from the scheme previously outlined are:

(1) cerium   0.91 calories degree^{-1} mole^{-1}

(2) praseodymium 1.07 calories degree^{-1} mole^{-1}

(3) neodymium   1.22 calories degree^{-1} mole^{-1}

(4) samarium   1.84 calories degree^{-1} mole^{-1}

The outer or conduction electronic contribution to the heat capacity varies linearly with temperature. Gerstein et al. (1957), through a private communication from Boorse, reported the temperature coefficient (γ) to be 2.4×10^{-3} (calories degree^{-2} mole^{-1}) for lanthanum. This value is used for the conduction electronic contribution to the heat capacity for praseodymium and neodymium. Clasius and Franzosini (1956) measured the low temperature heat capacity of thorium and reported the coefficient equal to 1.6×10^{-3} (calories degree^{-2} mole^{-1}). Because of the similarity between thorium and cerium, this value is used for the γ for cerium. Roberts (1957) measured the heat capacity of samarium from $2^\circ K$ to $20^\circ K$ and the value of γ computed from her data is 3.1×10^{-3} (calories degree^{-2} mole^{-1}). The conduction electronic contribution at $1000^\circ K$ for the rare earth metals studied are thus:

(1) cerium   1.6 calories degree^{-1} mole^{-1}

(2) praseodymium 2.4 calories degree^{-1} mole^{-1}

(3) neodymium   2.4 calories degree^{-1} mole^{-1}

(4) samarium   3.1 calories degree^{-1} mole^{-1}

The dilatation difference between C_p and C_v was computed at room temperature using formula 21. The values of

the room temperature compressibility were obtained from the
data of Bridgman (1954). The coefficients of thermal ex-
pansion of cerium, praseodymium and neodymium were given by
Barson et al. (1957). The coefficient of expansion of sama-
rium was obtained from the unpublished data of Barson (1957).
The values of the x-ray density necessary to compute the
molar volumes were obtained from Spedding et al. (1957b).
The ratio of C_p/C_v can be calculated at any other tempera-
ture by means of the equation:

$$C_p/C_v = 1 + 3\gamma\alpha_1 T, \tag{71}$$

where α_1 is the linear coefficient of expansion and γ (Gru-
neisen constant) is equal to $(3\alpha_1 V)(\beta C_v)$. In this expres-
sion for Gruneisen's constant α_1 is the linear coefficient
of expansion, v is the molar volume, β is the compressibil-
ity and C_v is the lattice heat capacity. The dilatation
correction was evaluated at room temperature, and from the
ratio of the heat capacities, the value of 3γ was calcu-
lated. By utilizing equation 71, the dilatation correction
can be computed at any temperature if the value of the lin-
ear coefficient of expansion is known at that temperature.
The dilatation correction at $1000°K$ for the rare earth met-
als studied are:

(1) cerium   0.09 calories degree^{-1} mole^{-1}

(2) praseodymium   0.07 calories degree^{-1} mole^{-1}

(3) neodymium   0.13 calories degree^{-1} mole^{-1}

(4)   samarium   0.11 calories degree^{-1} mole^{-1}

The theoretically calculated and measured values of C_p for the rare earths studied are tabulated below, respectively:

(1)   cerium   8.54 & 9.12 calories degree^{-1} mole^{-1}

(2)   praseodymium   9.48 & 9.77 calories degree^{-1} mole^{-1}

(3)   neodymium   9.69 &10.03 calories degree^{-1} mole^{-1}

(4)   samarium   10.99 &10.96 calories degree^{-1} mole^{-1}

In the cases of cerium, praseodymium and neodymium the theoretical value is about 0.5 calories degree^{-1} mole^{-1} lower than the measured one. For samarium the agreement is very good and may be fortuitous. Because of the qualitative character of the calculations, little can be said regarding the discrepancies. Anharmonicity of the lattice vibrations, neglecting crystal field splitting, magnetic effects, the analogies used to determine the outer electronic contributions for cerium, praseodymium and neodymium and the treatment of the inner electronic contributions as trivalent ions may all contribute to the differences.

Since most of the physical properties of europium and ytterbium are similar to those of the alkaline earths, they probably exhibit much divalency in the metallic state. With the metals in the divalent state, the 4f electrons would be in an S state and there is only the ground J state in the multiplet; with two electrons in the conduction band, the free electronic contribution would be less and hence the

total heat capacities may be the smallest of the rare earths.
If, on the other hand, europium exhibits trivalency in metal
and the treatment of the promotion energy of the 4f electrons
is valid, one would expect a higher contribution to the heat
capacity for europium than for samarium because europium's J
states in the multiplet are closer to the ground state.
Calculations have been carried out for europium showing that
this effect would contribute 1.87 and 2.42 calories per de-
gree per mole at $300^{\circ}K$ and $1000^{\circ}K$, respectively. If the
other contributions to the heat capacity are about the same
as for samarium, the total C_p at $1000^{\circ}K$ would be 11.6 calo-
ries per degree per mole. The heat capacity of trivalent
metallic ytterbium would be expected to be less than for
trivalent europium because it has only one higher J state
with a larger energy above the ground state. Since lantha-
num has no 4f electrons, one might expect a total heat capa-
city of about 8.5 calories per degree per mole at $1000^{\circ}K$.

The small decrease in the heat capacity, when passing
from the room temperature to the high temperature form of
the metal, may be due to fitting the data with an empirical
equation. The explanation for the large increase in the
heat capacity upon melting and the constant value exhibited
by the liquid metal is not apparent. The 300-degree temper-
ature range investigated for liquid cerium should be suffi-
cient to detect a temperature coefficient but in the cases

of neodymium and samarium, the temperature interval studied
for the liquid may be too small.

Richard's rule states that the entropy of fusion of a
close-packed metal with 12 nearest neighbors is about two
calories per degree per mole. The metals investigated have
a close-packed structure with 12 nearest neighbors at room
temperature and assuming the transition is a crystalline
transition, then the entropy of transition plus the entropy
of fusion should be about two entropy units. The total en-
tropy changes from the room temperature close-packed solid
to the liquid metal for cerium, neodymium and samarium are
1.85, 1.94 and 2.16 entropy units, respectively, which are
the right order of magnitude for Richard's generalization.

The changes in entropy for the room temperature struc-
ture to the transition state are 0.70, 0.67, 0.63 and 0.63
entropy units for cerium, praseodymium, neodymium and sama-
rium, respectively. Daane et al. (1954) reported the struc-
ture of samarium to be rhbdr while Spedding et al. (1956)
reported cerium as fcc and praseodymium and neodymium as
hcp with a double c axis. All are close-packed structures
and the entropies of transition should be about the same if
the high temperature structures are the same. The values
are the right order of magnitude for this to be true. By
averaging the entropies of fusion for cerium, neodymium and
samarium, the value of 1.33 entropy units was obtained. If

the high temperature structure of these metals is bcc, then
the entropy of fusion of a rare earth which is bcc should be
about the same. Europium which is bcc (Spedding et al.,
1956) exhibits no transitions before melting and should have
an entropy of fusion of 1.33 entropy units while the heat of
fusion would be 1340 calories per mole. If europium is con-
sidered to be more similar to samarium whose entropy of
fusion is 1.53 entropy units, then the heat of fusion would
be about 1540 calories per mole. It would be interesting to
compare the entropy of fusion of europium with that of ytter-
bium since they are quite similar in many of their properties.
By a comparison with cerium, one might expect lanthanum to
have a heat of transition of 700 calories per mole and a
heat of fusion of 1400 calories per mole.

An accumulation of the high temperature thermodynamic
properties of the remainder of the rare earths will aid in
a more complete correlation of their physical properties.
It is noted that gadolinium and lanthanum might not be sus-
ceptible to this type of calorimetric study because of the
quenchable allotropic transition of lanthanum at 300°C and
the Curie point of gadolinium near room temperature; these
metals may not return to a reproducible energy state at 0°C
when dropped from a higher temperature.

SUMMARY

A Bunsen drop calorimeter and a high temperature furnace have been designed and constructed. The performance of the apparatus was verified by measuring the high temperature heat content of α- Al_2O_3 from $0^\circ C$ to $1100^\circ C$ at 100-degree intervals. The data from this work compared within experimental error with the values determined by the National Bureau of Standards.

The high temperature heat content of cerium has been determined from $0^\circ C$ to $1100^\circ C$. The equation which fits the enthalpy (calories mole^{-1}) as a function of temperature from $0^\circ C$ to $730^\circ C$ is:

$$\Delta H]_0^t = 6.366t + 1.474\text{x}10^{-3}t^2 + 3.954\text{x}10^{-7}t^3, \qquad (72)$$

with an average deviation of the calculated from the observed values of 0.14%. Between the transition temperature ($730^\circ C$) and the melting point ($804^\circ C$), the enthalpy (calories mole^{-1}) may be expressed as a function of temperature by the equation:

$$\Delta H]_0^t = 9.047t - 318, \qquad (73)$$

with an average deviation of 0.02% while the enthalpy (calories mole^{-1}) of the liquid metal to $1100^\circ C$ follows the relationship:

$$\Delta H]_0^t = 9.345t + 680, \qquad (74)$$

with an average deviation of 0.04%. The heat of transition was found to be 700 ± 8 calories per mole while the heat of fusion is 1238 ± 4 calories per mole.

The enthalpy as a function of temperature was determined for praseodymium to about 100 degrees above the transition temperature of 798°C. The equation which expressed the enthalpy (calories mole^{-1}) as a function of temperature from 0°C to 798°C is:

$$\Delta H]_0^t = 6.592t + 5.104 \times 10^{-4}t^2 + 1.543 \times 10^{-6}t^3, \qquad (75)$$

with an average deviation of the calculated from the observed values of 0.26%. The heat of transition was determined to be 722 ± 19 calories per mole at 798°C.

The heat content of neodymium was measured from 0°C to 1100°C at 100-degree intervals except near the transition temperature and melting point where more closely spaced measurements were made. The equation which represents the data from 0°C to 862°C is:

$$\Delta H]_0^t = 6.518t + 1.239 \times 10^{-3}t^2 + 1.085 \times 10^{-6}t^3, \qquad (76)$$

where $\Delta H]_0^t$ is the enthalpy (calories mole^{-1}) relative to 0°C and t is the temperature (°C). The average deviation of the calculated from the observed values is 0.2%. In the transition range from 862°C to 1024°C, the enthalpy (calories mole^{-1}) is expressed by the equation:

$$\Delta H]_0^t = 10.654t - 1238, \qquad (77)$$

where the calculated values agree within 0.003% with the measured ones. In the liquid region from 1024°C to 1100°C, the enthalpy (calories mole^{-1}) varies linearly with temperature and may be expressed as:

$$\Delta H]_0^t = 11.661t - 564, \tag{78}$$

with an average deviation of 0.17%. The heat of transition was found to be 713 ± 15 calories per mole at 862°C and the heat of fusion to be 1705 ± 19 calories per mole at 1024°C.

The plot of the heat content versus temperature for samarium shows a departure from the shape of the curves determined for the other rare earths studied. The enthalpy (calories mole^{-1}) as a function of temperature from 0°C to 917°C is given by:

$$\Delta H]_0^t = 11.804t + 4.776 \text{x} 10^{-4} t^2$$
$$- 3.477 \text{x} 10^3 \log(t + 273.2)/273.2, \tag{79}$$

with an average deviation of 0.4%. In the transition range from 917°C to 1072°C the expression for the enthalpy (calories mole^{-1}) is:

$$\Delta H]_0^t = 11.216t - 538, \tag{80}$$

with an average deviation of 0.05%. In the liquid range from 1072°C to 1125°C, the enthalpy (calories mole^{-1}) was fitted by the equation:

$$\Delta H]_0^t = 14.041t - 1505, \tag{81}$$

with an average deviation of 0.09%. The heat of transition

at 917°C was found to be 744 ± 36 calories per mole while the heat of fusion at 1072°C is 2061 ± 15 calories per mole.

An attempt has been made to correlate the high temperature thermodynamic quantities of the rare earth metals studied.

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