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High temperature thermodynamic properties of some of the rare earths

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HIGH TEMPERATURE THERMODYNAMIC PROPERTIES OF SOME OF THE RARE EARTHS

by

John Richard Berg

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INTRODUCTION

In thermodynamics, the branch of science dealing with the relation of heat energy to other forms of energy, the fundamental laws are based on extensive experiments; it is possible starting with these postulates to derive many equations which have proved extremely useful in chemistry, physics and engineering. These equations relate pressure, temperature, volume and chemical potential to energy. If the thermodynamic functions are known for a substance, they permit the calculation of the possibility for a reaction of this substance to take place under a given set of conditions and thus avoid much extensive experimental labor.

Studies are being conducted on the thermodynamic properties of matter in many laboratories; however, there is still much work to be done as many of the thermodynamic functions of known elements are yet to be described. This is particularly true in the case of those elements which have not been readily available, and the rare earth elements have been in this category. These elements, in a unique position in the periodic table, normally have three valence electrons; since the chemical properties of an element depend upon these outer electrons, the properties of these elements in aqueous solutions are very similar thus making it difficult to separate them from one another by ordinary chemical procedures. In the past, this difficulty in obtaining the pure elements led to the term "rare" earths; however, these elements are reasonably abundant in nature.

The first discovery of one of these elements occurred in the late 1700's, and started the studies to characterize this family of elements. A great deal of scientific knowledge concerning the properties of the elements has been gained since that time; however, the laborious procedures used in the past to obtain pure materials has limited many phases of their investigation. Not until the application of ion exchange techniques to their separation at the Ames Laboratory starting in 1944, were they available in high purity and large quantity.

The tables of the elements as devised by Mendeleff and by Meyer predict one element of atomic number 57, lanthanum, but they do not account for the fourteen elements which follow, i.e., atomic numbers 58 through and including 71. Clarification of this situation followed Mosely's work on x-ray spectra and Bohr's theory of atomic structure which conclusively showed that fourteen elements should follow lanthanum. All of these can exist in the trivalent state, where the outer electronic configurations are essentially the same. These fourteen elements are sometimes called the lanthanide elements, or the lanthanons, after lanthanum.

Hund proposed that the ground state electronic configuration of the rare earth elements in the crystalline state and as ions in solution should have the ground state configuration of xenon plus $4f^n$, and three associated valence electrons, where n increases from zero to fourteen electrons across the series. Meggers (1947) proposed from results of spectra studies that the gaseous atoms of the rare earths had the configuration of the ground state of xenon plus the $4f^{n+1}6s^2$ levels populated except for lanthanum, gadolinium and lutetium; he indicated that these three had the ground state xenon configuration plus $4f^n5d^16s^2$ levels populated. In the condensed phase, the strong crystalline fields and valence bonding stabilize the configuration proposed by Hund; thus, in solution and as metals, a 4f electron is promoted, becoming a valence electron. This arrangement results in the unit increment increase of 4f electrons in the series starting with zero for lanthanum to fourteen for lutetium, and explains the characteristic trivalent state displayed by the series.

As the nuclear charge increases across the series, it is balanced by the filling in of the inner 4f electronic level. The electron shells shrink with increasing nuclear charge and atomic number, giving rise to the "lanthanide contraction". Parallel with the increase in atomic number and decrease in size, is the trend of other properties such as the increased tendency to form complexes, a decrease in basicity, etc. Most of the chemical properties remain nearly the same across the series. However, due to the shrinking of the atomic radii, there is a shift in the properties and the series provides a group of elements which are ideal to check chemical theories if the thermodynamic data are known.

Other valences, particularly in the oxides and the salts, are observed besides the trivalent state for some of these elements. Electronic configurations where the 4f orbital has zero, seven or fourteen electrons are especially stable from quantum mechanical calculations. This is verified by a number of physical observations, and is shown by the stability of the following ions under certain conditions; Ce^{+4} ion is isoelectronic with La^{+3}, Eu^{+2} ion and Tb^{+4} ion with Gd^{+3} ion and Yb^{+2} ion with Lu^{+3} ion. Other oxidation states which have been observed under special conditions are the Pr^{+4} ion which is isoelectronic with Ce^{+3} ion, Tm^{+2} ion with Yb^{+3} ion and Sm^{+2} ion with Eu^{+3} ion. Still other oxidation states have been observed for some of the rare earth elements in the oxides and salts. The chemical properties for the trivalent ions are in general the same; the physical properties on the other hand reflect the difference in the number of 4f electrons, as shown in the magnetic, optical and thermal properties.

Differences in the crystal structures of the metals are observed at room temperature with five different structures in the series, and transformations have been observed for most of the metals at higher temperatures or pressures. In the metals, the conduction electrons and their associated ions primarily define the structure of the metals. However, the structure is dependent on the "lanthanide contraction" and is very sensitive to those situations where the condensed state tends to stabilize a 4f electronic configuration which differs from that which gives rise to three conduction electrons. The metallic bonds involved in these structures will reflect the electronic configurations of the atoms. Combined with heat capacity measurements, knowledge of the energies involved in these transformations may aid in explaining the involvement of the 4f electrons in determining the nature of the condensed state.

The heat capacity of a material is defined by the expression $\text{đ}Q/\text{đ}T$, where the amount of heat added to a system, $\text{đ}Q$, causes a corresponding rise in temperature of the system, $\text{đ}T$. The heat capacity is mathematically undefined unless the independent variables are specified under the conditions of the temperature rise. The heat capacities of particular importance are those at constant volume and at constant pressure.

The heat capacity at constant volume, C_v is of interest from a theoretical viewpoint as it is directly related to the energy, E, of the system:

$$C_v = \left(\frac{dQ}{dT}\right)_v = \left(\frac{\partial E}{\partial T}\right)_v \,. \tag{1}$$

From an experimental viewpoint, it is easier to measure the heat capacity at constant pressure, C_p, which is expressed by:

$$C_p = \left(\frac{dQ}{dT}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p \,, \tag{2}$$

where H is the enthalpy of the system under observation.

The heat capacity of a solid can be arbitrarily divided into contributions of various energies. Most important of these is the contribution arising from the atomic vibrations within the crystal resulting from the increased motion of the atoms as heat is added to the crystal. If anharmonic vibration is neglected, this contribution approaches the classical value given by the law of Dulong and Petit which is 3R or about six calories per mole per degree for a metal at high temperatures. An electronic contribution adds to the heat capacity, which for the rare earth metals, results from two types of electrons, the inner 4f electrons, and outer or conduction electrons. Thermal excitation of the electrons in the inner shell can occur to higher energy states by increasing the temperature. In some cases, this energy may be sufficient to promote a 4f electron to the conduction band if the energy difference between the two states is of the order of kT. For the conduction electrons, thermal excitation can occur for the electrons in the vicinity of the Fermi level.

The heat capacity at constant pressure may be expressed in terms of the above contribution as:

$$C_p = C_{v_{(l)}} + C_{e_{(i)}} + C_{e_{(o)}} + \delta C \,, \qquad (3)$$

where $C_{v_{(l)}}$ is the lattice contribution at constant volume, $C_{e_{(i)}}$ is the contribution arising from the different electronic states in which the 4f electrons are involved, $C_{e_{(o)}}$ is the contribution due to the temperature dependence of the conduction electrons, and δ C is the dilatation term, i.e., the difference between C_p and C_v. Experimental anomalies in the curves of heat capacity vs. temperature will be found in solids at the Curie point and the Neel point for those exhibiting magnetism, at order-disorder transitions, from Schottky effects, at crystal transformations and at the melting points. Thus the intercomparison of the physical properties of the rare earths will aid in the explanation of their properties and to a lesser extent, the properties of other transition metals.

A transition metal ion in the normal state has unpaired electrons whereas the non-transition metal ion in the normal state has all electrons paired. For the latter ion, the spins are paired giving rise to a spherical charge distribution which to a first approximation is magnetically independent thus displaying no net angular momentum or magnetic moment. However, in the presence of a magnetic field, this type of ion may have a fairly large diamagnetic term as result of the paired electrons. For the transition metal ion, even if the spins are paired there may be a magnetic moment since in the incomplete shell the magnetic effects of the electrons with opposed spins no longer necessarily cancel one another. For these ions, there is a degeneracy in the field-free ground state and in general, electric crystal fields are not sufficient to remove the degeneracy.

For the transition metal ion, there are several different charge distributions of the same energy in the ground state giving rise to the degeneracy. This degeneracy for the free ion will be partly reduced by the external surroundings for the ion in the condensed state. In an external force field the different states will behave differently and have different energies. The splitting of the degenerate levels by the surroundings is the most important factor in determining light absorption in the transition metal compounds, thus establishing their color.

The energy differences, magnetic moments and spectroscopic splitting factors established by means of paramagnetic resonance studies, magnetic susceptibility studies, spectroscopic studies and thermal studies on the metals and their compounds can be related to models. From a combination of all the observed properties, these models can be tested.

Through a critical study of these data may come a unified theory concerning the nature of the transition elements. This work is undertaken in an effort to gain knowledge towards that end.

HISTORICAL

Method

The ice "drop" calorimeter was devised by Robert Bunsen in 1870 and the essential idea of his instrument is still used in many calorimetric studies at the present. In this type of instrument, the heat content of a sample is measured by dropping a sample from a furnace at a known temperature into a calorimeter chamber where the heat is exchanged with an ice mantle frozen on the outer wall of the chamber. The ice is in equilibrium with distilled water and mercury, and is enclosed in a constant volume chamber open to the atmosphere through a line filled with mercury, attached to a reservoir also filled with mercury. The heat liberated from the sample melts some of the ice resulting in a volume decrease which is compensated for by mercury being drawn into the chamber. From the heat of fusion for the ice and from the amount of mercury drawn into the system, the heat content of the sample can be computed. Bunsen's apparatus consisted of a glass tube sealed at the bottom which served as the calorimeter chamber. Sealed about this central tube was a glass chamber which contained the water and mercury. A glass capillary at the bottom of the chamber led to the reservoir. This instrument was surrounded with packed snow to isolate it from the surroundings. Bunsen calibrated his instrument by introducing water of known weight and temperature into the calorimeter chamber and measuring the mercury intake caused by the change in volume of ice melting to water.

Later improvements were made in the design and calibration of the instrument by Dieterici (1905). He used a copy quite similar to that of Bunsen's, but calibrated it by electrical means as well as with water. He placed a heater of known resistance in the calorimeter well, and passed a current at a measured voltage through the heater. Then in a given length of time, a measured amount of heat was supplied to the calorimeter resulting in a weight change of the mercury, and from these quantities, he obtained his calibration factor. Griffiths (1913) reduced the heat leak (i.e., the rate at which the ice mantle melts as a result of heat flowing into the calorimeter from the surroundings), by a factor of ten by adding another coaxial, closed-bottom, glass tube about the other glass vessel. He filled the space between the vessels with dry air to insulate it from local temperature variations in the surrounding bath. By calibrating his instrument electrically, he obtained a calibration factor within experimental error of that reported by Dieterici.

Sachse (1929) devised a calorimeter in which he substituted diphenyl ether (M.P. 26.55°C) for the distilled water. The calibration factor (calories per gram of mercury) for the ether is lower by a factor of nearly three compared to that of water, arising from the smaller ratio of the heat of fusion to the change of specific volume of the ether in melting. Thus, the mercury intake for the same amount of heat will be three times greater using the ether instead of water. In addition, the reference temperature is nearer to the standard temperature of 25°C, on which thermodynamic data are reported. However, using such an instrument, neither Sachse nor Giguere et al. (1955) were able to exceed the reproducibility of the ice calorimeter, i.e., 0.2 percent. Jessup (1955) reported that he was able to measure quantities of heat of the order of 38 calories with a precision of 0.05 percent using diphenyl ether. Work at the National Bureau of Standards would indicate that the ether used by Sachse (melting point reported above) was not pure, as the National Bureau of Standards reported the melting point of diphenyl ether as 26.87 ± 0.01°C.

Swietoslawski et al. (1933) placed their calorimeter deeper in the ice bath and used a differential manometer in the mercury line in an effort to reduce the heat leak. The mercury delivery line was also covered as much as possible. They suggested that as little distilled water be used as possible with half of it as ice of the mantle to obtain best results.

Ginnings and Corruccini (1947) constructed a calorimeter from metal and glass. The inner calorimeter tube was made from thin walled copper, and a series of fins were soldered near its bottom on the outer wall. This increased the rate of heat transfer from the sample to the ice, and the metal construction made the instrument less susceptible to damage. They added a tube which entered the calorimeter well at its bottom through which they passed dry carbon dioxide to free the calorimeter from condensed water vapor of the air. In addition they provided a gate radiation shield which was housed below the ice-water level of the constant temperature bath, but above the calorimeter proper. This gate was kept closed except during the time of the actual drop. The mercury-water interface of this instrument was in a bulb outside of the calorimeter vessel but below the surface of the constant temperature bath. A water filled glass capillary led from the inner calorimeter vessel to the bulb. The bulb was filled approximately half with water and half with mercury. The capillary from the top of the bulb, filled with mercury, led to the reservoir. Electrical calibration of this instrument agreed with the value given by Dieterici within experimental error.

Ginnings _et al_. (1950) made several improvements in the 1947 calorimeter. They eliminated the bulb in the mercury line and returned the water-mercury interface to the inner glass calorimeter vessel. This interface was large so that a change in the melting of the ice created a very small change in the height of the mercury level thus producing a very small change in the pressure exerted by the mercury. In addition, they tin plated the fins about the central well to effect a faster heat exchange.

Leake and Turkdogan (1954) eliminated the necessity of filling the space between glass vessels with dry air or carbon dioxide by maintaining a vacuum in this space. To eliminate the mechanical strain imposed on the inner vessel by the vacuum, they formed a shoulder on the inner vessel by winding a band of string ½ inch wide just below the open end of this vessel and cemented it in place with synthetic resin; this string flange mated to a brass screw collar which screwed to the head plate on the system. They waxed the lip of the glass vessel in a groove cut in the head plate, and the brass collar was then tightened to snugly fit the string shoulder.

Smith (1955) devised a new method for freezing the ice mantle about the central tube. Prior experimenters had lowered a copper cylinder filled with dry ice into the calorimeter well to freeze the mantle. Smith passed air through a copper coil which was cooled in a dry ice bath. The air passed down a tube inserted into the calorimeter, and he controlled the shape of the mantle by adjustment of the height of the tube.

Spedding _et_ _al_. (1960) improved the technique of freezing the mantle by passing the helium through copper coils immersed in liquid nitrogen. The cooled helium passed down a tube into the calorimeter well in a manner similar to that described above as used by Smith. They also reduced the heat leak of the calorimeter by adding a few milliliters of methyl alcohol to the ice bath; this lowered the temperature of the bath, and by adjusting the concentration of alcohol in the bath, the heat entering the calorimeter through the metal connections, supports, etc., could be balanced as closely as desired by the heat leaving the calorimeter to the slightly colder ice bath. The magnitude and direction of the heat leak were determined for each measurement.

The instruments discussed above were used for determining the enthalpy of materials to 1100°C or below. This temperature limitation was imposed by the materials used in the construction of the furnace, or in some cases, the calorimeters constructed of glass. Some experimenters were also limited to relatively low temperatures as the materials used to jacket the samples would react with the samples.

Lanthanum[1]

Hillebrand (1876) determined the mean specific heat of two samples of electrolytically reduced lanthanum - 0.8911

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[1] The results of previous investigations in the temperature range from 0° to 1700°C are compared to those of this study in a tabular form in the "Discussion" section, page 121 for all metals studied.

and 1.6828 grams - between 0° and 100°C using an ice calorimeter. Analysis indicated the following elements; 93.74% lanthanum, 4.59% neodymium and praseodymium, 1.23% iron, 0.28% silicon and 0.16% aluminum. By correcting for the impurities, he reported a value of 0.04485 calories per degree per gram for the mean specific heat, or 6.23 calories per degree per mole using 139 as the atomic weight of lanthanum.

Lewis and Gibson (1917) used the third law of thermodynamics to calculate the entropy of lanthanum at room temperature as S_{298}= 13.7 e.u.

Jaeger et al. (1936, 1938) used a copper block calorimeter to measure the mean specific heat of a 18.7912 gram sample of lanthanum between 300° and 725°C. It was contained in 27.5209 grams of platinum, and was analyzed as: 98.8% lanthanum, 1% iron, and traces of carbon, silicon, aluminum and magnesium. Above 650°C they found it necessary to separate the sample from the container with a thin mica sheet to prevent reaction. From heating curves, thermal arrests indicated transitions at 548°, 665° and 725°C. Quenching of the intermediate crystal structure was observed in the low temperature structure, and occurred when the sample was dropped between 420° and 665°C; this made their results too complicated in this region for easy interpretation. The mean specific heat is reported for the following temperature ranges:

0.04964 calories per degree per gram between 20° and 300°C
0.05048 calories per degree per gram between 20° and 420°C
0.05241 calories per degree per gram between 20° and 628°C
They estimated the mean specific heat between 0° and 20°C as 0.04725 calories per degree per gram. In addition, they indicated that the specific heat at higher temperatures fell in the following ranges:

672° to 701°C: from 8 to 11 calories per degree per mole;
711° to 750°C: from 10 to 12 calories per degree per mole.

They noted that at room temperature, the value of C_p exceeded the value of 3R predicted by the law of Dulong and Petit.

From a thermal analysis study of lanthanum, Cavallaro (1943) reported a heat of fusion of 5 kilocalories per mole.

Brewer (1950) estimated the heat of fusion of lanthanum as 2.3 kilocalories per mole, with an entropy of 2.0 e.u. He used the room temperature entropy calculation of Lewis and Gibson (1917) to estimate the thermodynamic functions from 500° to 2000°K.

Parkinson et al. (1951) measured the atomic heat of lanthanum from 2° to 180°K. A spectroscopic analysis of their 54 gram sample detected the following metal impurities which were present but below the lower limit of a quantitative analysis by this method: 0.05% calcium, 0.01 % beryllium and 0.002% iron. The sample contained both the face-centered cubic and hexagonal close-packed structures at room temperature. They reported a transition at 4.37°K, and a value of 6.20 calories per degree per mole for the heat capacity at constant pressure at 180°K. By extrapolating to 300°K, they reported $S_{300} - S_0$ as 13.64 e.u. and $H_{300} - H_0$ as 1582 calories per mole.

Stull and Sinke (1956) estimated the heat of fusion as 2700 calories per gram atom.

Kolsky _et al_. (1957) calculated the thermodynamic functions of lanthanum as an ideal monatomic gas from 0° to 8000°K.

Berman _et al_. (1958) measured the heat capacity of lanthanum from 1.6 to 6.5°K; they found superconducting transitions at 4.8°K and at 5.9°K, associated with the hexagonal close-packed and the face-centered cubic modifications respectively. Their samples contained approximately 1.1 moles of lanthanum; spectroscopic analysis failed to show any other metal impurities although the lower limit of such a method is usually 500 ppm of tantalum and 50 ppm of calcium or iron. Twenty ppm of nitrogen and 200 ppm of carbon were detected by other means but the oxygen content was unknown.

Kelley (1949, 1960) has estimated the heat capacity of solid and liquid lanthanum, and the heat of fusion; these are given for the solid as:

$$H_T - H_{298.15} = 6.17T + 0.80\times10^{-3}T^2 - 1911 \text{ calories/mole} \qquad (4)$$

(298° to 1193°K);

$$C_p = 6.17 + 1.60 \times 10^{-3} T \text{ calories/degree-mole} \quad (298° \text{ to } 1193°K) . \qquad (5)$$

The heat of fusion was estimated as 2750 calories per mole. For the liquid range:

$$H_T - H_{298.15} = 8.00T - 200 \text{ calories/mole} \quad (1193° \text{ to } 3000°K); \qquad (6)$$

$$C_p = 8.00 \text{ calories/degree-mole} \quad (1193° \text{ to } 3000°K) . \qquad (7)$$

Enthalpy and entropy values based on the above formulas are tabulated from 400° to 3000°K at 100° intervals.

Praseodymium

Kelley (1936) reported the work of Canneri (1934a, 1934b) on studies of the praseodymium-silver and praseodymium-copper systems. The heat of fusion was calculated to be 2750 and 2650 calories per mole respectively from the two studies. Kelley suggested that 2700 calories per mole be used as the heat of fusion.

Rossi (1934) studied the praseodymium-gold system. He reported that the mean heat capacity of a praseodymium sample which melted at 950°C was 0.0486 ± 0.0007 calories per degree per gram in the temperature range of 20° to 100°C, or C_p = 6.85 calories per degree per mole. His sample was reported to be free of other rare earth elements, and contained 0.5% impurities, chiefly silicon and carbon.

Cavallaro (1943) studied the heat of fusion of a 75 gram sample of praseodymium, approximately 99% pure, and obtained a value of 3100 calories per mole using thermal analysis.

Parkinson et al. (1951) investigated the heat capacity of praseodymium from 2.5° to 170°K. Their 65 gram sample contained no detectable amount of other rare earth elements but had less than the following amounts of metal impurities: $\leq$ 0.1% magnesium, $\leq$ 0.05% calcium and $\leq$ 0.07% iron as determined by spectroscopic analysis. The heat capacity was found to be 6.50 calories per degree per mole at 170°K, and by extrapolation, the enthalpy and entropy at 300°K were reported as 1708 calories per mole and 17.49 e.u. respectively.

Stull and Sinke (1956) estimated the heat capacity of solid praseodymium to the melting point based on the work of Parkinson et al. (1951). The former also estimated a heat of transition for praseodymium as 320 calories per mole and a heat of fusion of 2400 calories per mole. They estimated the heat capacity of the liquid as 8.00 calories per degree per mole.

Kelley (1960) used the estimated values of Stull and Sinke (1956), and tabulated the enthalpy and entropy values of praseodymium from 400° to 3000°K at 100° intervals, except for transition temperatures which were also listed with their corresponding thermodynamic quantities. The estimated values of the enthalpy and heat capacity made by Stull and Sinke are given by Kelley as:

$$H_T - H_{298.15} = 5.50T + 1.60\text{x}10^{-3}T^2 - 1782 \text{ calories/mole} \quad (298° \text{ to } 1071°\text{K}) \ , \tag{8}$$

$$C_p = 5.50 + 3.20\text{x}10^{-3}T \text{ calories/degree-mole} \quad (298° \text{ to } 1071°\text{K}) \ ; \tag{9}$$

$$H_T - H_{298.15} = 8.00T - 2300 \text{ calories/mole} \quad (1071° \text{ to } 1208°\text{K}) \ , \tag{10}$$

$$C_p = 8.00 \text{ calories/degree-mole} \quad (1071° \text{ to } 1208°\text{K}) \ ; \tag{11}$$

$$H_T - H_{298.15} = 8.00T + 500 \text{ calories/mole} \quad (1208° \text{ to } 3000°\text{K}) \ , \tag{12}$$

$$C_p = 8.00 \text{ calories/degree-mole} \quad (1208° \text{ to } 3000°\text{K}) \ . \tag{13}$$

McKeown (1958) measured the heat capacity of praseodymium in an ice calorimeter from 0° to 875°C; measurements were terminated at this upper temperature when the sample container ruptured. His data are given by:

$$H_t - H_0 = 6.59t + 5.10\text{x}10^{-4}t^2 + 1.54\text{x}10^{-6}t^3 \text{ calories/mole} \quad (0° \text{ to } 798°\text{C}) \ , \tag{14}$$

$$C_p = 6.59 + 1.02\text{x}10^{-3}t + 4.63\text{x}10^{-6}t^2 \text{ calories/degree-mole} \quad (0° \text{ to } 798°\text{C}) . \qquad (15)$$

He determined a heat of transition of 722 calories per mole. His 21.3512 gram sample was analyzed spectrographically and contained $< 0.5\%$ calcium, $< 0.01\%$ iron, $< 0.1\%$ cerium, $< 0.1\%$ lanthanum, $< 0.1\%$ neodymium, $< 0.02\%$ silicon and $< 0.1\%$ tantalum.

Europium

Based on the work of Skochdopole et al. (1955) on the low temperature heat capacities of neighboring elements, Stull and Sinke (1956) estimated the entropy of europium at 298°K as 17 e.u. They also estimated the heat capacity of the solid and liquid, and proposed a value for the heat of fusion of 2500 calories per mole. Kelley (1960) formulated their estimates by:

$$H_T - H_{298.15} = 5.81T + 0.99\text{x}10^{-3}T^2 - 1820 \text{ calories/mole} \quad (298° \text{ to } 1100°\text{K}) , \qquad (16)$$

$$C_p = 5.81 + 1.98\text{x}10^{-3}T \text{ calories/degree-mole} \quad (298° \text{ to } 1100°\text{K}) ; \qquad (17)$$

$$H_T - H_{298.15} = 8.00T - 530 \text{ calories/mole} \quad (1100° \text{ to } 1700°\text{K}) , \qquad (18)$$

$$C_p = 8.00 \text{ calories/degree-mole} \qquad (1100° \text{ to } 1700°K) . \tag{19}$$

Kelley has tabulated the enthalpy and entropy values based on these equations for 100° intervals from 400° to 1700°K.

Ytterbium

Stull and Sinke (1956) estimated the heats of transition and fusion for ytterbium as 300 and 2200 calories per mole respectively. They estimated the solid and liquid heat capacities which are presented by Kelley (1960):

$$H_T - H_{298.15} = 5.41T + 0.99\times10^{-3}T^2 - 1701 \text{ calories/mole} \qquad (298° \text{ to } 1071°K) , \tag{20}$$

$$C_p = 5.41 + 1.98\times10^{-3}T \text{ calories/degree-mole} \qquad (298° \text{ to } 1071°K) ; \tag{21}$$

$$H_T - H_{298.15} = 7.70T - 2717 \text{ calories/mole} \qquad (1071° \text{ to } 1097°K) , \tag{22}$$

$$C_p = 7.70 \text{ calories/degree-mole} \qquad (1071° \text{ to } 1097°K) ; \tag{23}$$

$$H_T - H_{298.15} = 7.50T - 300 \text{ calories/mole} \qquad (1097° \text{ to } 1800°K) , \tag{24}$$

$$C_p = 7.50 \text{ calories/degree-mole} \qquad (1097° \text{ to } 1800°K) . \tag{25}$$

Kelley has tabulated the enthalpy and entropy values at 100° intervals except for transition temperatures from 400° to 1800°K based on the above equations.

Yttrium

Brewer (1950) estimated the heat of fusion of yttrium at 1750°K as 4000 calories per mole with an entropy of fusion of 2.3 e.u., the entropy at 298°K as 11 e.u. and the enthalpy from 500° to 2000°K (based on 298°K).

Stull and Sinke (1956) list Brewer's data as well as that based on a communication from Kelley. This later information is supplied in mathematical form by Kelley (1960):

$$H_T - H_{298.15} = 5.72T + 0.50\times10^{-3}T^2 - 1750 \text{ calories/mole} \quad (298° \text{ to } 1773°\text{K}) \text{ ,} \tag{26}$$

$$C_p = 5.72 + 1.00\times10^{-3}T \text{ calories/degree-mole} \quad (298° \text{ to } 1773°\text{K}) \text{ ;} \tag{27}$$

$$\Delta H_f = 4100 \text{ calories/mole } (1773°\text{K}) \text{ ;} \tag{28}$$

$$H_T - H_{298.15} = 8.00T - 120 \text{ calories/mole} \quad (1773° \text{ to } 3000°\text{K}) \text{ ,} \tag{29}$$

$$C_p = 8.00 \text{ calories/degree-mole} \quad (1773° \text{ to } 3000°\text{K}) \text{ .} \tag{30}$$

Kolsky _et_ _al_. (1957) calculated the free energy functions of yttrium considered as an ideal monatomic gas from 0° to 8000°K.

Jennings et al. (1960) measured the low temperature heat capacity of yttrium. They reported the heat capacity at 298.15°K to be 6.34 calories per degree per mole, and the corresponding entropy to be 10.63 e.u.

Simmons et al. (1958) reported the enthalpy and instantaneous specific heat of a yttrium sample encapsuled in molybdenum from 0° to 1000°C. Measurements were performed using an ice drop calorimeter.

METHOD AND THEORY

In the selection of a calorimetric method for the study of high temperature thermodynamic properties, certain requirements and restrictions should be considered. Among these are the amount of time required to obtain the data; the reproducibility, reliability and accuracy of the method; the limits imposed upon the equipment and sample by temperature; and, the nature of the sample itself. Any study made of the rare earth metals at elevated temperatures will first be concerned with the latter two items. The reactivity of the elements with the atmosphere and with the sample containers at high temperatures necessarily required that the study be conducted so that the sample is protected by an inert atmosphere or by a vacuum, and contained in an inert metal such as tantalum, tungsten or niobium. Furthermore, since these containers sufficiently inert to the rare earth metals are attacked by air at elevated temperatures, they, too, must be similarly protected.

Three general methods currently employed in calorimetric studies are:

(1) thermal analysis studies,

(2) adiabatic methods, and

(3) isothermal or "drop" methods.

Certain adaptations have been made of these methods, and some of them will be briefly described and compared to each other.

The thermal analysis method consists of heating and cooling a massive sample at a known rate and measuring the change in temperature vs. time. These rates are compared to those run under similar conditions on a known material. It is a rapid method, but its accuracy and reproducibility are limited, and when compared to the other two methods, it is only an approximation. This method was used by Cavallaro (1943) in determining the heat of fusion of praseodymium. A recent modification of this method is described by Butler and Inn (1958). They heated samples of gold, silver, nickel, molybdenum, copper and platinum coated with platinum black in an evacuated chamber, using radiation from a carbon arc, to a constant temperature (in the range of 1000°C), and then allowed the sample to cool by radiation. The rate of cooling was followed by means of a thermocouple attached to the sample. They reported an accuracy of ± 5%.

The adiabatic method is used to directly measure the heat capacity of a sample by adding a known amount of heat and observing the temperature rise. It is less rapid than the thermal analysis method, but considerably faster than the drop method, as the measurements can be performed continuously from low to high temperatures. It is reproducible and reliable; however, because conditions must be maintained so that the sample is in adiabatic surroundings, proper radiation shielding becomes very difficult at elevated temperatures.

The range of this method is being extended; Stansbury et al. (1959) measured the thermodynamic properties of nickel from 0° to 1000°C using an adiabatic calorimeter with a reported accuracy of ± 0.5%. An adaptation of the adiabatic method was used by Wallace (1960) to study the specific heat of thorium from room temperature to 1000°C. A wire sample was heated to an equilibrium temperature and then pulse heated by means of an electrical current; the rise in temperature of the sample was then measured. The error for this method was given as less than 2%. Of course, this method is limited to nonvolatile solid samples.

The "drop" method is used to determine the heat content (enthalpy) of a sample at constant pressure at some known temperature relative to the temperature of the calorimeter. There are two types of this calorimeter in use. One uses the heat liberated from the sample to melt a solid such as ice or solid diphenyl ether, and the resultant volume change displaces an equal volume of mercury, which is measured. The other method uses the heat of the sample to raise the temperature of a massive metal block.

The Bunsen ice calorimeter has certain advantages over the diphenyl ether and copper block calorimeters.

(1) Diphenyl ether is rather hard to purify and protect from oxidation.

(2) Elaborate devices to measure the temperature increase

of a copper block are not necessary.

(3) Electrical calibration of the ice calorimeter should not be necessary provided outgassed conductivity water and pure mercury are used.

(4) The precision of the calorimeter does not decrease with an increase of heat liberated as in the copper block method.

Some disadvantages of the Bunsen calorimeter are:

(1) It requires a long time to establish the heat content of a sample over a temperature range.

(2) Measurements are made relative to 0°C whereas thermodynamic data are reported at 25°C. Both the copper block and diphenyl ether calorimeters are nearer to the latter temperature.

(3) The volume of the calorimeter system must remain constant.

(4) The sample must return to the same energy state after each drop, and thus high temperature modifications of the sample must not be quenchable.

The advantages of the Bunsen calorimeter coupled with its successful operation in this laboratory resulted in its choice for the following work.

As noted previously, this method is used to measure the enthalpy of a sample at constant pressure and a known temperature relative to 0°C; thus, the change in enthalpy from

0°C to some other temperature, t, can be expressed as a function of the temperature:

$$H_t - H_o = \Delta H\Big]_o^t = f(t) \ . \qquad (31)$$

Various empirical equations may be used to express the data. One of the most common types is a power series of the form:

$$\Delta H\Big]_o^t = a + bt + ct^2 + \ldots , \qquad (32)$$

where t is in degrees centigrade. This expression can be transformed into one based on absolute temperature, T, to give:

$$\Delta H\Big]_{273.15}^T = A' + BT + CT^2 + \ldots \qquad (33)$$

By computing Equation 32 at 25°C and subtracting from Equation 33, the enthalpy will be expressed relative to the thermodynamic standard temperature of 298.15°K, giving:

$$\Delta H\Big]_{298.15}^T = A + BT + CT^2 + \ldots \qquad (34)$$

As the measurements are made at constant pressure, the heat capacity of the sample can be obtained by differentiating Equation 34:

$$C_p = B + 2CT + 3DT^2 + \ldots \qquad (35)$$

This expression then may be used to compute the change in entropy, S, by using the relationship:

$$\Delta S = \int \frac{C_p}{T} dT \ . \qquad (36)$$

The free energy function, F, may be written as:

$$-(F_T - H_{298.15})/T = S_T - S_0 - (H_T - H_{298.15})/T \ , \qquad (37)$$

thus combining the entropy as determined from low and high temperature studies with enthalpy from high temperature studies. The above formulas are a basis for expressing the data as determined by this method. However, the various thermodynamic functions may be expressed in more complex mathematical form by using rigorous derivations based on models of the solid state.

The liberated heat of the sample is accounted for by an intake of mercury into the calorimeter. A calibration factor expressed in calories per gram intake of mercury is given by:

$$K = \Delta H_{ice}/(\overline{V}_{ice} - \overline{V}_{H_2O})d_{Hg} \ , \qquad (38)$$

where ΔH_{ice} is the heat of fusion of ice, $\overline{V}_{ice}$ is the specific volume of ice, $\overline{V}_{H_2O}$ is the specific volume of water and d_{Hg} is the density of mercury. Ginning and Corruccini (1947) determined this calibration factor through electrical means as 64.631 ± 0.014 calories per gram mercury intake.

APPARATUS AND PROCEDURE

Apparatus

Two calorimeter assemblies were used for the measurements described in this study. One, a conventional Bunsen type, was described by Spedding et al. (1960), and used for observations from 0° to 1100°C, operated in air. The other was a modified Bunsen calorimeter which operated in a high vacuum with an increased temperature range to attain temperatures to 1700°C and higher.

The metal samples used in the 0° to 1100°C apparatus were sealed under helium first in tantalum crucibles, which were then sealed in platinum crucibles. They were heated to equilibrium in a platinum-13% rhodium wire wound resistance furnace which was limited to a maximum temperature of approximately 1300°C. The melting points of a number of the rare earth metals exceed this temperature, however, and some melt above the melting point of platinum. However, the "drop" method seemed feasible for measurements at higher temperatures if the apparatus was modified.

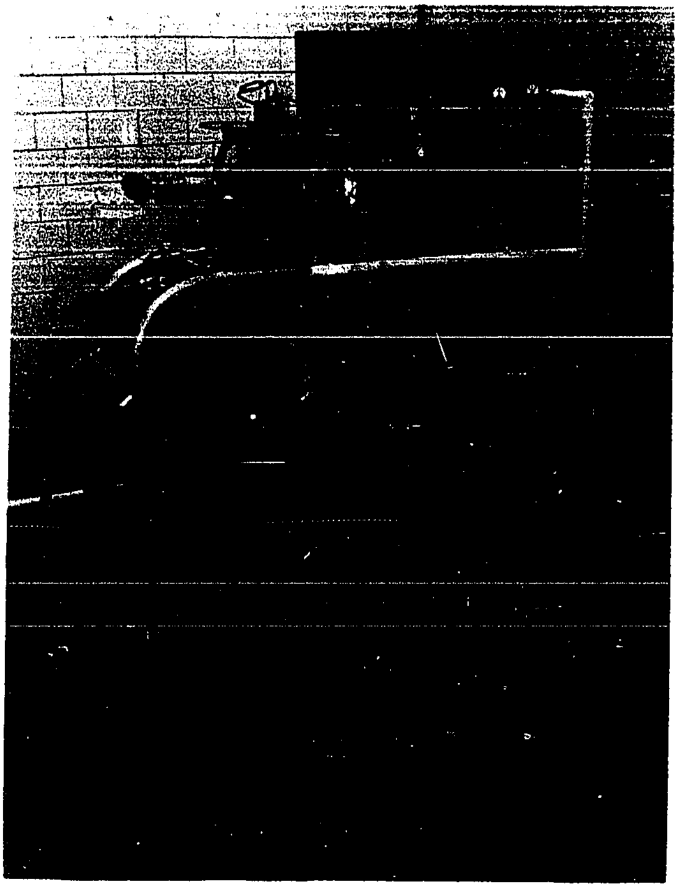
Three metals, tantalum, tungsten and molybdenum, were considered for use in constructing a high temperature furnace. All three would require that operation would be conducted in a vacuum or inert atmosphere. Favorable fabrication and high temperature properties of the tantalum resulted in its choice for this study. An apparatus that would work in a static vacuum was chosen over an inert atmosphere for two reasons:

(1) To obtain a clean atmosphere quickly would require a vacuum first.

(2) In a vacuum, the heat loss to the surroundings would be by radiation only.

Figure 1 shows the assembled high temperature system. The vacuum was maintained by a Welch 1397 Duo Seal vacuum mechanical forepump and a three stage MCF 300-011 Consolidated Electrodynamics Corporation oil diffusion pump. A National Research Corporation thermocouple gauge, Type 501, was connected between the pumps; a Westinghouse WL-5966 ion gauge as described by Alpert (1953), served on the high vacuum side of the pumps for pressure measurements. A sliding 4-inch gate valve manufactured by Consolidated Electrodynamics Corporation served to isolate the pumps from the rest of the system when not operating, and a stainless steel liquid nitrogen cold trap was located between this valve and the diffusion pump. A pair of $\frac{1}{4}$ inch Hoke vacuum valves on either side of the large valve were used as bleeder valves during the pump down operation, and permitted the introduction of helium into the system at the conclusion of a run. These valves were connected to each other and to a helium tank with rubber vacuum tubing. A "T" next to the helium valve was

Figure 1. High temperature vacuum Bunsen type calorimeter in operation



used to connect a small pump during the pump down operation.

Power was supplied for heating the furnace from a 208v. line stabilized by a 5.0 KVA Superior Electric Company Stabline voltage regulator. The line voltage was controlled by a 7.5 KVA Superior Electric Company Powerstat which fed a water cooled 10 KVA 230 v input, 8 - 20 v output step-down transformer manufactured by Banner Welder, Inc. The transformer was connected to the furnace lugs with 4/0 welding cable. The temperature of the furnace was measured with a Leeds and Northrup Co. optical pyrometer.

The vacuum line was made from 4 inch seamless copper tubing, and connections were made with O-ring seals bolted between flanges. All vacuum joints were silver soldered. The furnace, diffusion pump, vacuum line and electrical circuits for the ion gauges and drop mechanism were mounted on an iron pipe frame.

Figures 2 and 3 are schematic drawings of the furnace and calorimeter assemblies. The furnace assembly is water cooled as shown by the water inlets, 1, and outlets, 2. A Plexiglass head plate, 3, 4 3/8 inches in diameter and ½ inch thick, holds the copper burn-off electrode holders, 4. The plate is fastened to its water cooled mounting with six screws, and an O-ring between the two provides a vacuum seal. The electrode holders are sealed to the top plate with O-rings drawn tight with compression nuts which are screwed on the

Figure 2. Schematic diagram of the furnace assembly for the high temperature vacuum calorimeter

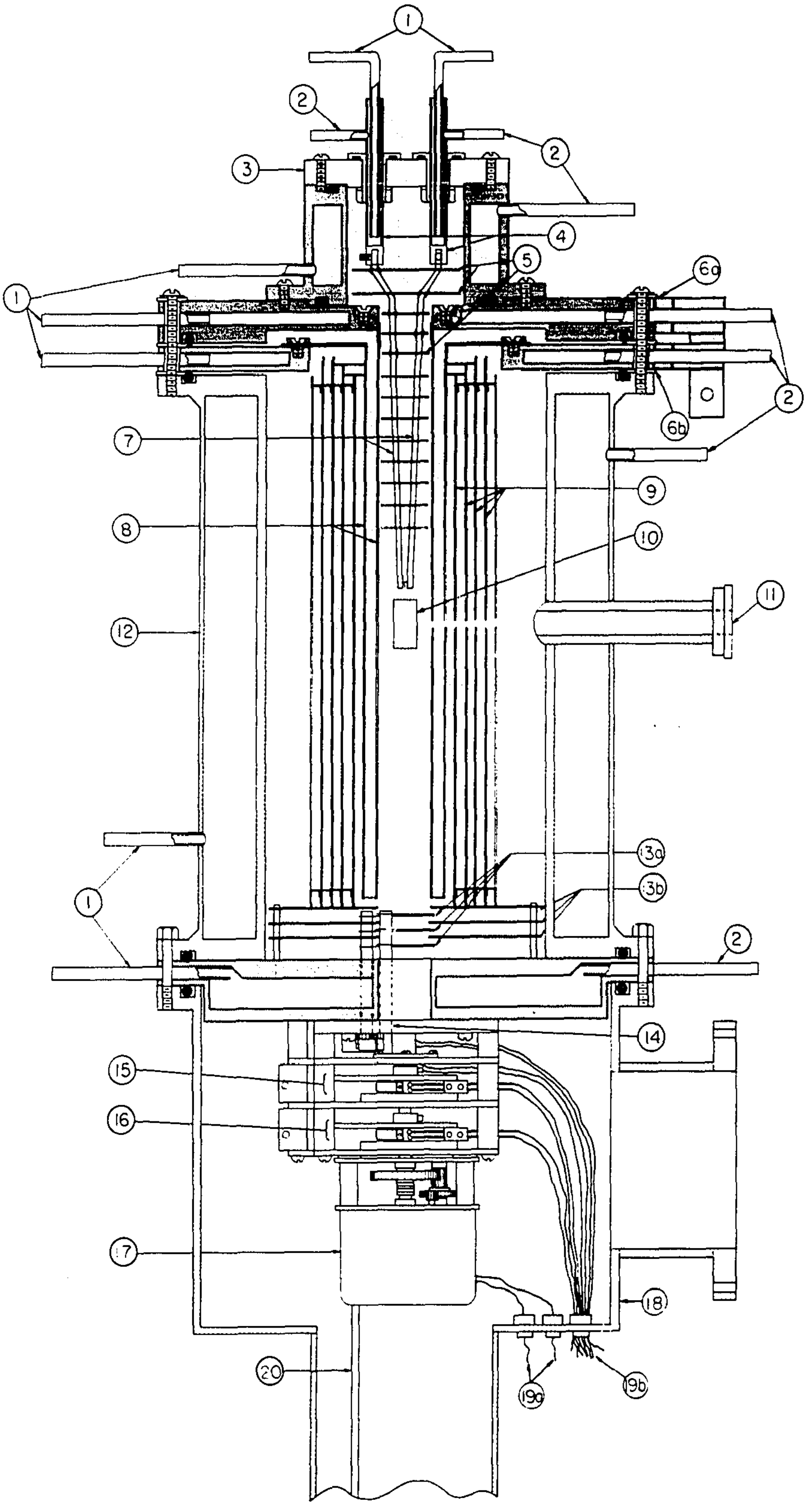
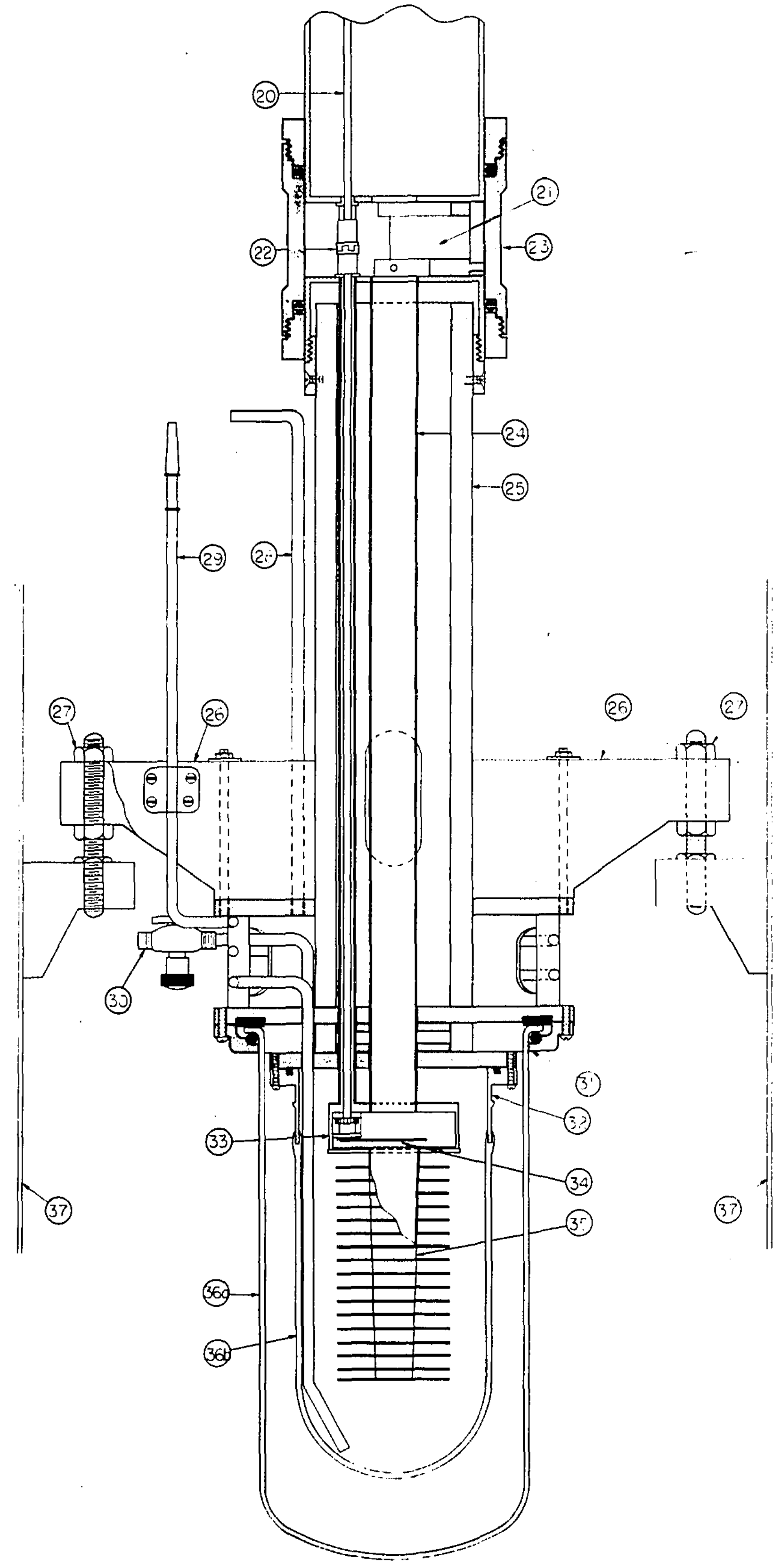

1
2
2
3
4
5
6a
1
2
6b
2
7
9
8
10
11
12
13a
13b
1
2
14
15
16
17
18
20
19a
19b

Figure 3. Schematic diagram of the calorimeter assembly for the high temperature vacuum calorimeter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36a
36b

bottom of the holders. The holders extend into the system approximately 1 3/4 inches. The tantalum burn-off electrodes, 7 are mounted with set screws in the holders. These electrodes are 6 7/8 inches long, and extend to within 3/4 inches of the furnace center. Tantalum radiation shields are mounted on the electrodes in such a manner that alternate shields are attached to one electrode, and the intervening shield to the opposite electrode and separated from the first electrode by a slot in the shield for electrical insulation. The sample, 10, is suspended from the electrodes with 10 mil tantalum wire so that the center of the sample corresponds to the center of the furnace; the sample and its bail are approximately 1 3/4 inches long.

The top water cooled brass plate, 6a, is 10 5/8 inches in diameter and 7/8 inches thick; it serves as one electrode for the furnace, 8. Note the lug connector attached to this plate. The second plate, 6b, acts as the other furnace electrode. It is ½ inch thick and is also water cooled. Between the plates and the furnace jacket, 12, rubber 9 inch O-rings provide a vacuum seal. Electrical insulation of the plates from one another and from the furnace jacket is accomplished by means of 5/8 inch Synthane washers, 1/16 inches thick, and Synthane sleeves. The sleeves are mounted in the plates. The bolts pass through the sleeves and the washers, with washers placed between the bolt head and top plate, between the plates, and between the bottom plate and the furnace jacket. The bolts are threaded into the furnace jacket and provide the compression for the vacuum seal on the O-rings.

The furnace element, 8, is made from 2½ mil tantalum sheet. It consists of two concentric cylinders formed by spot welding the tantalum sheet. The two elements are joined at the bottom by arc welding a 5 mil tantalum ring between them. There are 10 mil tantalum sleeves spot welded to the tops of the elements, and the heavier material is used to make electrical contact to the furnace plates, 6a and 6b, through brass compression rings.

The furnace is shielded on the sides by molybdenum radiation shields, 9, and on the bottom by the tantalum gates, 13a, and shields, 13b. A 1/8 inch sight hole is drilled through shields, 9, and the furnace element. Temperature sightings on the sample are made with an optical pyrometer taken through the quartz window, 11, attached to the system with Apiezon-W wax. The furnace and shielding is enclosed by a double walled water cooled steel jacket, 12, 12 inches long with an inside diameter of 6 inches. The inside surface of the jacket is silver plated for additional shielding.

The upper radiation gates, 13a, are approximately hemispherical. A pivoting action created by the action of a follower arm on a cam, 15, causes the gates to scissor open and close. One set of gates is mounted on the shaft, 14, which is attached to the follower arm. A pair of gears transfers the motion to the other set of gates mounted on a parallel shaft. The shafts above the water cooled plate are of tantalum, and are joined to stainless steel shafts which extend through the plate to the gear box and to the drive mechanism. Holes 1 1/16 inches in diameter in the radiation shields, 13b, which also served as a stand for shield 9, are opened and closed by the action of the gates.

The cam mechanism, 16, is connected to lower gate, 34, which is located in the calorimeter, by an aluminum gate shaft, 20. The cams are driven by 17, a 150 rpm 115 v synchronous motor, similar to Type DYAZ 20F2, obtained from the Barber Coleman Company. Electrical leads for the motor, 19a, and for the solenoids and cam mechanism, 19b, are sealed in Stupakoff seals with Apiezon-W wax. The Stupakoff seals are soldered into brass plugs which form a vacuum seal with the steel housing, 18, with O-rings compressed by nuts screwed on the ends of the plugs.

The furnace assembly is fastened to an iron pipe frame by means of three 3/8 inch leveling bolts. These bolts pass through the furnace can and motor assembly mounting plate, and are screwed into the flange of the motor housing, 18. Six ¼ inch bolts also act as compression bolts for the O-rings between the furnace can, motor assembly mounting plate, and motor housing flanges, and screw into the latter. The leveling bolts continue through a steel collar, with leveling nuts on the top side of the collar. Nuts tightened from the underside of the collar serve to secure the mechanism to the pipe frame.

The calorimeter assembly is positioned below the furnace assembly with the aid of a steel guide, 21, which is attached to the head of the calorimeter assembly and is locked into a stop attached to the bottom of the motor housing can. A rachet coupler, 22, is used to couple the lower gate shaft, 20, to its drive mechanism, 16. A vacuum seal is made between the furnace and calorimeter assemblies with O-rings in the aluminum and brass sliding coupler, 23.

A 10 mil Monel tube, 24, 18 7/16 inches long and 1 1/16 inches i.d. is silver soldered to the lower gate housing at the bottom end, and is sealed to the assembly head at the top with a rubber O-ring compressed with a plate bolted to the underside of the head. A similar tube, 3/8 o.d., is used to enclose the gate shaft; it is fastened in the same manner.

A 3 ½ inch o.d. Synthane tube, with ½ inch thick walls, 25, is used to support the calorimeter. It is pinned at the top to the assembly head and bolted to brass head plate at the bottom. Mounting fins, 26, of 1 inch Synthane support the assembly on leveling bolts, 27, threaded into aluminum supports bolted to a 30 gallon stainless steel barrel, 37.

A ¼ inch stainless steel vacuum line, 28, is used to maintain a static vacuum between the glass chambers, 36a and 36b. The vacuum serves to reduce temperature gradients which may be present in the ice bath. A mercury delivery tube, 29, is made from $\frac{1}{4}$ inch stainless steel. A tapered section arc welded at the top of this tube, is sealed with Apiezon-W wax to a glass delivery tube as shown in Figure 1. A Hoke vacuum valve, 30, is silver soldered to a $\frac{1}{4}$ inch stainless steel tubing which enters the inner chamber, 36b, and is used in filling this chamber with water and mercury.

A 8 inch brass collar, 31, bolted to a brass head, compresses a 6 inch i.d. O-ring against the underside of the lip of the outer glass chamber, 36a. The upper lip of this chamber is ground flat, and is compressed against a rubber gasket. The chamber is made of Pyrex glass, 5 7/8 inches o.d., and approximately 12 inches long.

The inner calorimeter vessel, 36b, is $4\frac{1}{2}$ inches o.d. It has a 1 5/8 inch long Kovar ring, 32, obtained from Larson Electronic Glass, sealed into the top of the glass. The Kovar is arc welded to a stainless steel flange at the top; this flange is bolted to a brass head with a 4 5/8 inch i.d. O-ring between. Overall length of the glass and Kovar is 9 inches.

The lower gate housing, 33, is made of brass. The tantalum gate shields, 34, operate in a similar manner as described for the top gates. Soldered to the gate housing, is the tapered copper calorimeter well and its fin assembly, 35. The outer surfaces are silver plated to aid heat transfer.

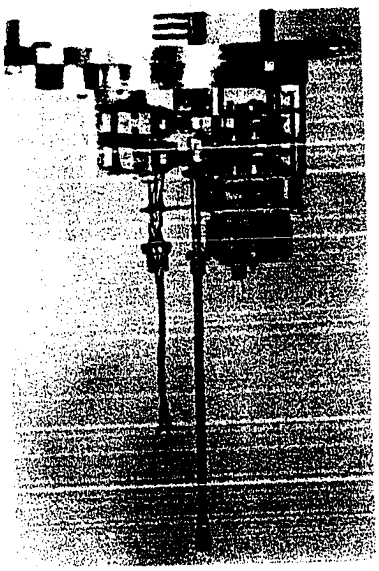
The calorimeter assembly, mounted in the barrel, is enclosed in a double walled plywood box which is mounted on an angle iron frame with casters. The 4 inch space between the box walls is filled with diatomaceous earth insulation, and the space between the barrel and the inner box wall is insulated with carpet felt. The box was covered by a split plywood cover which fitted over the box and around the upper part of the calorimeter assembly.

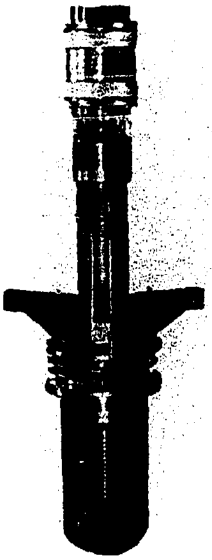
The electronic circuit used for the dropping mechanism was designed by J. Goss of the electronic section of the Ames Laboratory, and a circuit diagram is included in the Appendix.

The details of the motor and cam mechanism are shown in Figure 4. The motor, middle right center, is geared to drive the cams, upper right center, at 150 r.p.m. Tension springs attached to the mounting brackets in rear, not shown, and to the follower arms, upper left center, hold nylon riders mounted in the follower arms to the cams. The pivoting action of the follower arms opens and closes the gates. In the position shown, the cams are at the high points with the iron plates attached to the follower arms flush with the solenoid faces, upper left, so that the gates are closed. The solenoids are mounted on an aluminum mounting plate which is bolted to the water cooled brass mounting plate.

Figure 4. Motor and cam mechanism

Figure 5. Assembled calorimeter assembly





By turning the power switch of the electrical drop mechanism "ON" and rotating the cams by turning the motor switch "ON", the follower arms will be picked up and held by the solenoids in the position shown. By turning the "RUN-STOP" switch to "RUN" and pushing the "START" button, the fields of the solenoids will be released for approximately one revolution as described below, permitting the gates to open and close. If the "RUN-STOP" switch is in the "STOP" position and the "START" button is pushed, the fields of the solenoids are cut and the follower arms will ride the cams, opening and closing the gates as long as the motor is running. This permits the release of the follower arms from the solenoids without banging the faces of the cams.

Mounted on each cam is a Synthane disk; each disk has a copper shorting bar imbedded in it. Two brass spring electrical contacts ride on each disk. With the power of the drop circuit "ON", the "RUN" switch on, and the motor switch "ON", pushing the "START" button activates a circuit which will close when the top cam disk is rotated to the position where electrical contact can be made between the spring contacts through the shorting bar. The point at which this electrical contact is made is such that the high dwell point of the cam is located beneath the follower arm nylon rider. The completed circuit fires a thyrotron tube releasing the field of the top solenoid momentarily, permitting the follower arm and rider to ride the cam thus opening the top gates. At the same time, a circuit is closed allowing 110v to flow through the drop line fusing the wire holding the sample and permitting it to drop. After a time delay, the circuit to the lower cam's disk contacts is reactivated. The released follower arm rides its cam for one revolution, opening and closing the top gates; during this time, the sample will have reached and passed through the gate opening. Before the cam has made its first full revolution, the field of the top solenoid will have been again activated, and will pick up and hold the follower arm as it reaches the high point of the cam thus keeping the top gates closed.

The lower cam will now have rotated so that the shorting bar will make contact with the spring contacts. Another thyrotron tube is fired so that the field is released on the bottom solenoid, its action is similar to that of the top solenoid. The lower gate is then opened and closed in a manner similar to that described for the top gates.

Positioning of the cams on the gate shaft is critical for gate timing. Rough settings were made from calculations involving the distance and time of fall of the sample. Fine adjustment was made after the process was observed using a Fastax high speed motion camera manufactured by the Wollensak Optical Company.

Procedure

The procedure followed in the use of the 0° to 1100° calorimeter is the same as described by McKeown (1958). The process for filling the calorimeter vessels with conductivity water and mercury was similar for both instruments, and is described below for the higher temperature instrument.

The assembled high temperature calorimeter is shown in Figure 5. The inner chamber and calorimeter well were thoroughly flushed with distilled water to remove the soluble solder flux salts used in attaching the well and fin assembly to the gate housing. The calorimeter well was rinsed with absolute alcohol and dried with a purified air jet. The inner chamber was carefully rinsed twice with conductivity water and dried using an infra red lamp and a purified air stream.

Conductivity water was placed in a clean four-liter suction flask which was stoppered with a rubber stopper thinly coated with Dow Corning Silicone vacuum grease. One arm of a three way stopcock attached to the bottom of the suction flask, was bent up at a right angle; this arm was connected to a rubber vacuum line. The single arm of the stopcock ended with a ball joint which was sealed with Apiezon-W wax to a glass tube that extended downwards. On the other end of this tube was a 7/25 standard taper joint which was waxed to the mercury delivery tube, 29, in Figure 3, with Apiezon-W wax. The calorimeter assembly was clamped at an angle such that the valve, 30, and the calorimeter axis defined a vertical plane. A vacuum hose connected to the valve, 30, contained a "T" which was attached to the angled arm of the three way stopcock. The other end of the "T" was similarly attached to a glass tube sealed in a two hole rubber stopper in the top of an empty two-liter suction flask. A vacuum hose connected to a glass tube in the other hole of the stopper led to the side arm of the suction flask containing the conductivity water. The empty suction flask served as a safety trap and was attached in series to two sulfuric acid bubble traps and a dry ice-acetone cold trap and could be isolated from one another with cut-off valves in the line. The cold trap was attached to a mechanical forepump. The system was carefully pumped down, outgassing the conductivity water and the calorimeter.

The system was allowed to outgas from six to eight hours. The two way stopcock was then turned to allow the outgassed water to fill the calorimeter. Pumping on the calorimeter chamber was continued during the filling process through valve 30. An infra-red lamp was turned on the fin assembly to heat this area to aid in the removal of adsorbed gases. A small six watt light inserted into the calorimeter well also helped to remove gases. The chamber was filled after all gas bubbles had been pumped out. Valve 30 was then turned off, and atmospheric pressure returned to the system. The ball joint on the stopcock was opened, and a funnel with a ball joint on its end attached to the angled glass tube on the delivery tube after the calorimeter had been clamped upright. Outgassed triply-distilled mercury which had been air distilled and filtered to remove base metals, was introduced into the system by passing through a filter placed in the funnel. Water in the upper section of the delivery tube, 29, was replaced by the mercury, and this water was discarded. The pool of mercury at the bottom of the inner chamber was formed by opening valve 30 as the mercury entered the system. The level of the mercury pool was allowed to rise from ½ to 3/4 of an inch above the end of the delivery tube. It is important that no water is trapped in the delivery line; after filling was completed, the calorimeter assembly was disconnected and gently precessed, to spiral trapped water out of the line. The water was easier to remove from the line if the coils in the line were tapped during this process. When no more water could be removed, the line had been filled with mercury. The glass tube was removed from the delivery line, the calorimeter assembly set on its mounts in the barrel, and leveled.

The front section of the box cover was bolted into place. The glass capillary delivery tube was waxed into place with Apiezon-W wax and filled with mercury from a 10 ml. glass beaker which served as a reservoir; see Figure 1. The vacuum line was attached to line 28 of Figure 3, and the space between the chambers evacuated. The barrel was then filled with a crushed ice-distilled water bath; approximately 40 mls. of methanol was added to the bath to depress the freezing point of the bath to counteract heat entering the calorimeter from the surroundings. The system was allowed to equilibrate for approximately 24 hours.

An ice mantle then was frozen on the fin assembly. A stream of helium was passed through copper coils immersed in liquid nitrogen, and the cooled helium introduced into the calorimeter well through a ½ inch o.d. metal tube centered in the well by two slotted rubber stoppers. The tube was positioned at the bottom of the well and freezing in this position was continued until approximately 12 mls. of mercury were displaced from the calorimeter vessel. The tube was replaced by another ½ inch metal tube, pinched off at the bottom, with horizontal jets along the side. This tube was initially positioned ½ inch from the bottom of the calorimeter well, and 5 mls. of mercury were removed through freezing. The tube was elevated another ½ inch, and 5 mls. of mercury removed. The tube was finally raised another ½ inch, and 3 mls. of mercury removed. The mantle thus formed had been found to be of the desired size and shape for measurements. The system was allowed to equilibrate overnight.

Each day thereafter, water was removed from the bath and replaced by approximately five gallons of crushed ice; from 15 to 25 mls. of methanol were replaced in the bath to maintain a heat leak near zero.

The purpose for sealing the sample within two concentric tantalum crucibles instead of in one vessel was twofold. First, the outer vessel provided a safety container should the inner vessel fail from weakening caused by the strain imposed by the dropping process or from attack by the sample. Second, since the enthalpy of the sample is determined by subtracting the heat of the blank (the empty containers) from the heat of the containers and enclosed sample, the heat of the containers must be the same whether they contain a sample or not. This will be true only if the heat lost by radiation during the drop from the furnace into the calorimeter is the same in both instances. For two vessels, the inner one would serve as a heat reservoir that would tend to be the same whether it contained a sample or not, as the outer crucible would act as a radiation shield cutting down on the heat lost from the sink. Heat lost by the sample during the drop would have to occur by conduction through the inner vessel, then by radiation and conduction to the outer vessel, then by conduction through the outer vessel where it could finally be lost by radiation from the outer surface of this vessel. Thus, the inner vessel would tend to slow down the heat lost from the sample whereas a single capsule enclosing a sample would tend to lose more heat from the sample which would serve as the only heat reservoir.

The inner crucible was prepared by sealing a bottom to a 1 1/8 inch long tantalum tube cut to ~ 9 mil wall thickness from a ½ inch o.d., 15 mil tube. The bottom was arc welded in a helium atmosphere, forming a flat surface. The outer crucible was prepared from a 1 ½ inch long, ½ inch i.d., 10 mil tantalum tube, and similarly welded. The two crucibles and their lids were outgassed thoroughly in a vacuum of $< 5\times10^{-6}$ millimeters of mercury at 1700°C.

In the case of the blank, a lid was welded on under a reduced atmosphere of helium. For the samples, a weighed sample was sealed in this inner crucible. The inner crucible was then sealed in the larger outer crucible, again under a reduced pressure. The total weight of the tantalum used in the inner crucible was 4.9882 grams, and for the outer crucible, 7.0397 grams. A tantalum bail was made from a 3/4 inch long 20 mil wire and spot welded to the butt weld of the outer crucible. The total weight of the tantalum used in the capsules and bail for each sample was 12.0967 grams.

The sample was hung between the burn-off electrodes on a 10 mil tantalum fuse wire fastened through a small hole drilled in each of the electrodes, and it was "V" shaped to center the sample in the furnace. The calorimeter was positioned directly below and coupled to the furnace assembly.

The entire system was rough pumped through the bleeder valve by the auxillary mechanical vacuum pump thus allowing the diffusion pump on the system to remain on, cutting down on the pumping time. After the system was rough pumped, the bleeder valve was closed, and the main forepump allowed to pump the system through the bleeder valves. The main sliding gate valve was then opened, the bleeder valves shut, and liquid nitrogen added to the cold trap.

After the system had pumped down to $< 1x10^{-5}$ millimeters of mercury, the cooling water to the furnace assembly was turned on. The radiation gates were closed by turning on the power to the drop circuit and running the motor for several seconds. Power was supplied to the furnace, and the temperature gradually increased while maintaining a pressure of less than $3x10^{-5}$ millimeters of mercury.

The sample was maintained at the equilibrium furnace setting for two hours for the blank, for four hours for the aluminum oxide calibration sample and for three hours for the yttrium sample. It was found that the sample reached equilibrium in the calorimeter within these times with three-fourths to one-half an hour to spare as a safety margin.

From one-half to one hour before the drop was made, the determination of the "before" heat leak was started. This was done by turning off the Teflon stopcock in the glass delivery tube connected to the reservoir. The capillary height and time were recorded, and the reservoir weighed. A cathetometer was used to read the mercury height in the capillary to ± 0.05 millimeters. Five minutes before the drop time, the temperature of the furnace was observed; five or six temperature readings were taken in the next four minutes and recorded. One minute before drop time, the capillary height and time were recorded, and the weighed mercury reservoir coupled to the line. The pressure of the system was noted, and one more furnace temperature reading was made. The drop line was coupled to the electrodes, and, at five seconds before the drop was made, the motor turned on. The drop was made by pushing the "START" button, and the motor was then turned off. The furnace power was turned down gradually, and finally turned off within three minutes of the time the drop was made. An hour later, the cooling water to the furnace assembly was turned off.

After the specified time for equilibration given previously had elapsed, the mercury reservoir was adjusted to bring the height of the mercury column in the capillary to within a millimeter or less of its height prior to the coupling of the reservoir to the system before the drop, and the stopcock closed. The height of the mercury column was measured with the cathetometer, and the reservoir was weighed. The "after" heat leak was taken for two to three hours, at the end of which the height of the column again recorded.

The calibration of the capillary was made every time it was necessary to fill the calorimeter vessel with conductivity water and mercury to insure that water and air were not trapped in the mercury delivery line. This operation was done "in situ" prior to heating of the sample in the evacuated system. The mercury reservoir was coupled to the line and raised to produce a tall column in the capillary. The reservoir was detached and weighed. The capillary height was recorded, the reservoir immediately coupled and a lower column of mercury produced; the reservoir was again detached, and the new column height recorded. The reservoir again was weighed. This process was done ten times. From it, the average number of grams of mercury per millimeter of the capillary height was calculated.

The temperature calibration of the optical pyrometer and quartz window had been made previously by sighting on the center of a 1 inch long, ½ inch tantalum rod centered in the furnace. A platinum, platinum-13% rhodium thermocouple was placed in a 1/8 inch hole drilled to the center of the block from the top. Calibration of the pyrometer system *vs*. the thermocouple was made from 900° to 1300°C; the thermocouple was standardized against melting point standards obtained from the National Bureau of Standards. Above 1300°, the optical pyrometer and window system were calibrated against a standard tungsten filament light source calibrated at the

National Bureau of Standards.

With the above calibration and correction factors along with the observed data, the enthalpy of the sample at the observed temperatures could be calculated. The heat content is directly proportional to the net mercury intake. This net intake, W, is expressed by:

$$W = w_1 - w_2 - \frac{R_2 - R_1}{t_2 - t_1} C - t_T \frac{R_4 - R_3}{t_4 - t_3} C - (R_3 - R_2)C \ . \qquad (39)$$

where w_1 is the weight of the reservoir before the drop, w_2 is its weight after equilibrium has been attained; R_1 is the height of the capillary in millimeters at t_1, taken at the start of the before heat leak; R_2 is the height at t_2, one minute before drop time; C is the calibration factor of the capillary column in grams per millimeter; R_3 is the height of the capillary at t_3, after equilibrium is attained; w_2 is the weight of the mercury reservoir after heat exchange between sample and calorimeter is completed at t_3; R_4 is the height at t_4 at the end of the after heat leak; and T is the total time that the sample is in the calorimeter. $R_3 - R_2$ is the difference in capillary heights at the second and first weighings of the reservoir. This net weight, W, is converted to calories by multiplying by 64.631 calories per gram of mercury.

MATERIALS

A sample of α-Al_2O_3 (corundum) was obtained from Linde Air Products in the form of ½ inch diameter rod. A portion of this rod was ground to 0.480 inches in diameter and cut to form a sample weighing 4.2047 grams, fired overnight to 1000°C, cooled and sealed in a double tantalum jacket as described in the preceding section. It was used to calibrate the calorimeter from 1100° to 1700°C. A spectroscopic analysis of the rod is given in Table 1.

Ion-exchange techniques described by Spedding _et_ _al_. (1950, 1951, 1954) and Spedding and Powell (1954), were used in this laboratory to separate the rare earths from their ores and from each other. The lanthanum and praseodymium samples, weighing 13.3877 and 21.3845 grams respectively, were prepared by metalothermic reduction of the anhydrous fluorides with calcium as described by Spedding and Daane (1954, 1956). These samples were thoroughly heated in a high vacuum to remove any residual calcium. Analysis of the samples is given in Table 1.

The europium sample was prepared by reducing the sintered oxide with lanthanum metal. The europium was distilled away from the reactants and collected on a condensing plate in a method similar to that described by Spedding _et_ _al_. (1958). A sample of 10.9970 grams was studied from 0° to 1100°C, and its analysis is given in Table 1.

Table 1. Analysis of samples

Sample	Impurities										
	(Spectrographic quantitative analyses)										
	Nd	Pr	Ce	Ca	Mg	Cr	Ta				
Lanthanum	0.2%	< .03%	< .03%	≪ .05%	< .02%	< .01%	< .1%				
	Nd[a]	Si	Ce	Ca[a]	Mg	Fe[a]	Ta				
Praseodymium[a]	< .1%	< .3%	≤ .1%	≤ .05%	≤ .01%	< .01%	≤ .1%				
	La[a]										
	< .1%										
	Gd	Sm									
Europium	≤ .009%	≤ .02%									
	Sc	Lu	Tm	Er	Y	Ta					
Ytterbium	< .001%	≤ .001%	≤ .001%	≤ .002%	≤ .01%	< .05%					
	Si	Ca	Mg	Cr	Fe						
	.01%	.06%	.02%	.001%	< .01%						
	Ca	Fe	Ta	Si	Mg	Er					
Yttrium	< .05%	< .01%	> 1%	< .01%	< .005%	≤ .05%					
	Ho	Dy	Yb	Gd							
	≤ .05%	≤ .005%	≤ .05%	≤ .01%							
	(Spectrographic qualitative analyses)[b]										
	Al	Bi	Cu	Eu	Fe	Ga	Mn	Ni	Tm	Yb	
Lanthanum	T	T	T	TX	VW	FT	FT	T	FTX	FTX	
	Al										
Praseodymium	FTX										
	Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Si	Ta	Ti
Europium	TX	T	FT	T	T	VW	VW	T	VW	W	TX

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[a] Element detected.

[b] M = moderate, W = weak, VW = very weak, T = trace, FT = faint trace, X = interference.

Table 1. (Continued)

Sample	Impurities										
Ytterbium	Ag FT	Al FT	Bi T	Cu FT	Tm FTX						
Yttrium	Al FT	Cr VW	Cu T	Mg FT	Ti FT	Zr FT					
Corundum	Bi T	Ca T	Cr T	Cu FT	Fe W-M	Ga T	Mg T-VW	Mn VW	Ni FT	Si VW	V T
	(Analytical results)										
	Oxygen	Hydrogen	Nitrogen	Carbon							
Lanthanum	455 ppm	33 ppm	13 ppm	152 ppm							
Europium	190 ppm	12 ppm	30 ppm	45 ppm							
Ytterbium	225 ppm	35 ppm	1 ppm	117 ppm							
Yttrium	250 ppm		70 ppm	77 ppm							
			100 ppm Fluorine								

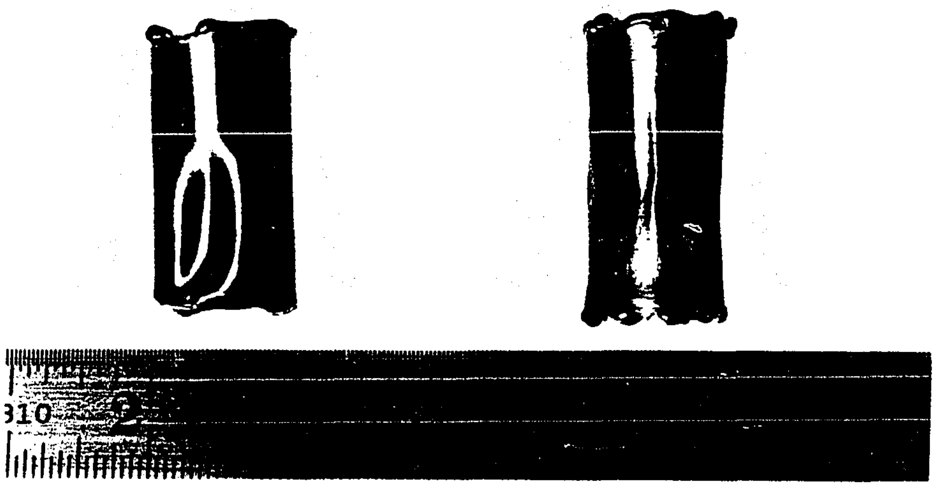
Two samples of ytterbium metal prepared from the same source metal and weighing 18.0404 and 17.3980 grams were used to study the heat content of this metal from 0° to 1100°C. The metal was prepared by reducing the oxide with lanthanum and distilling the ytterbium from the reactants as described by Daane _et al._ (1953) and Spedding and Daane (1954); its analysis is given in Table 1.

Yttrium metal weighing 9.5855 and 7.4528 grams from the same source metal was used in studies from 0° to 1100°C, and from 1100° to 1675°C, respectively. This metal was prepared by the metallothermic reduction of the anhydrous fluoride with calcium and subsequent distillation of the yttrium in a method to be described by Habermann (1960). The metal was obtained as crystals which were pressed into ½ inch diameter pieces and sealed in tantalum. Analysis of the metal is given in Table 1.

All of the samples except the yttrium were first cast into ½ inch rods and jacketed in tantalum. The praseodymium and first ytterbium and europium samples were encapsuled in crucibles prepared from 5 mil tantalum sheet. However, rupturing of the side and bottom seams of the capsules containing the ytterbium and europium forced a change in capsule design. This rupturing was probably caused by the expansion and contraction of the metals in the thermal cycling; the effect on the capsules is evident in Figure 6 which shows the lanthanum and ytterbium samples encased in tantalum after the studies to 1100°C had been completed. These samples were jacketed in tantalum crucibles prepared from ½ inch diameter tantalum tubing cut to ~ 7 mil wall thickness. Lids were sealed to the top and bottom by arc welding in helium. Note that the bottom of the ytterbium sample was not welded flush so the capsule had space to move under the strain of the expansion and contraction of the contents. These inner crucibles were tared to a total weight of 4.7584 grams of tantalum.

The outer platinum jackets used to cover the jacketed

Figure 6. Tantalum crucibles containing lanthanum (left) and ytterbium (right). Note the wrinkles introduced by the expansion and contraction of the metals caused by repeated heating and cooling in the studies to 1100°C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2

samples in the studies to 1100°C were obtained from the American Platinum Works. They were $1\frac{1}{4}$ inches long, 5/8 inches o.d., and had a 10 mil wall thickness. A platinum lid was arc welded on the crucible under a helium atmosphere. A #18 B and S gauge platinum wire was spot welded to the weld on the crucible to serve as a bail. Additional wire was spot welded to the lip to tare the weight to 13.3152 grams of platinum.

The samples used in the high temperature calorimeter were sealed in tantalum jackets as described in the preceding section.

RESULTS

Aluminum Oxide

The U. S. Calorimetry Conference in 1949 recommended the use of α-Al_2O_3 as a high temperature standard for the comparison of calorimeters. The calorimeter used in previous studies in this laboratory and in this study from 0° to 1100°C had been calibrated as reported by Spedding _et al_. (1960). The higher temperature instrument was calibrated from 1100° to 1700°C and compared to previous work reported in this temperature range as cited below.

Wilkes (1932) measured the mean specific heat of sintered alumina between 30° and 1700°C using an Emerson bomb calorimeter. Esser _et al_. (1933) measured the mean specific heat of fused alumina from 0° to 1200°C using a metal block calorimeter. Elsner von Gronow and Schwiete (1933) used a combination copper block-water calorimeter to study the mean specific heat of corundum from 0° to 1500°C. Shomate and Naylor (1945) made a study of natural saphire from 189° to 1514°C with a copper block calorimeter; Egan _et al_. (1950) made a similar study of corundum from 304° to 1299°C. Rodigina and Gomel'skii (1955) studied the heat content of corundum from 1100° to 1400°C using an ice calorimeter. Olette (1957) measured the heat content of corundum at 850° and 1227° using a Nernst-Magnus copper block calorimeter.

Kelley (1960) combined the results of the thermodynamic studies reported in literature and recommended that the enthalpy of aluminum oxide be calculated from a formula he derived from this review such that:

$$H_T - H_{298.15} = 27.49T + 1.41x10^{-3}T^2 + 8.38x10^5T^{-1} - 11,132 \text{ . calories/mole} \qquad (40)$$

From the present study, the enthalpy of the empty tantalum crucibles (blank) was determined at 100° intervals from 1100° to and including 1700°C. The values of the enthalpy of at least three measurements were made at each temperature and were averaged to obtain the heat content at that temperature. Crucibles similar to those used for the blank were prepared and used to contain the α-Al_2O_3. The heat content of the sample was obtained from at least three measurements at each temperature as described above for the blank. The enthalpy of the aluminum oxide was determined by subtracting the value of the enthalpy of the blank from that of the enclosed sample. The experimental values obtained for the enthalpy and the mean specific heat are listed in Table 2.

The enthalpies obtained from the 1100° to 1700°C study were combined with the results of Spedding _et al_. (1960) in the study from 0° to 1100°C, corrected to 298.15°K, and fitted to the following empirical equation by means of a least-squares treatment.

$$H_T - H_{298.15} = 27.01T + 1.45\times10^{-3}T^2 + 551{,}307T^{-1} - 10{,}367 \quad (41)$$

calories/mole

The values obtained from this equation are compared to the observed experimental values and to the values reported by the workers cited above in Figure 7 from 1100° to 1700°C;

Table 2. The heat content and mean specific heat of α-Al_2O_3

Furnace temp. °C	Measured heat of sample (calories/mole) $H_t - H_0$	Reproducibility (%)	Mean specific heat (cal./g-deg.)
1100 ± 3	30,409	0.20	0.2711
1200 ± 3	33,419	0.14	0.2731
1300 ± 3	36,399	0.18	0.2746
1400 ± 3	39,711	0.14	0.2782
1500 ± 4	42,854	0.13	0.2802
1600 ± 4	45,871	0.03	0.2812
1700 ± 4	49,423	0.10	0.2851

the values were corrected to 298.15°K (25°C) and the deviation from Equation 41 plotted *vs.* the temperature in degrees centigrade. The observed experimental enthalpy and mean specific heat were combined with those of Spedding *et al.* (1960), and are shown in Figures 8 and 9.

The reproducibility of the method is based on the standard deviation of the observed enthalpies from the average of at

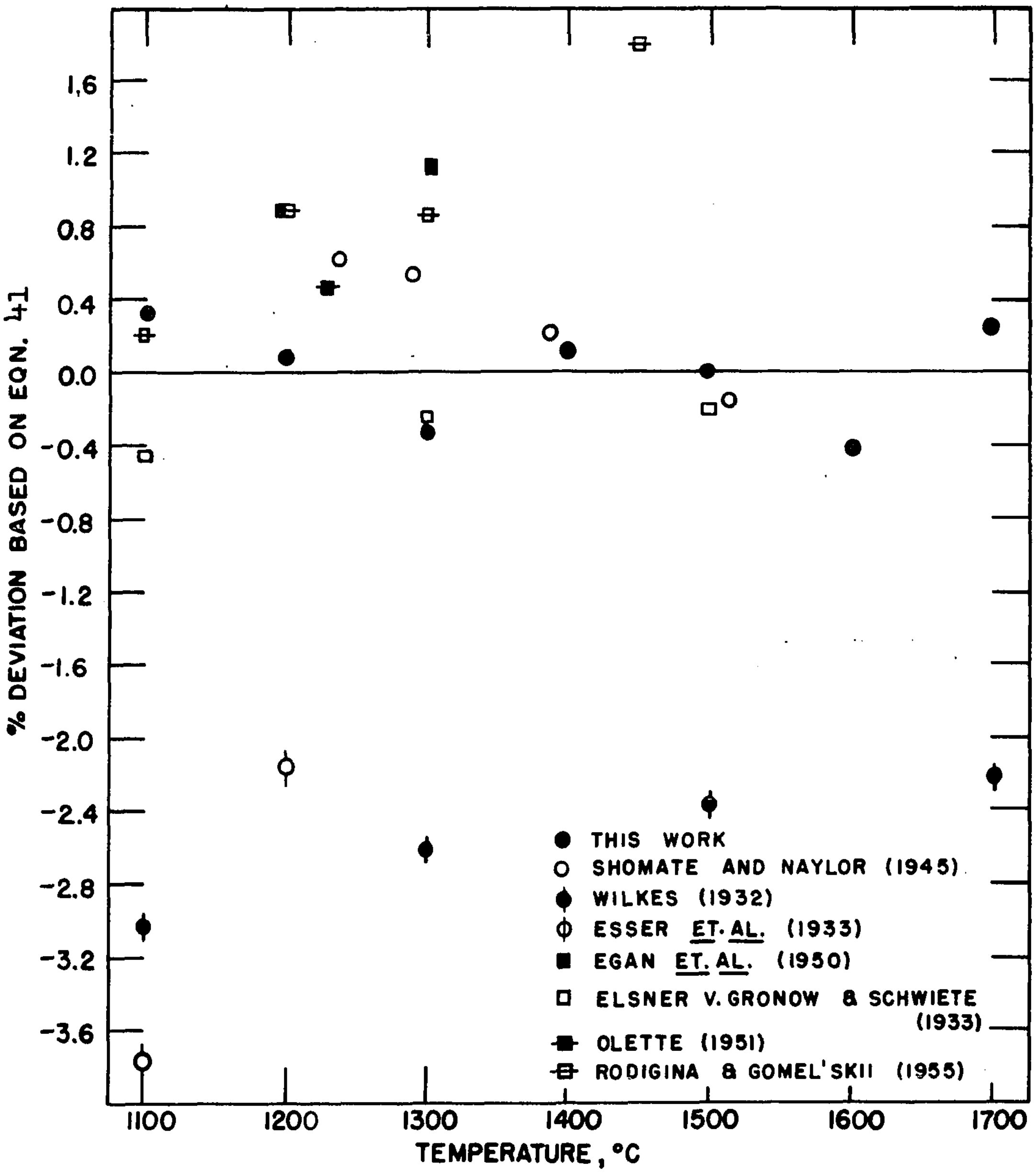

Figure 7. Deviation of observed values of the enthalpy of α-Al_2O_3 from Equation 41

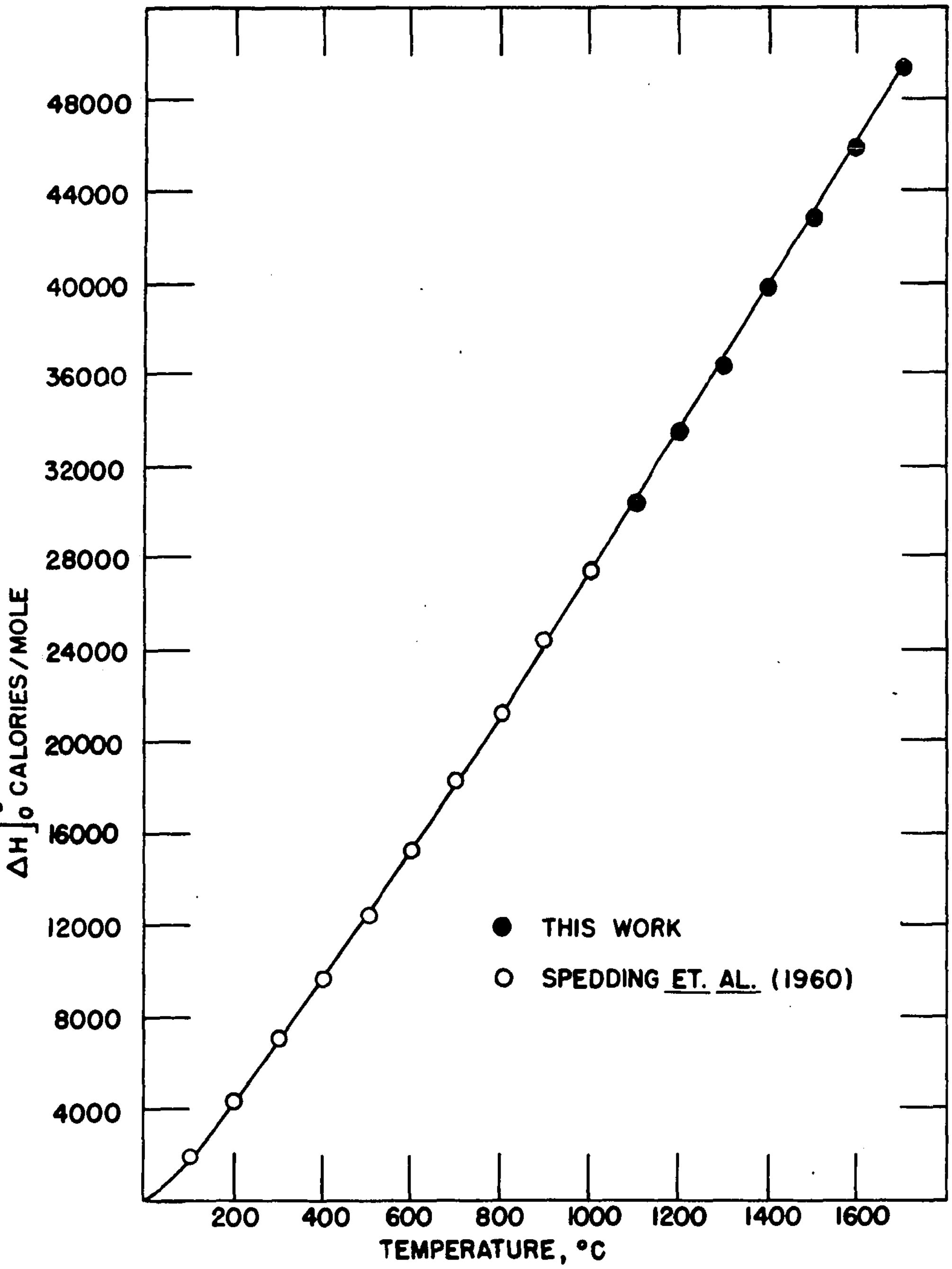

Figure 8. The measured enthalpy of aluminum oxide from 0° to 1700°C

least three measurements at each temperature. However, the greatest source of error introduced in the method is the measurement of the temperature. This is particularly noticeable in the mean specific heat where a difference of 3° to 4° in the temperature measurement at 1300° and 1600° would place the mean specific heat at these points in line on the curve shown in Figure 9.

Lanthanum

The heat content of lanthanum was determined from 0° to 1100°C at 100° intervals except near the transition temperatures and the melting point where observations were made over shorter temperature ranges. At least three drops were made at each temperature. The heat content of the sample was determined by subtracting the heat content of the blank from the total heat content of the enclosed sample. The enthalpy of the blank had been determined at 100° intervals. Temperatures between these intervals at which the sample were measured, i.e., in the vicinity of transformation temperatures, were interpolated by using an empirical quadratic equation the coefficients of which were determined by the enthalpy and temperature values nearest the temperature in question.

The study by Jaeger et al. (1936, 1938) indicated that an intermediate phase was quenched in the room temperature

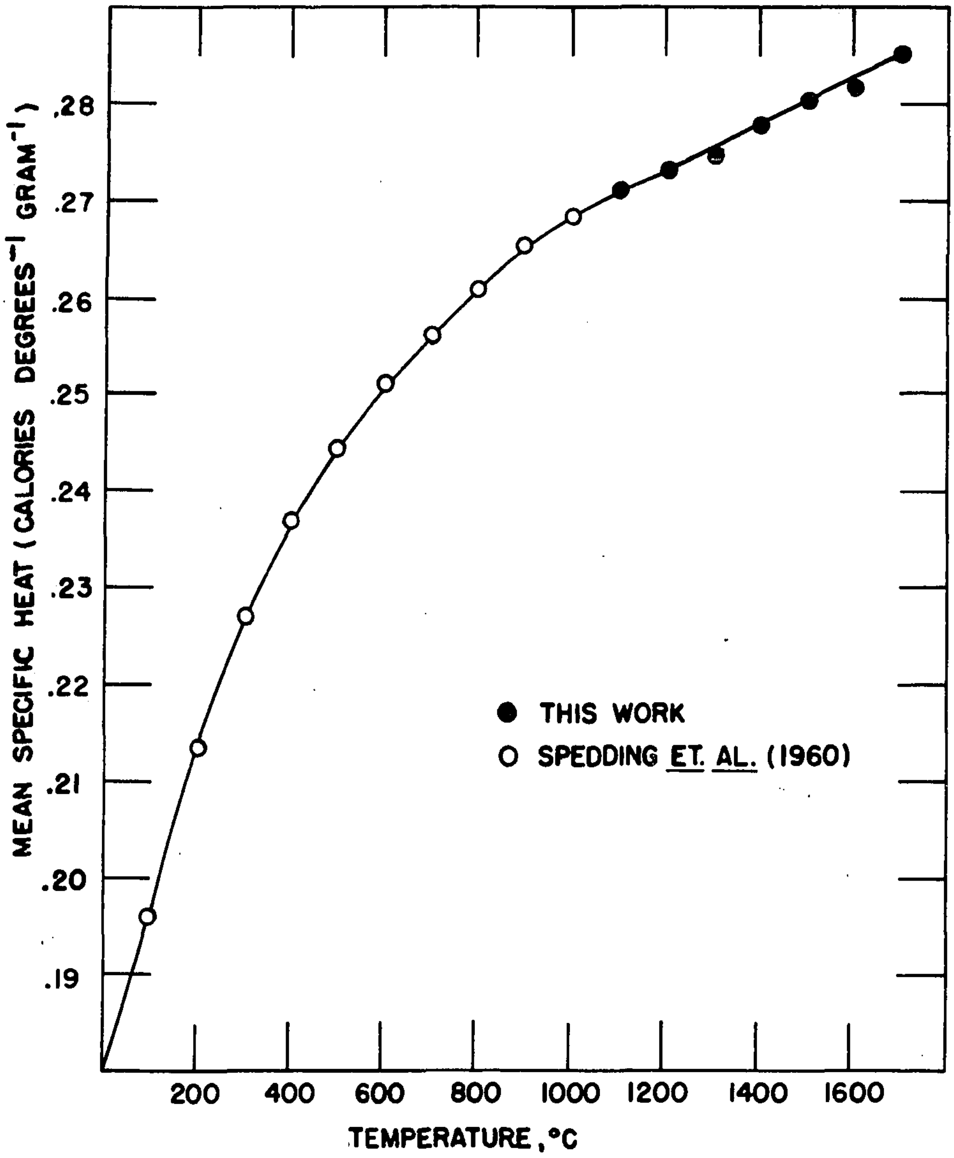

Figure 9. The calculated mean specific heat of aluminum oxide from 0° to 1700°

form of lanthanum metal. Studies conducted in this laboratory showed that the fcc modification of lanthanum indeed could be quenched in the hcp room temperature form of lanthanum. Immediately above the transition temperature of 310°C, results for the heat content measurements were not reproducible. Less heat was liberated after each drop even though the temperature did not vary more than 0.4°C. It was found that by annealing the sample for about one-half to one hour approximately 10° to 20° above the melting point in an auxillary furnace and then slowly cooling the sample to room temperature by raising it out of the hot zone reproducible results could be obtained. Thereafter, at the conclusion of each drop, the sample was so annealed. Therefore, the metal measured above the fcc transition contained an unknown but apparently uniform amount of the higher energy form of lanthanum in the fcc modification, as reproducible results were obtained that were within the error reported for other rare earth metals studied. This unknown amount of the face centered modification would result in low values for the thermodynamic functions reported in the temperature ranges above the transition.

The measured enthalpy of the sample, the reproducibility, the calculated enthalpy from empirical equations based on the observed enthalpy as a function of temperature and the deviation of the observed enthalpy from the calculated enthalpy at each temperature are given in Table 3. The calculated

Table 3. Heat content measurements of lanthanum metal

Furnace temp. (°C)	Observed heat of sample calories/mole	Reproducibility (%)	Calculated heat of sample calories/mole	Deviation of obs. values from calc. values (%)
99.0	622.4	0.32	625.4	-0.48
198.8	1284.8	0.09	1281.7	+0.24
292.5	1920.5	0.09	1921.6	-0.06
347.9	2361.6	0.12	2362.6	-0.04
397.5	2700.2	0.03	2698.5	+0.06
496.6	3390.1	0.11	3391.3	-0.04
599.8	4146.7	0.06	4145.1	+0.04
699.2	4900.9	0.04	4903.9	-0.06
800.0	5711.3	0.06	5707.8	+0.06
854.4	6155.0	0.05	6156.7	-0.03
881.2	7149.2	0.05	7148.7	+0.01
888.6	7217.5	0.04	7218.6	-0.01
896.1	7290.0	0.05	7289.5	+0.01
934.3	9114.9	0.05	9114.5	---
1020.1	9818.5	0.05	9819.3	-0.01
1099.9	10475.2	0.03	10474.8	+0.01

thermodynamic functions of lanthanum based on 298.15°K are given at 50° intervals in Table 4, along with the same information at the transformation temperatures. The value for the entropy at 298.15°K is taken from the information given

Table 4. Thermodynamic properties of lanthanum metal (calories per degree per mole)

T°K	C_p	$S^o_T - S^o_0$	$\frac{H^o_T - H^o_{298.15}}{T}$	$-\frac{(F^o_T - H^o_{298.15})}{T}$
298.15	6.253	13.606	0.000	13.606
300	6.258	13.645	0.038	13.607
350	6.389	14.619	0.936	13.683
400	6.519	15.481	1.626	13.855
450	6.649	16.256	2.177	14.079
500	6.780	16.963	2.631	14.332
550	6.910	17.616	3.014	14.602
583.15	6.997	18.023	3.238	14.785
583.15	6.594	18.138	3.353	14.785
600	6.641	18.326	3.444	14.882
650	6.784	18.864	3.696	15.168
700	6.931	19.372	3.922	15.450
750	7.081	19.855	4.127	15.728
800	7.236	20.317	4.317	16.000
850	7.395	20.760	4.493	16.267
900	7.558	21.188	4.659	16.529
950	7.725	21.601	4.816	16.785
1000	7.896	22.001	4.965	17.036
1050	8.071	22.391	5.109	17.282
1100	8.250	22.770	5.248	17.522
1141.15	8.400	23.076	5.359	17.717
1141.15	9.450	23.736	6.019	17.717

Table 4. (Continued)

T°K	C_p	$S_T^o - S_0^o$	$\frac{H_T^o - H_{298.15}^o}{T}$	$-\frac{(F_T^o - H_{298.15}^o)}{T}$
1150	9.450	23.809	6.045	17.764
1193.15	9.450	24.157	6.168	17.989
1193.15	8.214	25.399	7.410	17.989
1200	8.214	25.446	7.415	18.031
1250	8.214	25.781	7.447	18.334
1300	8.214	26.104	7.476	18.628
1350	8.214	26.414	7.504	18.910
1373.15	8.214	26.553	7.516	19.037

by Jennings *et al*. (1960).

The observed enthalpy for lanthanum is shown as a function of temperature from 0° to 1100°C in Figure 10. The discontinuities shown in this figure are at the hcp-fcc, fcc-bcc and bcc-liquid transitions. The computed heat capacity is shown as a function of the temperature from 298.15° to 1373.15°K in Figure 11.

The data were treated by a least-squares method to obtain four empirical equations to express the enthalpy as a function of temperature in the four regions. In the bcc and liquid regions, the data were found to fit linear equations. The enthalpy is expressed by:

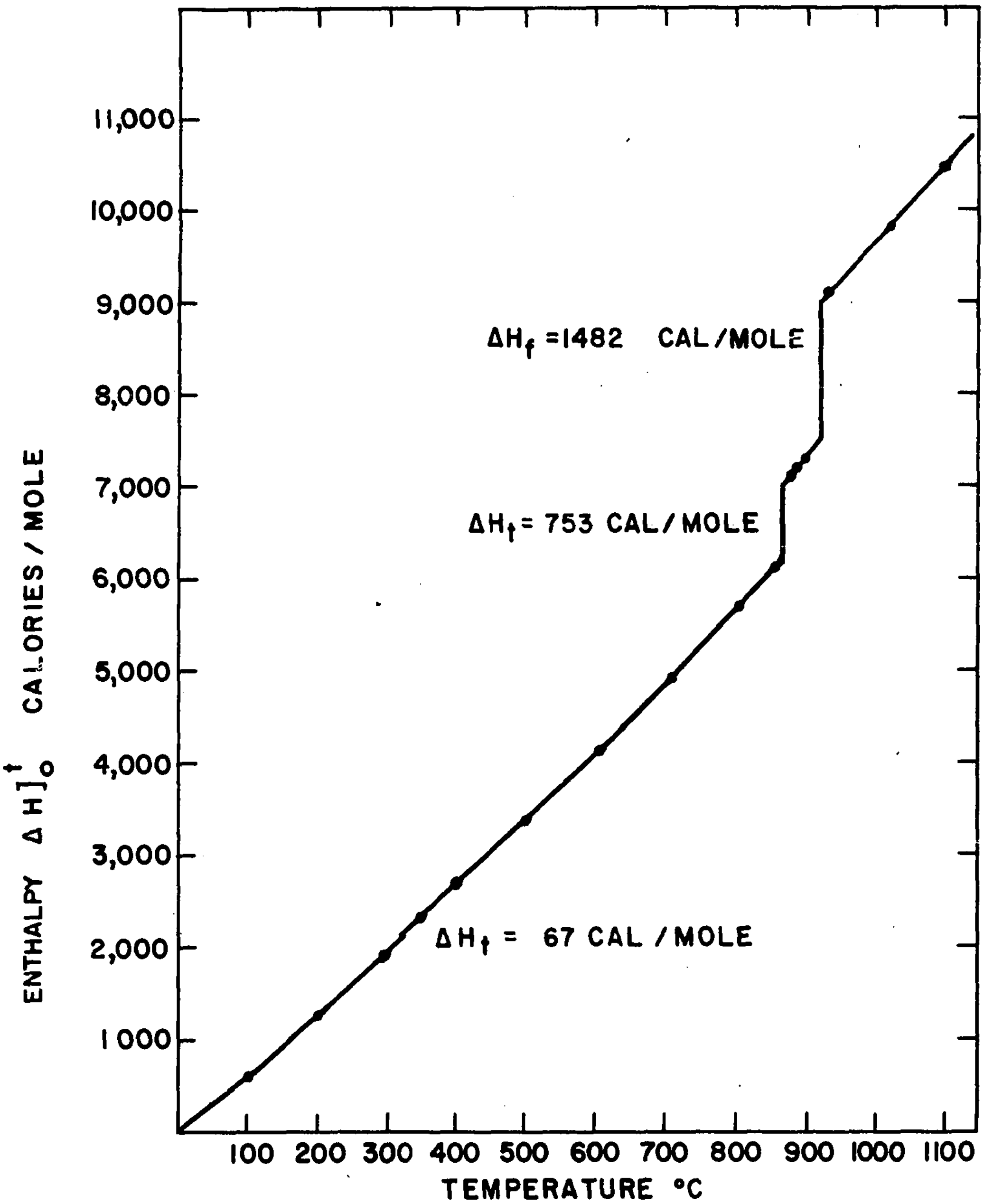

Figure 10. The measured enthalpy of lanthanum metal from 0° to 1100°C

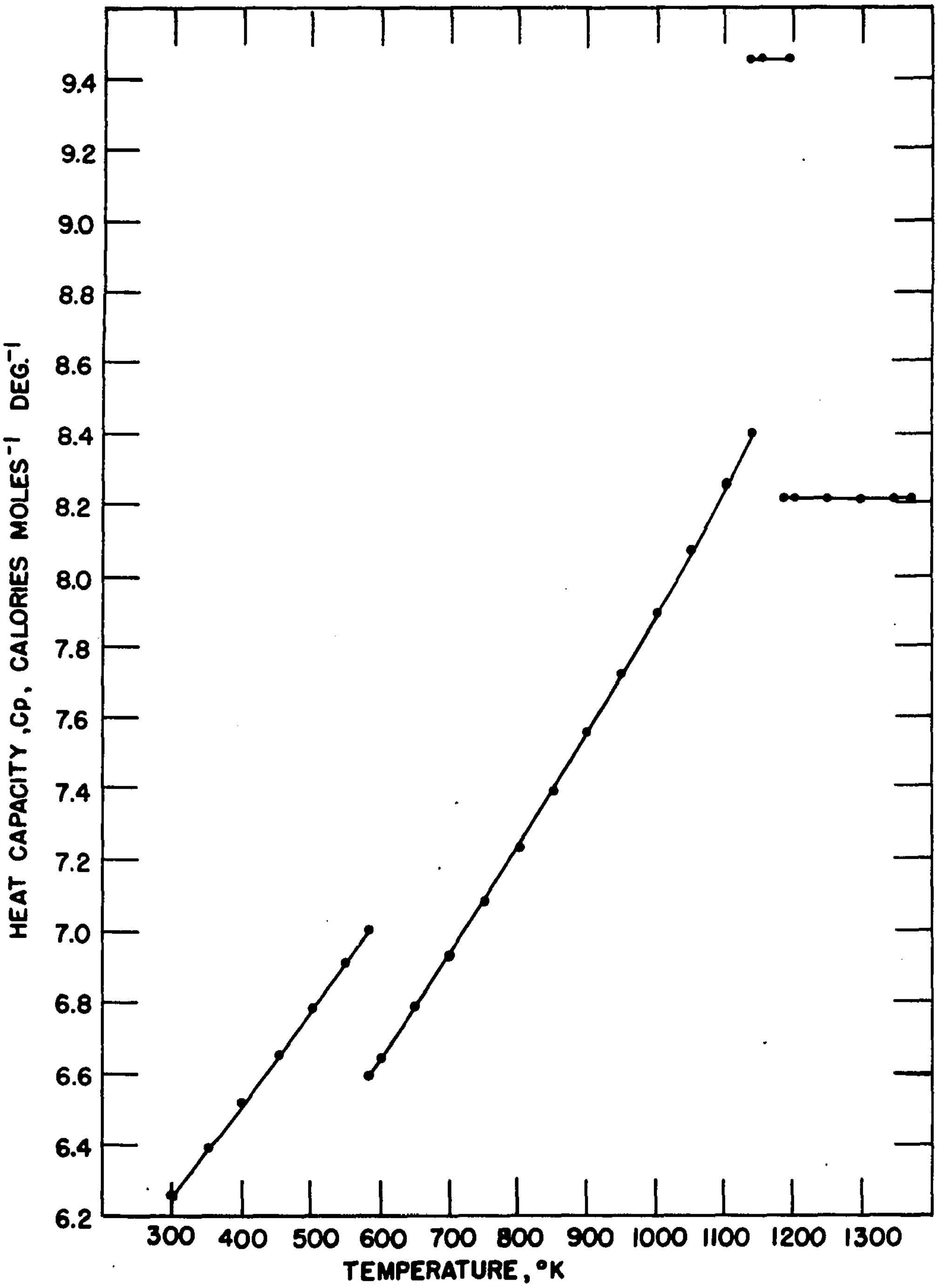

Figure 11. The calculated heat capacity of lanthanum metal from 298.15° to 1373.15°K

$$\Delta H\Big]_0^t = 6.1880t + 1.3043\times10^{-3}t^2 \text{ calories/mole} \qquad (42)$$

(0° to 310°C, average deviation of observed values from calculated values, ± 0.26%)

$$\Delta H\Big]_0^t = 5.8097t + 1.1395\times10^{-3}t^2 + 2.7093\times10^{-7}t^3 + 192.05 \text{ calories/mole} \qquad (43)$$

(310° to 868°C, average deviation of observed values from calculated values, ± 0.05%)

$$\Delta H\Big]_0^t = 9.4502t - 1178.8 \text{ calories/mole} \qquad (44)$$

(868° to 920°, average deviation of observed values from calculated values, ± 0.01%)

$$\Delta H\Big]_0^t = 8.2142t + 1440.0 \text{ calories/mole} \qquad (45)$$

(920° to 1100°C, average deviation of observed values from calculated values, ± 0.01%)

These equations were recomputed to express the thermodynamic functions at the reference temperature of 298.15°K; thus:

$$\Delta H\Big]_{298.15}^T = 5.4755T + 1.3043\times10^{-3}T^2 - 1748.5 \text{ calories/mole} \qquad (46)$$

(298.15° to 583.15°K)

$$\Delta H\Big]_{298.15}^T = 5.2478T + 9.1751\times10^{-4}T^2 + 2.7093\times10^{-7}T^3 - 1470.9 \qquad (47)$$

calories/mole (583.15° to 1141.15°K)

$$\Delta H\Big]_{298.15}^T = 9.4502T - 3915.7 \text{ calories/mole} \qquad (48)$$

(1141.15° to 1193.15°K)

$$\Delta H\Big]_{298.15}^T = 8.2142T - 959.2 \text{ calories/mole} \qquad (49)$$

(1193.15° to 1373.15°K)

The heat capacity at constant pressure is obtained by differentiating the enthalpy with respect to the temperature, so that:

$$C_p = 5.4755 + 2.6086\text{x}10^{-3}T \text{ calories/degree-mole} \quad (298.15° \text{ to } 583.15°K) \tag{50}$$

$$C_p = 5.2478+1.8350\text{x}10^{-3}T+8.1279\text{x}10^{-7}T^2 \text{ calories/degree-mole} \quad (583.15° \text{ to } 1141.15°K) \tag{51}$$

$$C_p = 9.4502 \text{ calories/degree-mole} \quad (1141.15° \text{ to } 1193.15°K) \tag{52}$$

$$C_p = 8.2142 \text{ calories/degree-mole} \quad (1193.15° \text{ to } 1373.15°K) \tag{53}$$

The entropy is obtained utilizing the following integration:

$$\Delta S = \int \frac{C_p}{T} dT , \tag{54}$$

and the entropy for the various temperature ranges becomes:

$$\Delta S\Big]_{298.15}^{T} = 5.4755 \ln T/298.15+2.6086\text{x}10^{-3}(T-298.15) \text{ calories/degree-mole } (298.15° \text{ to } 583.15°K) \tag{55}$$

$$\Delta S\Big]_{583.15}^{T} = 5.2478 \ln T/583.15+1.8350\text{x}10^{-3}(T-583.15) +4.0640\text{x}10^{-7}(T^2-(583.15)^2) \text{ calories/degree-mole } (583.15° \text{ to } 1141.15°K) \tag{56}$$

$$\Delta S\Big]_{1141.15}^{T} = 9.4502 \ln T/1141.15 \text{ calories/degree-mole} \quad (57)$$

(1141.15° to 1193.15°K)

$$\Delta S\Big]_{1193.15}^{T} = 8.2142 \ln T/1193.15 \text{ calories/degree-mole} \quad (58)$$

(1193.15° to 1373.15°K)

The transition temperature for the hcp-fcc transition was taken as 310°C based on this work and on that of Barson et al. (1957) who studied the thermal expansion of some of the rare earths. The fcc-bcc transition was reported by Spedding and Daane (1954) to be 868°C from thermal analysis studies, and verified by Spedding et al. (1960) in high temperature x-ray studies of the rare earths. The melting point was reported to be 920° from thermal analysis studies by Spedding and Daane (1954); this temperature was used as the melting point of lanthanum although some pre-melting occurred 15° below this temperature. This was analogous to the behavior observed for lanthanum by Barson et al. (1957).

The heats of transition and of fusion were obtained by computing the enthalpies at the corresponding temperatures at which these changes occurred from the empirical enthalpy equation; thus from Equations 43-42, 44-43 and 45-44, values of 67 ± 6 calories per mole, 753 ± 4 calories per mole and 1482 ± 2 calories per mole were obtained for the hcp-fcc, fcc-bcc and bcc-liquid transitions. The errors for these values were computed from the average deviation of the observed enthalpies from the calculated enthalpies for the respective temperature ranges on either side of the transition. The corresponding entropy values are: 0.115 ± 0.010, 0.660 ± 0.004 and 1.242 ± 0.002 calories per degree per mole for the above transitions.

Praseodymium

The heat content of praseodymium was studied from 0° to 1100° in the same manner as described for lanthanum. The observed heat contents, reproducibilities, calculated heat contents and deviation of observed from calculated values are listed in Table 5. The thermodynamic functions for praseodymium are given in Table 6 based on the empirical equations given below. The entropy value at 298.15°C was taken from the work of Parkinson *et al.* (1951).

The enthalpy observed in this study is plotted in Figure 12 from 0° to 1100°C, and the heat capacity based on Equations 65, 66 and 67 is plotted in Figure 13 from 298.15° to 1373.15°K.

A least-squares treatment of the observed enthalpy data as a function of the centigrade temperature gave the following empirical equations:

$$\Delta H\Big]_0^t = 6.3806t + 1.4285\text{x}10^{-3}t^2 + 7.3585\text{x}10^{-7}t^3 \text{ calories/mole} \quad (59)$$

(0° to 798°C, average deviation of observed values from calculated values, ± 0.12%)

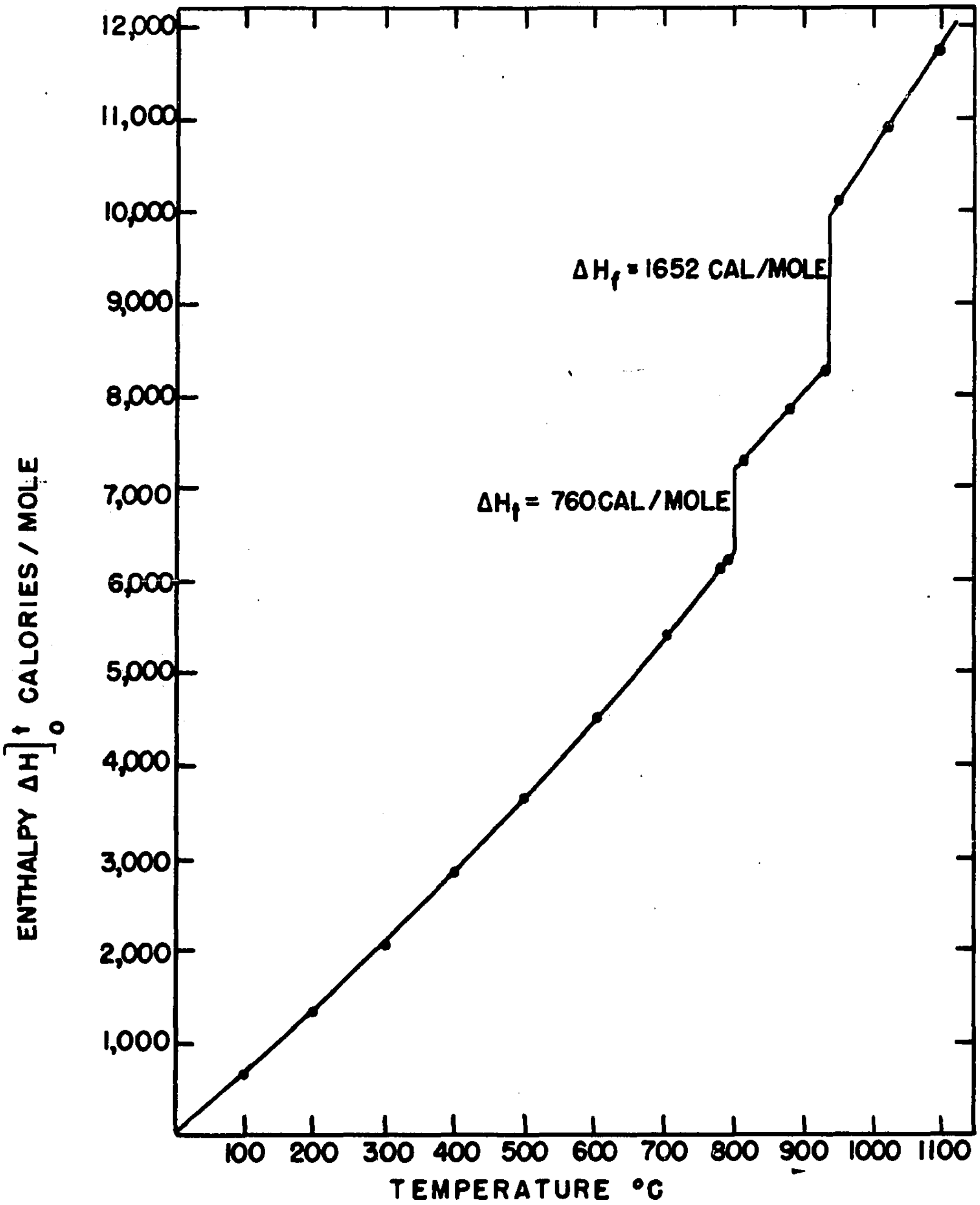

Figure 12. The measured enthalpy of praseodymium metal from 0° to 1100°C

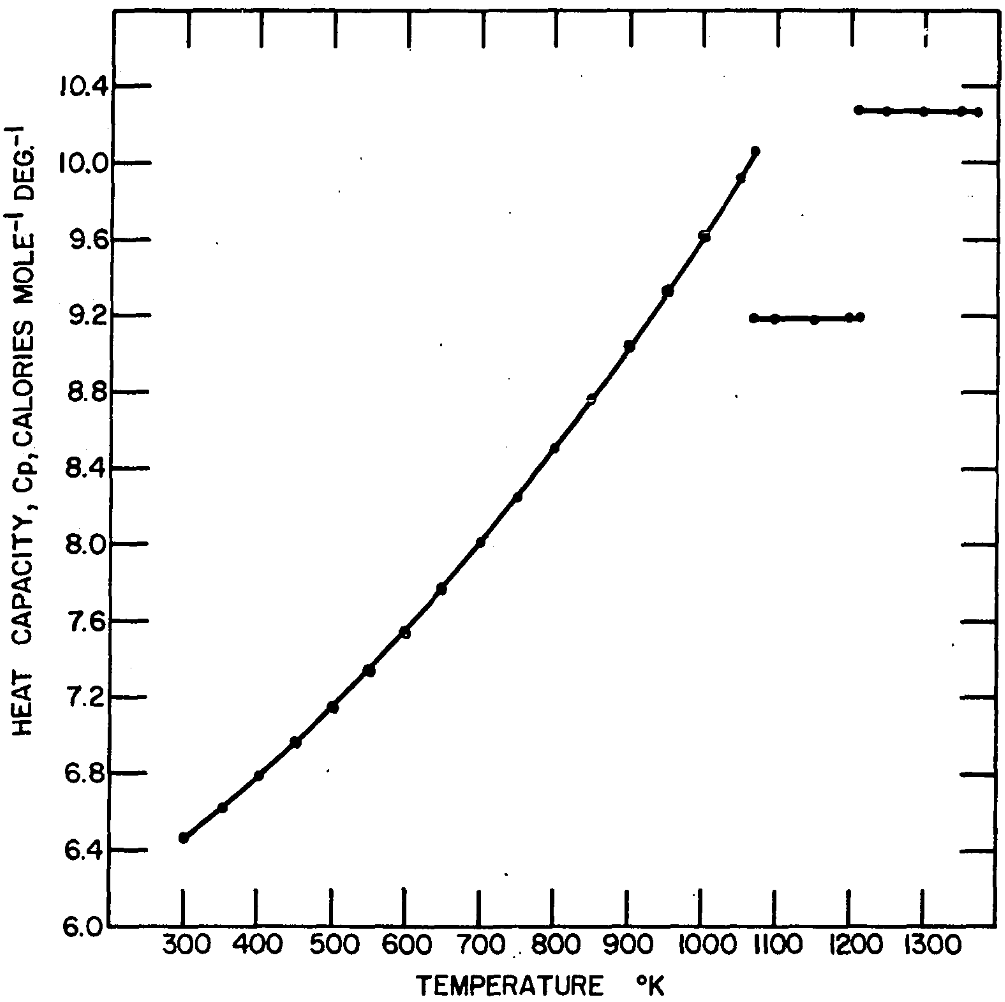

Figure 13. The calculated heat capacity of praseodymium metal from 298.15° to 1373.15°K

Table 5. Heat content measurements of praseodymium metal

Furnace temp. (°C)	Observed heat of sample (calories/mole)	Reproducibility (%)	Calculated heat of sample (calories/mole)	Deviation of obs. values from calc. values (%)
100.3	657.3	0.53	655.1	+0.34
199.9	1336.7	0.16	1338.5	-0.13
299.9	2059.7	0.08	2061.9	-0.11
400.4	2832.7	0.15	2831.1	+0.06
500.3	3642.3	0.07	3641.9	+0.01
601.9	4523.1	0.05	4518.5	+0.10
700.6	5415.6	0.05	5424.5	-0.16
776.7	6169.5	0.03	6162.4	+0.11
788.7	6279.0	0.02	6282.0	-0.05
809.5	7238.8	0.08	7240.4	-0.02
871.3	7811.8	0.05	7808.3	+0.04
924.7	8297.1	0.04	8299.0	-0.02
940.3	10100.1	0.03	10099.0	---
1019.5	10912.9	0.03	10913.4	---
1100.8	11748.7	0.04	11748.5	---

$$\Delta H\Big]_0^t = 9.1889t - 198.0 \text{ calories/mole} \qquad (60)$$

(798° to 935°C, average deviation of observed values from calculated values, ± 0.03%)

$$\Delta H\Big]_0^t = 10.2717t + 441.39 \text{ calories/mole} \qquad (61)$$

(935° to 1100°C, average deviation of observed values from calculated values, ± 0.01%)

Table 6. Thermodynamic function of praseodymium metal (calories per degree per mole)

T°K	C_p	$S^o_T - S^o_0$	$\frac{H^o_T - H^o_{298.15}}{T}$	$-\left(\frac{F^o_T - H^o_{298.15}}{T}\right)$
298.15	6.453	17.450	0.000	17.450
300	6.459	17.490	0.040	17.450
350	6.613	18.497	0.968	17.529
400	6.778	19.391	1.684	17.707
450	6.955	20.199	2.259	17.940
500	7.142	20.942	2.738	18.204
550	7.341	21.632	3.148	18.484
600	7.550	22.279	3.506	18.773
650	7.771	22.892	3.825	19.067
700	8.002	23.476	4.115	19.361
750	8.245	24.037	4.382	19.655
800	8.498	24.577	4.632	19.945
850	8.763	25.100	4.867	20.233
900	9.039	25.609	5.091	20.518
950	9.325	26.105	5.306	20.799
1000	9.623	26.591	5.515	21.076
1050	9.932	27.068	5.718	21.350
1071.15	10.066	27.267	5.802	21.465
1071.15	9.189	27.976	6.511	21.465
1100	9.189	28.220	6.581	21.639
1150	9.189	28.629	6.695	21.934
1200	9.189	29.020	6.799	22.221

Table 6. (Continued)

T°K	C_p	$S^o_T - S^o_0$	$\frac{H^o_T - H^o_{298.15}}{T}$	$-\left(\frac{F^o_T - H^o_{298.15}}{T}\right)$
1208.15	9.189	29.082	6.815	22.267
1208.15	10.272	30.449	8.182	22.267
1250	10.272	30.799	8.252	22.547
1300	10.272	31.202	8.330	22.872
1350	10.272	31.589	8.402	23.187
1373.15	10.272	31.764	8.433	23.331

These equations, when converted to the standard reference temperature, become:

$$\Delta H\Big]_{298.15}^{T} = 5.7649T + 8.2546\times10^{-4}T^2 + 7.3585\times10^{-7}T^3 - 1811.7 \quad (62)$$
calories/mole (298.15° to 1071.15°K)

$$\Delta H\Big]_{298.15}^{T} = 9.1889T - 2868.3 \text{ calories/mole} \quad (63)$$
(1071.15° to 1208.15°K)

$$\Delta H\Big]_{298.15}^{T} = 10.2717T - 2524.7 \text{ calories/mole} \quad (64)$$
(1208.15° to 1373.15°K)

The heat capacities corresponding to these temperature ranges are:

$$C_p = 5.7649 + 1.6509\times10^{-3}T + 2.2076\times10^{-6}T^2 \text{ calories/degree-mole} \quad (65)$$
(298.15° to 1071.15°K)

$$C_p = 9.1889 \text{ calories/degree-mole} \quad (1071.15° \text{ to } 1208.15°\text{K}) \tag{66}$$

$$C_p = 10.2717 \text{ calories/degree-mole} \quad (1208.15° \text{ to } 1373.15°\text{K}) \tag{67}$$

The entropies are given by:

$$\Delta S\Big]_{298.15}^{T} = 5.7649 \ln T/298.15 + 1.6509\text{x}10^{-3}(T-298.15) + 1.1038\text{x}10^{-6}(T^2-(298.15)^2) \text{ calories/degree-mole} \quad (298.15° \text{ to } 1071.15°\text{K}) \tag{68}$$

$$\Delta S\Big]_{1071.15}^{T} = 9.1889 \ln T/1071.15 \text{ calories/degree-mole} \quad (1071.15° \text{ to } 1208.15°\text{K}) \tag{69}$$

$$\Delta S\Big]_{1208.15}^{T} = 10.2717 \ln T/1208.15 \text{ calories/degree-mole} \quad (1208.15° \text{ to } 1373.15°\text{K}) \tag{70}$$

The values of 798° and 935° were reported as the transition and melting points of praseodymium by Spedding and Daane (1954) from thermal analysis studies. By computing Equations 60-59 and 61-60 at these temperatures, the heat of transition was found to be 760 ± 10 calories per mole and the heat of fusion to be 1652 ± 3 calories per mole, where the error was computed from the average deviation of the observed and calculated values for the empirical equations involved. The entropies of transition and fusion, computed by dividing the appropriate heat by the respective temperature, were found to be 0.709 ± 0.009 and 1.367 ± 0.002 calories per degree per mole.

Europium

The thermodynamic functions for europium metal were determined from 0° to 1100°C in the same manner as described for lanthanum. The data reported here are from a fourth run of the metal. The first run ended at 700°C when the sample container ruptured above this temperature. The second and third runs produced results higher than observed for the first run and did not agree with one another. It was suspected that a high oxygen content in the metal probably produced these discrepancies, although no analysis for oxygen in europium metal had been devised at the time these runs were made. A fourth sample of europium was very carefully prepared by distilling the metal from thoroughly outgassed and sintered oxide with lanthanum as the reductant. This sample was studied over the temperature range from 0° to 1100°C, and gave slightly lower results than the first run where enthalpies could be compared. After the conclusion of the study, the sample was analyzed (see Table 1), and the first oxygen determination in europium metal was made in the Analytical Section of the Ames Laboratory. The method consisted of fusing the metal in a tin capsule within a graphite crucible, where the oxygen present in the metal was converted to carbon monoxide which in turn was oxidized to carbon dioxide, and then determined.

All four samples showed a discontinuity in the enthalpy and heat capacity curves in the vicinity of 503°K. It was of such small magnitude that it was difficult to ascertain whether this was merely a change in slope of the enthalpy, or a definite break in the curve. Empirical equations were fitted to the data above and below this break, and the results listed below.

The observed heat contents of europium metal, reproducibilities, calculated heat contents and deviations of observed values from calculated values are listed in Table 7. The thermodynamic functions for europium are listed at 50° intervals and at the transition temperatures in Table 8. No reliable data for the room temperature entropy were available, and the usual form for reporting the calculated free energy function was thus omitted; the entropy was reported relative to 298.15°K.

The measured enthalpy of europium metal is presented in Figure 14 and the calculated heat capacity in Figure 15.

The data were fitted to the following empirical equations:

$$\Delta H\Big]_0^t = 6.4265t + 1.025\times10^{-3}t^2 \text{ calories/mole} \qquad (71)$$

(0° to 230°C, estimated deviation, ± 0.33%)

$$\Delta H\Big]_0^t = 7.2608t - 1.1189\times10^{-3}t^2 + 2.1735\times10^{-6}t^3 - 92.6 \qquad (72)$$

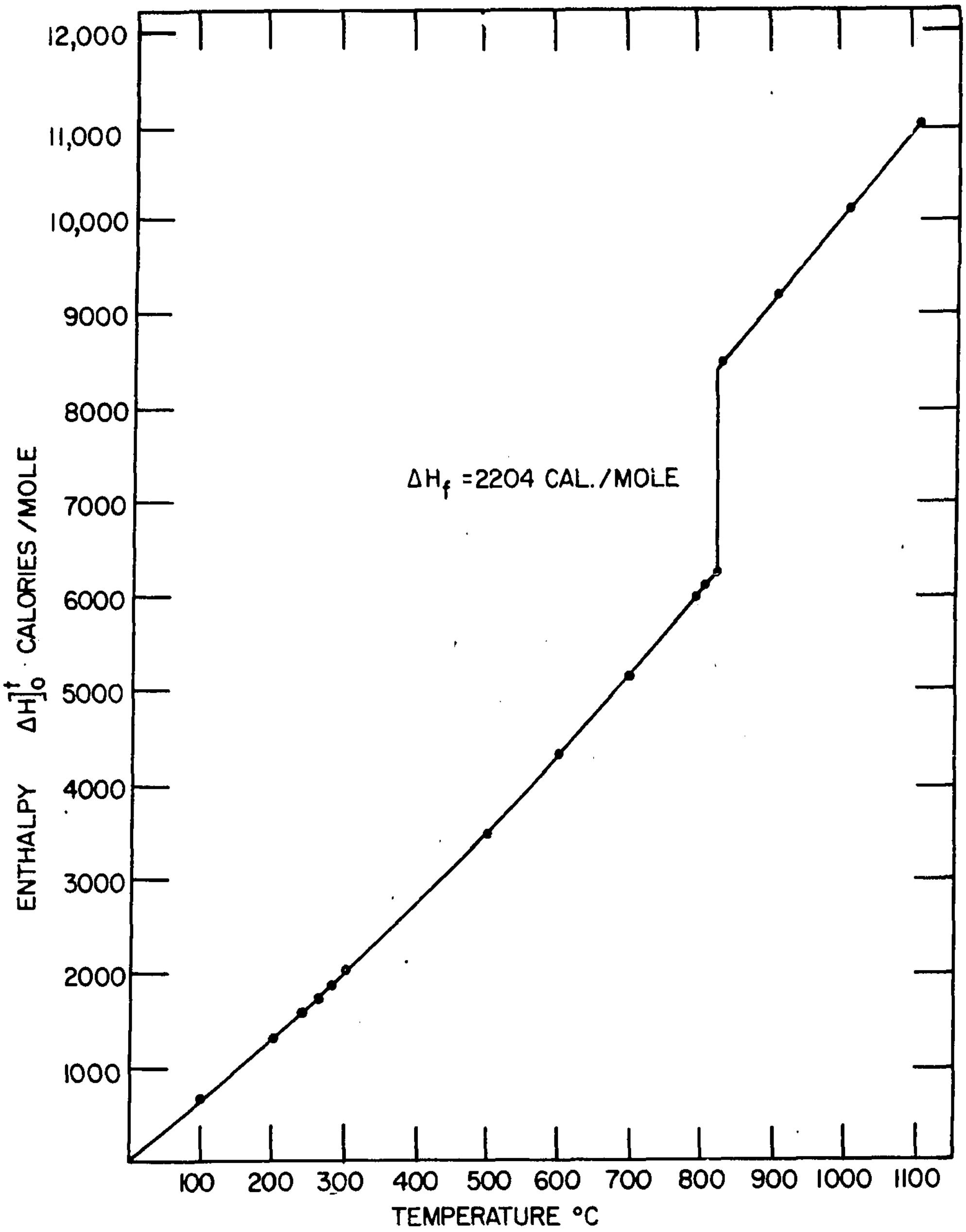

Figure 14. The measured enthalpy of europium metal from 0° to 1100°C

Figure 15. The calculated heat capacity of europium metal from 298.15° to 1373.15°K. The large break in the heat capacity curve at 503.15°K is the result of fitting the observed enthalpies above and below the break to two empirical equations; the break is exaggerated, and is probably smaller than shown

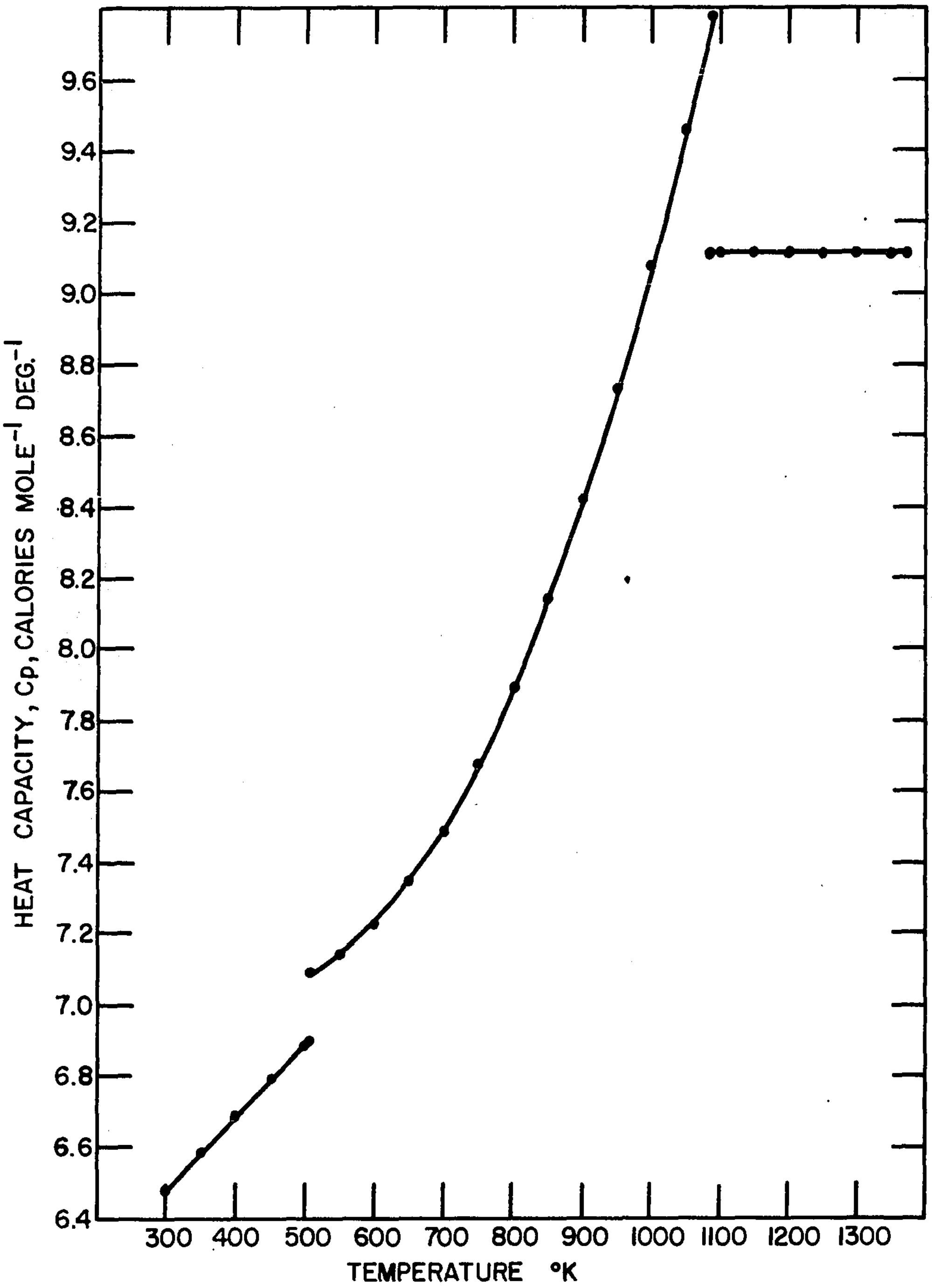
HEAT CAPACITY, Cp, CALORIES MOLE^{-1} DEG.$^{-1}$
9.6
9.4
9.2
9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
300
400
500
600
700
800
900
1000
1100
1200
1300
TEMPERATURE °K

Table 7. Heat content measurements of europium metal

Furnace temp. (°C)	Observed heat of sample (calories/mole)	Reproducibility (%)	Calculated heat of sample (calories/mole)	Deviation of obs. values from calc. values (%)
100.0	652.9	0.44	652.9	---
200.0	1326.3	0.18	1326.3	---
240.1	1618.6	0.14	1616.3	+0.14
259.6	1755.0	0.12	1755.0	---
279.9	1901.4	0.15	1899.7	+0.09
301.0	2045.2	0.14	2050.8	-0.27
399.6	2769.7	0.12	2768.9	+0.03
500.3	3530.0	0.18	3532.1	-0.06
600.1	4341.5	0.06	4331.4	+0.23
700.3	5179.1	0.06	5189.9	-0.21
791.0	6030.0	0.08	6026.3	+0.06
801.0	6158.1	0.09	6122.4	+0.42
826.4	8561.2	0.12	8567.4	-0.07
901.2	9246.4	0.09	9249.1	-0.03
1001.9	10189.3	0.10	10166.8	+0.22
1100.1	11047.9	0.11	11061.7	-0.12

calories/mole (230° to 817°C, average deviation of observed values from calculated values, ± 0.15%)

$$\Delta H\Big]_0^t = 9.1132t + 1036.3 \text{ calories/mole} \qquad (73)$$

(817° to 1100°C, average deviation of observed values from calculated values, ± 0.11%)

Table 8. Thermodynamic functions of europium metal (calories per degree per mole)

T °K	C_p	$S^o_T - S^o_{298.15}$	$\frac{H^o_T - H^o_{298.15}}{T}$
298.15	6.478	0.000	0.000
300	6.482	0.040	0.040
350	6.584	1.047	0.967
400	6.687	1.933	1.676
450	6.789	2.726	2.238
500	6.892	3.447	2.699
503.15	6.898	3.490	2.725
503.15	7.091	3.515	2.750
550	7.141	4.148	3.121
600	7.226	4.773	3.460
650	7.344	5.356	3.754
700	7.494	5.905	4.015
750	7.676	6.428	4.253
800	7.892	6.930	4.474
850	8.140	7.416	4.682
900	8.420	7.889	4.882
950	8.733	8.353	5.076
1000	9.079	8.809	5.267
1050	9.458	9.261	5.458
1090.15	9.785	9.622	5.611
1090.15	9.113	11.644	7.632
1100	9.113	11.726	7.646

Table 8. (Continued)

T °K	C_p	$S^o_T - S^o_{298.15}$	$\frac{H^o_T - H^o_{298.15}}{T}$
1150	9.113	12.131	7.710
1200	9.113	12.519	7.768
1250	9.113	12.891	7.822
1300	9.113	13.248	7.871
1350	9.113	13.592	7.917
1373.15	9.113	13.747	7.938

Expressed relative to the standard temperature of 298.15°K, the thermodynamic functions become:

$$\Delta H\Big]^{T}_{298.15} = 5.8665T + 1.025\times10^{-3}T^2 - 1840.2 \text{ calories/mole} \quad (298.15° \text{ to } 503.15°\text{K}) \tag{74}$$

$$\Delta H\Big]^{T}_{298.15} = 8.3586T - 2.9000\times10^{-3}T^2 + 2.1735\times10^{-6}T^3 - 2364.9 \text{ calories/mole} \quad (503.15° \text{ to } 1090.15°\text{K}) \tag{75}$$

$$\Delta H\Big]^{T}_{298.15} = 9.1132T - 1614.3 \text{ calories/mole} \quad (1090.15° \text{ to } 1373.15°\text{K}) \tag{76}$$

For the heat capacity,

$$C_p = 5.8665 + 2.0500\times10^{-3}T \text{ calories/degree-mole} \quad (298.15° \text{ to } 503.15°\text{K}) \tag{77}$$

$$C_p = 8.3586 - 5.8000\times10^{-3}T + 6.5205\times10^{-6}T^2 \text{ calories/degree-mole} \tag{78}$$

(503.15° to 1090.15°K)

$$C_p = 9.1132 \text{ calories/degree-mole} \qquad (79)$$

(1090.15° to 1373.15°K)

For the entropy,

$$\Delta S\Big]_{298.15}^{T} = 5.8665 \ln T/298.15 + 2.05\times10^{-3}(T-298.15) \qquad (80)$$

calories/degree-mole (298.15° to 503.15°K)

$$\Delta S\Big]_{503.15}^{T} = 8.3586 \ln T/503.15 - 5.8000\times10^{-3}(T-503.15) + 3.2603\times10^{-6}(T^2-(503.15)^2) \qquad (81)$$

calories/degree-mole (503.15° to 1090.15°K)

$$\Delta S\Big]_{1090.15}^{T} = 9.1132 \ln T/1090.15 \text{ calories/degree-mole} \qquad (82)$$

(1090.15° to 1373.15°K)

The melting point of europium metal was reported by Spedding _et_ _al_. (1958) as 826 ± 10°C. The results of this study indicated that europium melts at 817 ± 5°C. The heat of the anomalous transition was computed from Equations 72-71 to be 12 ± 7 calories/mole. The heat of fusion was computed from Equations 73-72 as 2204 ± 18 calories per mole. The entropies of these transitions are 0.025 ± 0.014 and 2.022 ± 0.017 calories per degree per mole.

Ytterbium

Three samples of ytterbium were prepared before the studies to 1100°C were completed. The first sample ruptured above 700°C. A new sample was prepared and studied from 100° to 814°C; above this temperature, it ruptured. New tantalum crucibles were designed and fabricated from tubing thus eliminating the troublesome side seam where the metal fractured. A third sample was prepared, and check points made at several points in the temperature range made with the second sample; the data were in agreement, and the study was completed to 1100°C. The measured heat contents, reproducibilities, calculated heat contents and deviation of the observed values from the calculated values are given in Table 9. The thermodynamic functions of ytterbium metal are given at 50° intervals and the transformation temperatures in Table 10. Low temperature studies on ytterbium were not completed at the time of this study; therefore, the calculated free energy functions were omitted from the table, and the entropy is reported from 298.15°K to T.

The enthalpy studies of this metal showed a small but definite break in the curve of the enthalpy, Figure 16, at 553°K. From the empirical equations used to fit the data, this anomaly appeared to be twice as large as that reported in europium at 503°K. The large break in the heat capacity at 553°, Figure 17, is the result of the empirical equations

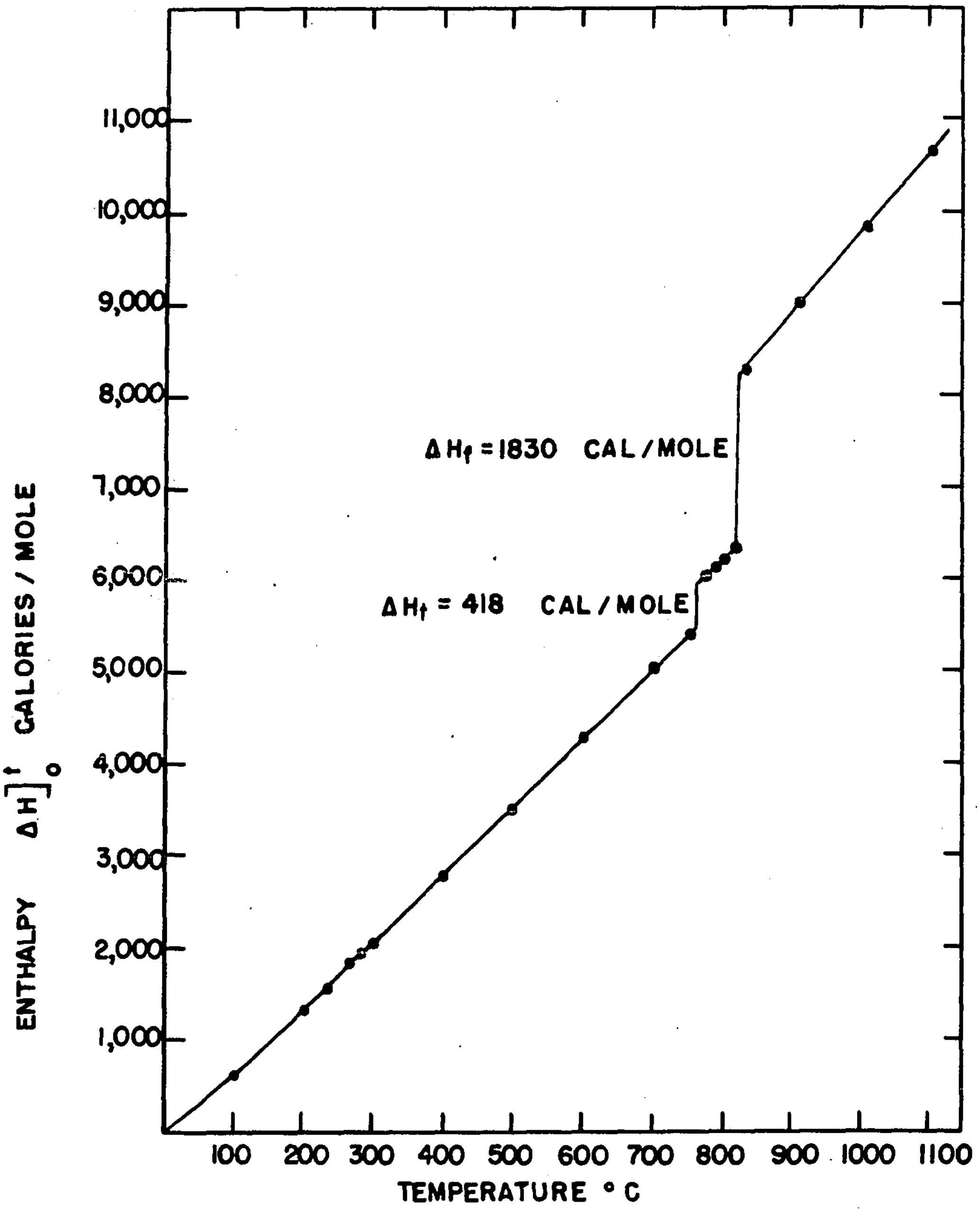

Figure 16. The measured enthalpy of ytterbium metal from 0° to 1100°C

Figure 17. The calculated heat capacity of ytterbium metal from 298.15° to 1373.15°K. The large break in the heat capacity curve at 553.15° is the result of fitting the observed enthalpies above and below the break to two empirical equations; the break is exaggerated, and is smaller than shown. The empirical equations are also sensitive to changes in slope, and the downward curvature of the heat capacity may be magnified in the figure

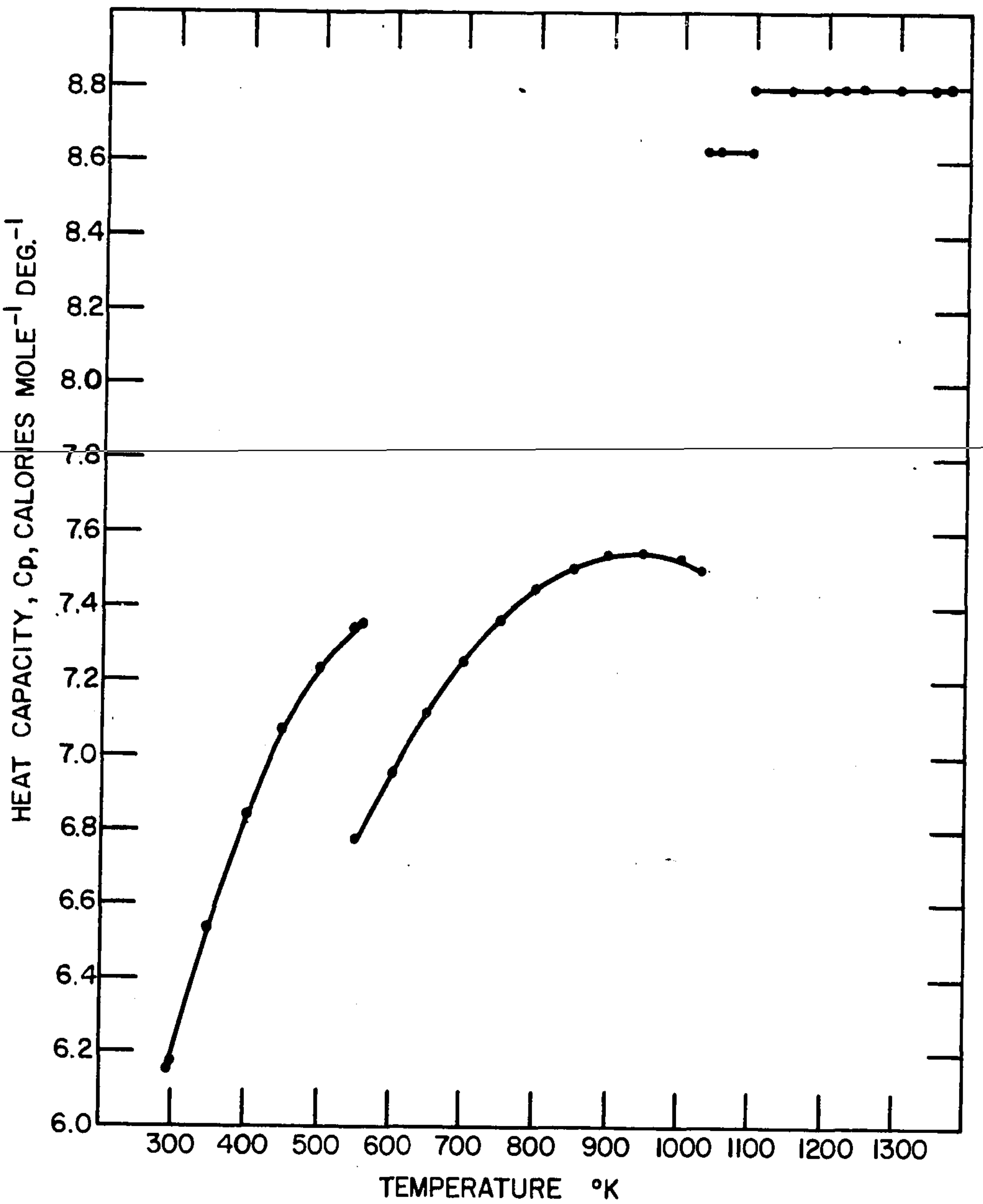
HEAT CAPACITY, Cp, CALORIES MOLE^{-1} DEG.$^{-1}$
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
300
400
500
600
700
800
900
1000
1100
1200
1300
TEMPERATURE °K

Table 9. Heat content measurements of ytterbium metal

Furnace temp. (°C)	Observed heat of sample (calories/mole)	Reproducibility (%)	Calculated heat of sample (calories/mole)	Deviation of obs. values from calc. values (%)
99.9	634.5	0.27	632.9	+0.25
200.2	1321.6	0.10	1328.4	-0.51
233.7	1571.3	0.23	1569.7	+0.10
244.8	1658.0	0.18	1650.4	+0.46
253.7	1717.1	0.13	1715.2	+0.11
268.6	1818.4	0.14	1824.2	-0.32
294.2	2030.8	0.18	2031.6	-0.04
300.4	2073.9	0.15	2074.0	---
399.6	2774.1	0.06	2770.7	+0.12
499.8	3497.8	0.08	3502.1	-0.12
600.4	4255.4	0.04	4254.0	+0.03
700.1	5007.5	0.02	5005.9	+0.03
749.9	5379.5	0.05	5380.7	-0.02
774.2	5996.2	0.05	5997.2	-0.02
786.3	6102.4	0.05	6101.6	+0.01
799.4	6215.5	0.06	6214.7	+0.01
814.2	6341.5	0.05	6342.4	-0.01
830.9	8291.1		8317.6	-0.32
912.6	9037.3	0.04	9036.1	+0.01
1004.0	9838.5	0.06	9839.9	-0.01
1100.1	10686.2	0.04	10685.0	+0.01

Table 10. Thermodynamic functions of ytterbium metal (calories per degree per mole)

T °K	C_p	$S^o_T - S^o_{298.15}$	$\frac{H^o_T - H^o_{298.15}}{T}$
298.15	6.156	0.000	0.000
300	6.171	0.038	0.038
350	6.532	1.017	0.941
400	6.829	1.910	1.659
450	7.063	2.728	2.247
500	7.233	3.482	2.738
550	7.339	4.176	3.151
553.15	7.343	4.218	3.175
553.15	6.770	4.268	3.225
600	6.948	4.825	3.508
650	7.112	5.388	3.780
700	7.250	5.920	4.023
750	7.362	6.425	4.242
800	7.448	6.903	4.440
850	7.507	7.356	4.618
900	7.540	7.786	4.780
950	7.546	8.194	4.925
1000	7.526	8.581	5.056
1033.15	7.499	8.826	5.135
1033.15	8.630	9.231	5.540
1050	8.630	9.370	5.589
1097.15	8.630	9.749	5.720

Table 10. (Continued)

T °K	C_p	$S^o_T - S^o_{298.15}$	$\frac{H^o_T - H^o_{298.15}}{T}$
1097.15	8.794	11.417	7.388
1100	8.794	11.441	7.392
1150	8.794	11.831	7.453
1200	8.794	12.206	7.509
1250	8.794	12.565	7.560
1300	8.794	12.910	7.608
1350	8.794	13.242	7.652
1373.15	8.794	13.391	7.671

and probably is not as large as is indicated in the figure.

The empirical equations used to fit the observed enthalpies as a function of the centigrade temperature are as follows:

$$\Delta H\Big]_0^t = 5.950t + 4.2755\times10^{-3}t^2 - 4.2571\times10^{-6}t^3 \text{ calories/mole} \qquad (83)$$

(0° to 280°C, average deviation of observed values from calculated values, ± 0.29%)

$$\Delta H\Big]_0^t = 5.2240t + 3.4973\times10^{-3}t^2 - 1.7552\times10^{-6}t^3 + 236.68 \qquad (84)$$

calories/mole (280° to 760°C, average deviation of observed values from calculated values, ± 0.05%)

$$\Delta H\Big]_0^t = 8.6299t - 684.17 \text{ calories/mole} \qquad (85)$$

(760° to 824°C, average deviation of observed values from calculated values, ± 0.01%)

$$\Delta H\Big]_{0}^{t}=8.7944t + 1010.7 \text{ calories/mole} \qquad (86)$$

(824° to 1100°C, average deviation of observed values from calculated values, ± 0.09%)

Conversion to the Kelvin temperature scale and 298.15°K as the reference temperature, the thermodynamic functions can be expressed:

$$\Delta H\Big]_{298.15}^{T}=2.6615T+7.7640\text{x}10^{-3}T^{2}-4.2571\text{x}10^{-6}T^{3}-1370.9 \qquad (87)$$

calories/mole (298.15° to 553.15°K)

$$\Delta H\Big]_{298.15}^{T}=2.9206T+4.9357\text{x}10^{-3}T^{2}-1.7552\text{x}10^{-6}T^{3}-1045.0 \qquad (88)$$

calories/mole (553.15° to 1033.15°K)

$$\Delta H\Big]_{298.15}^{T}= 8.6299T - 3192.8 \text{ calories/mole} \qquad (89)$$

(1033.15° to 1097.15°K)

$$\Delta H\Big]_{298.15}^{T}= 8.7944T - 1542.9 \text{ calories/mole} \qquad (90)$$

(1097.15° to 1373.15°K)

For the heat capacity, differentiation of the enthalpies gives:

$$C_p=2.6615+1.5528\text{x}10^{-2}T-1.2771\text{x}10^{-5}T^{2} \text{ calories/degree-mole} \qquad (91)$$

(298.15° to 553.15°K)

$$C_p= 2.9206 + 9.8714\text{x}10^{-3}T - 5.2656\text{x}10^{-6}T^{2} \qquad (92)$$

calories/degree-mole (553.15° to 1033.15°K)

$$C_p= 8.6299 \text{ calories/degree-mole} \qquad (93)$$

(1033.15° to 1097.15°K)

$$C_p = 8.7944 \text{ calories/degree-mole} \quad (1097.15° \text{ to } 1373.15°K) \tag{94}$$

The entropy is expressed as:

$$\Delta S\Big]_{298.15}^{T} = 2.6615 \ln T/298.15 + 1.5528\times10^{-2}(T-298.15) - 6.3856\times10^{-6}(T^2-(298.15)^2) \text{ calories/degree-mole } (298.15° \text{ to } 553.15°K) \tag{95}$$

$$\Delta S\Big]_{553.15}^{T} = 2.9206 \ln T/553.15 + 9.8714\times10^{-3}(T-553.15) - 2.6328\times10^{-6}(T^2-(553.15)^2) \text{ calories/degree-mole } (553.15° \text{ to } 1033.15°K) \tag{96}$$

$$\Delta S\Big]_{1033.15}^{T} = 8.6299 \ln T/1033.15 \text{ calories/degree-mole } (1033.15° \text{ to } 1097.15°K) \tag{97}$$

$$\Delta S\Big]_{1097.15}^{T} = 8.7944 \ln T/1097.15 \text{ calories/degree-mole } (1097.15° \text{ to } 1373.15°K) \tag{98}$$

The transformation temperature for the fcc-bcc transformation was observed to be 760 ± 5°C in this study. The melting point was reported as 824° by Spedding and Daane (1954), and confirmed in this study. The enthalpies of the transformations and fusion were computed from Equations 84-83, 85-84, and 86-85 at the respective temperatures, and found to be 27 ± 6, 418 ± 3 and 1830 ± 8 calories per mole. The corresponding entropies were obtained by dividing these enthalpies by the respective transformation temperatures, and are: 0.049 ± 0.011, 0.405 ± 0.003 and 1.668 ± 0.007 calories per degree per mole.

Yttrium

The heat content of yttrium metal was determined from 0° to 1100° in the low temperature apparatus, and from 1100° to 1675°C in the high temperature vacuum apparatus. Two samples were used, both from the same source metal.

The measured heat contents, reproducibilities, calculated heat contents and deviation of the observed values from the calculated values are presented in Table 11. At least three measurements of the heat content were made at each temperature up to and including 1434°C. Above this temperature, single determinations were made over shorter temperature intervals in an effort to maintain as low a tantalum content in the yttrium as possible, and prevent undue attack of the tantalum crucibles. Measurements were made over the narrower temperature ranges to 1675°C; it had been planned to study this sample to 1700°C, but a leak in the furnace during the heating period at this temperature, ruined the sample. Five measurements had been made in the liquid range, and the studies were terminated.

The calculated thermodynamic functions for yttrium metal are presented in Table 12. The measured enthalpy of yttrium as a function of the temperature is shown in Figure 18 with

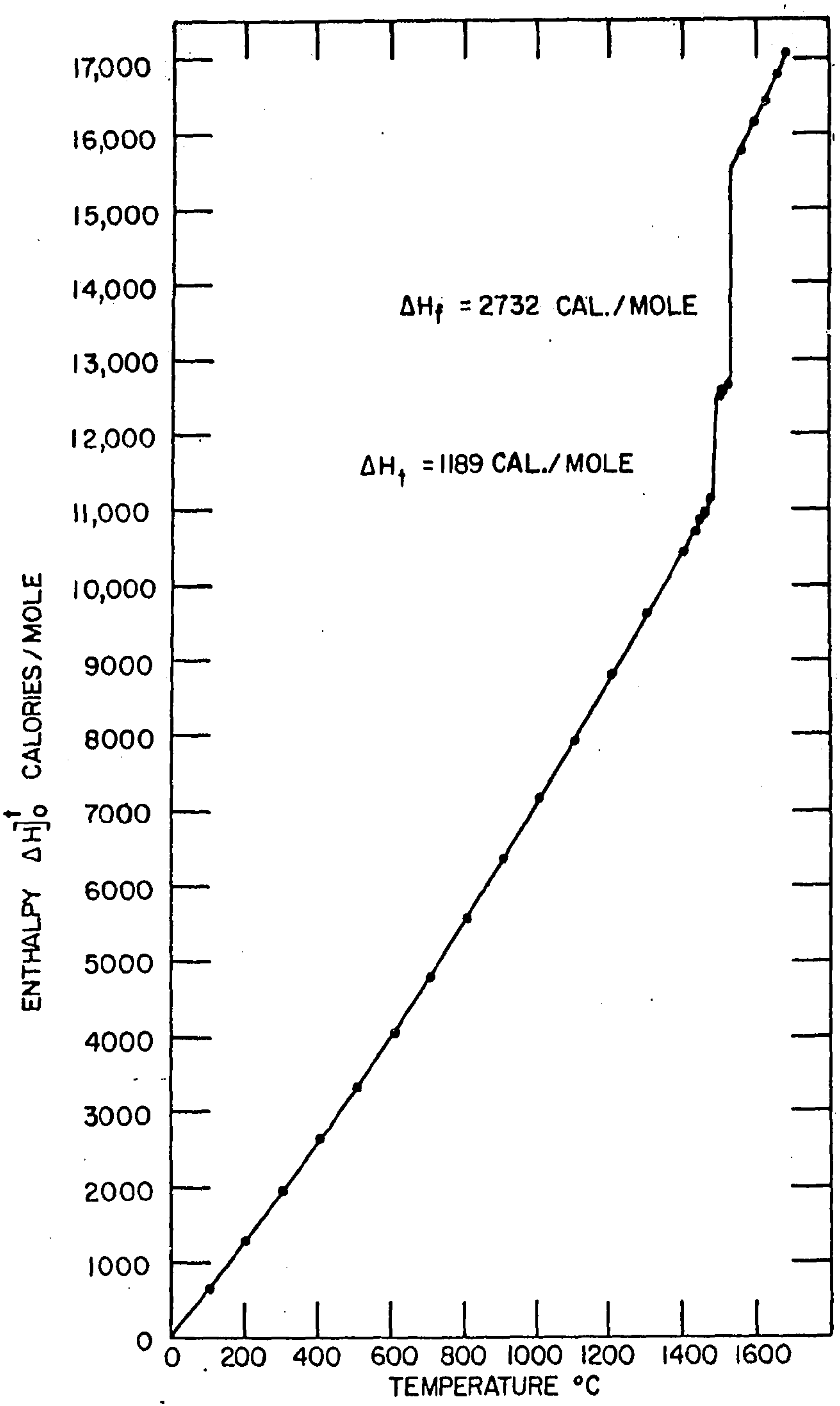

Figure 18. The measured enthalpy of yttrium metal from 0° to 1675°C

Table 11. Heat content measurements of yttrium metal

Furnace temp. (°C)	Observed heat of sample (calories/mole)	Reproducibility (%)	Calculated heat of sample (calories/mole)	Deviation of obs. values from calc. values (%)
100.9	640.3	0.26	644.3	-0.62
199.8	1292.8	0.10	1291.7	+0.09
299.5	1964.9	0.08	1960.2	+0.24
399.7	2650.0	0.06	2648.5	+0.06
499.2	3337.2	0.08	3348.6	-0.34
599.0	4059.6	0.05	4067.7	-0.20
698.8	4793.6	0.04	4804.1	-0.22
799.7	5576.3	0.06	5566.4	+0.18
901.4	6367.9	0.05	6353.3	+0.23
998.9	7153.7	0.08	7125.4	+0.40
1099.6	7962.1	0.08	7941.3	+0.26
1100	7898.5	0.61	7944.6	-0.58
1200	8811.0	0.27	8773.9	+0.42
1300	9593.6	0.13	9622.4	-0.30
1400	10439.7	0.19	10490.3	-0.48
1434	10744.8	0.19	10789.9	-0.42
1438	10842.2		10825.3	+0.16
1447	10893.8		10905.1	-0.10
1460	11013.3		11020.6	-0.07
1467	11119.9		11082.9	+0.36
1471	11170.0		11118.6	+0.46

Table 11. (Continued)

Furnace temp. (°C)	Observed heat of sample (calories/mole)	Reproducibility (%)	Calculated heat of sample (calories/mole)	Deviation of obs. values from calc. values (%)
1497	12523.3		12533.1	-0.08
1504	12611.5		12591.7	+0.16
1511	12640.5		12650.3	-0.08
1553	15779.9		15778.0	+0.01
1588	16152.5		16138.6	+0.09
1619	16435.1		16458.0	-0.14
1651.5	16786.4		16792.9	-0.04
1675	17048.6		17035.0	+0.08

Table 12. Thermodynamic functions of yttrium metal (calories per degree per mole)

T °K	C_p	$S^o_T - S^o_0$	$\frac{H^o_T - H^o_{298.15}}{T}$	$-\left(\frac{F^o_T - H^o_{298.15}}{T}\right)$
298.15	6.348	10.630	0.000	10.630
300	6.351	10.669	0.039	10.630
350	6.429	11.654	0.946	10.708
400	6.508	12.518	1.637	10.881
450	6.588	13.289	2.182	11.107
500	6.668	13.987	2.627	11.360
550	6.750	14.627	2.998	11.629
600	6.832	15.217	3.314	11.903
650	6.914	15.768	3.588	12.180

Table 12. (Continued)

T °K	C_p	$S^o_T - S^o_0$	$\frac{H^o_T - H^o_{298.15}}{T}$	$-\left(\frac{F^o_T - H^o_{298.15}}{T}\right)$
700	6.998	16.283	3.828	12.455
750	7.082	16.769	4.043	12.726
800	7.167	17.228	4.235	12.993
850	7.253	17.665	4.410	13.255
900	7.340	18.082	4.570	13.512
950	7.427	18.482	4.719	13.763
1000	7.515	18.865	4.856	14.009
1050	7.604	19.234	4.985	14.249
1100	7.694	19.590	5.106	14.484
1150	7.785	19.934	5.221	14.713
1200	7.876	20.267	5.329	14.938
1250	7.968	20.590	5.433	15.157
1300	8.061	20.905	5.532	15.372
1350	8.155	21.210	5.628	15.582
1400	8.249	21.509	5.720	15.789
1450	8.344	21.799	5.808	15.991
1500	8.440	22.084	5.894	16.190
1550	8.537	22.363	5.978	16.385
1600	8.634	22.635	6.060	16.575
1650	8.732	22.902	6.139	16.763
1700	8.832	23.165	6.217	16.948
1750	8.931	23.422	6.293	17.129

Table 12. (Continued)

T °K	C_p	$S^\circ_T - S^\circ_0$	$\frac{H^\circ_T - H^\circ_{298.15}}{T}$	$-\left(\frac{F^\circ_T - H^\circ_{298.15}}{T}\right)$
1758.15	8.948	23.464	6.305	17.158
1758.15	8.371	24.140	6.982	17.158
1800	8.371	24.279	7.014	17.265
1803.15	8.371	24.289	7.016	17.273
1803.15	10.303	25.804	8.531	17.273
1850	10.303	25.955	8.576	17.379
1900	10.303	26.112	8.621	17.491
1950	10.303	26.266	8.665	17.601

breaks shown for the crystal transformation and the melting point. The calculated heat capacity is shown in Figure 19.

The heat content data were fitted to the following empirical equations as a function of the centigrade temperature:

$$\Delta H\Big]_0^t = 6.3095t + 7.7325\times10^{-4}t^2 + 5.1636\times10^{-8}t^3 \qquad (99)$$

calories/mole (0° to 1485°C, average deviation of observed values from calculated values, ± 0.29%)

$$\Delta H\Big]_0^t = 8.3714t + 1.1 \text{ calories/mole} \qquad (100)$$

(1485° to 1530°C, average deviation of observed values from calculated values, ± 0.11%)

$$\Delta H\Big]_0^t = 10.3028t - 222.2 \text{ calories/mole} \qquad (101)$$

(1530° to 1675°C, average deviation of observed values from calculated values, ± 0.07%)

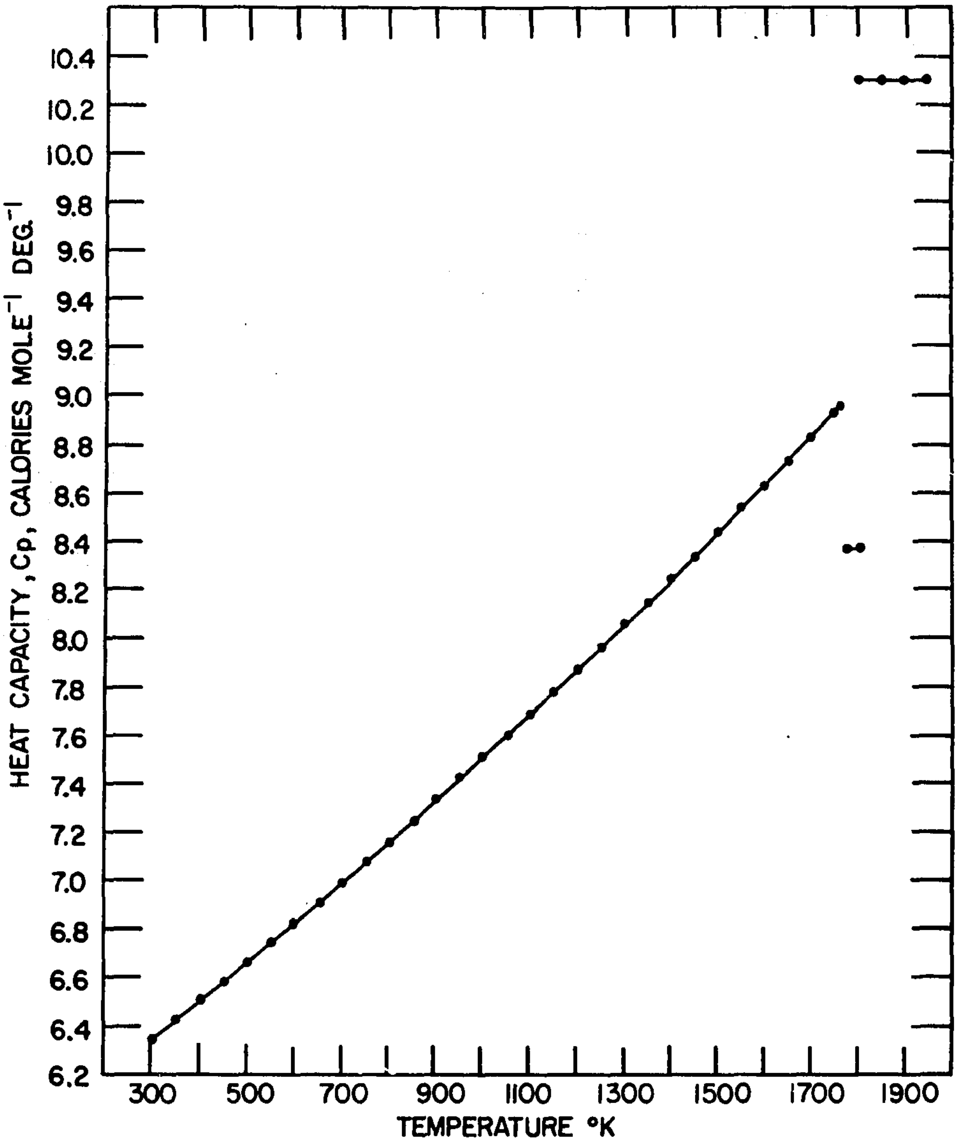

Figure 19. The calculated heat capacity of yttrium metal from 298.15°K to 1950.15°K

Expressed as a function of the Kelvin temperature with 298.15°K as the reference temperature, the thermodynamic functions starting with the enthalpy become:

$$\Delta H\Big]_{298.15}^{T}=5.8986T+7.3094\times10^{-4}T^2+5.1636\times10^{-8}T^3-1825 \quad (102)$$

calories/mole (298.15° to 1758.15°K)

$$\Delta H\Big]_{298.15}^{T}= 8.3714T - 2443.7 \text{ calories/mole} \quad (103)$$

(1758.15° to 1803.15°K)

$$\Delta H\Big]_{298.15}^{T}= 10.3028T - 3194.6 \text{ calories/mole} \quad (104)$$

(1803.15° to 1950.15°K)

The heat capacities are expressed by:

$$C_p= 5.8986 + 1.4619\times10^{-3}T + 1.5491\times10^{-7}T^2 \quad (105)$$

calories/degree-mole (298.15° to 1758.15°K)

$$C_p = 8.3714 \text{ calories/degree-mole} \quad (106)$$

(1758.15° to 1803.15°K)

$$C_p = 10.3028 \text{ calories/degree-mole} \quad (107)$$

(1803.15° to 1950.15°K)

The entropies are expressed by:

$$\Delta S\Big]_{298.15}^{T}=5.8986 \ln T/298.15+1.4619\times10^{-3}(T-298.15) +7.7454\times10^{-8}(T^2-(298.15)^2) \quad (108)$$

calories/degree-mole (298.15° to 1758.15°K)

$$\Delta S\Big]_{1758.15}^{T}=8.3714 \ln T/1758.15 \text{ calories/degree-mole} \quad (109)$$
(1758.15° to 1803.15°K)

$$\Delta S\Big]_{1803.15}^{T}=10.3028 \ln T/1803.15 \text{ calories/degree-mole} \quad (110)$$
(1803.15° to 1950.15°K)

The heat of fusion and transformation depend upon the slope of the curve fitted to the data in the bcc region of yttrium. The relatively large error in the temperature made it difficult to obtain data over the small temperature range as the transformation occurred over a 10° to 15° temperature range. The crystal transformation was observed at 1485 ± 8°C, which is 5° lower than reported by Eash (1959) and 26° higher than observed by Habermann (1960). The melting point was observed in this study at 1530 ± 8°C, and is 13 to 15° higher than the value reported by Eash, and 20° higher than reported by Habermann. The small amount of titanium present in the metal (see Table 1) may account for the differences.

The heats of transformation and fusion were computed from Equations 100-99 and 101-100. These values were 1189 ± 46 and 2732 ± 25 calories per mole. The entropies were determined by dividing the heats involved by the respective temperatures and found to be 0.676 ± 0.026 and 1.515 ± 0.014 calories per degree per mole.

The enthalpies and entropies of transition and fusion are summarized in Table 13.

Table 13. The enthalpies and entropies of transition and fusion of the rare earth metals

Element	Transition	T°K	ΔH_t $\frac{\text{cal.}}{\text{mole}}$	ΔS_t	Transition	T°K	ΔH_t $\frac{\text{cal.}}{\text{mole}}$	ΔH_t	Transition	T°K	ΔH_f $\frac{\text{cal.}}{\text{mole}}$	ΔS_f	$\Sigma \Delta S$
Y	---	---	--	---	hcp-bcc	1758	1189	0.676	bcc-liq.	1803	2732	1.515	2.191
La	hcp-fcc	583	67	0.115	fcc-bcc	1141	753	0.660	bcc-liq.	1193	1482	1.242	2.017
Ce[1]	---	---	--	---	fcc-bcc	1003	700	0.698	bcc-liq.	1077	1238	1.149	1.847
Pr	---	---	--	---	hcp-bcc	1071	760	0.709	bcc-liq.	1208	1652	1.367	2.076
Nd[1]	---	---	--	---	hcp-bcc	1135	713	0.628	bcc-liq.	1297	1705	1.314	1.942
Sm[1]	---	---	--	---	rhom-?	1190	744	0.625	? -liq.	1345	2061	1.532	2.157
Eu	?	503	12	0.025	---	----	---	----	bcc-liq.	1090	2204	2.022	2.047
Yb	?	553	27	0.049	fcc-bcc	1033	418	0.405	fcc-liq.	1097	1830	1.668	2.122

[1] Data obtained by Spedding *et al*. (1960).

DISCUSSION

In Tables 14, 15, 16, 17 and 18, the values of the thermodynamic functions reported for the rare earth metals in this study are compared to the values reported in the literature. The poor agreement found between this work and that done prior to 1950 is primarily attributable to the poor quality of the metal used in the earlier studies, and to the less precise and direct methods by which some of the data were obtained by those earlier workers. It therefore seems reasonable to assume that the present results are more accurate. It is interesting to note that the estimated values for the heats of fusion are considerably higher than those actually observed for these metals, whereas the heats of transition that had been estimated were found to be too low when compared to the data reported in this study. The heat of transition reported by McKeown (1958) for praseodymium is 5%, or some 22 calories per mole, lower than reported here. It is felt that the low value may be due to error in the slope of his enthalpy curves in this region. His sample capsule completely ruptured above 875°C, and may have caused sample contamination at temperatures below this.

From the comparison of the enthalpies of α-Al_2O_3 measured in this work to other reported values, it appeared that the vacuum calorimeter was functioning properly and was a suitable instrument for the measurement of high temperature

Table 14. Comparison of thermodynamic functions reported in literature to results reported in this investigation for lanthanum metal

Prior work by:	Function	Remarks	This Study
Hillebrand (1876)	$\bar{c}_p$=0.04485 cal./deg. gm. (0° to 100°C)	Sample 93.74% La, with Pr, Nd, Fe and Al	$\bar{c}_p$= 0.04526 cal./deg. gm. (observed, 0° to 99°C)
Lewis and Gibson (1917)	S_{298}= 13.7 e.u.	Calculation from 3rd law	--------
Jaeger *et al.* (1936, 1938)	$\bar{c}_p$=0.04964 cal./deg. gm. (20° to 300°C)	Sample 98.8% La with Fe, C, Si, Al and Mg	$\bar{c}_p$= 0.04755 cal./deg. gm. (calculated, 20° to 300°C)
	$\bar{c}_p$=0.05048 cal./deg. gm. (20° to 420°C)		$\bar{c}_p$= 0.04911 cal./deg. gm. (calculated, 20° to 420°C)
	$\bar{c}_p$=0.05241 cal./deg. gm. (20° to 628°C)		$\bar{c}_p$= 0.05011 cal./deg. gm. (calculated, 20° to 628°C)
	$\bar{c}_p$=0.04725 cal./deg. gm. (0° to 20°C)	Estimated	$\bar{c}_p$= 0.04473 cal./deg. gm. (calculated, 0° to 20°C)
	C_p= 8 to 11 cal./deg.mole (between 672° and 701°)	Estimated	C_p= 7.708 cal./deg. mole (at 672°C)
			C_p= 7.807 cal./deg. mole (at 701°C)

Table 14. (Continued)

Prior work by:	Function	Remarks	This study
	C_p=10 to 12 cal./deg. mole (between 711° and 750°)	Estimated	C_p= 7.841 cal./deg. mole (at 711°C) C_p= 7.976 cal./deg. mole (at 750°C)
Cavallaro (1943)	ΔH_{fus}=5000 cal./mole	Thermal analysis studies	ΔH_{fus}=1482 cal./mole (at 1193°K)
Brewer (1950)	ΔH_{fus}=2300 cal./mole (at 1160°K)	Estimated	ΔH_{fus}=1482 cal./mole (at 1193°K)
Parkinson *et al.* (1951)	S_{300}= 13.64 e.u.	Extrapolated from low temperature calorimetric studies	---
Stull and Sinke (1956)	ΔH_{fus}=2700 cal./mole (at 1193°K)	Estimated	ΔH_{fus}= 1482 cal./mole (at 1193°K)
Kelley (1960)	$C_p=6.17 + 1.60 \times 10^{-3}T$ cal./deg. mole (298° to 1193°K)	Estimated	$C_p= 5.48 + 2.61 \times 10^{-3}T$ cal./deg. mole (298° to 583°K) ΔH_{trans}= 67 cal./mole (at 583°K) $C_p= 5.25 + 1.84 \times 10^{-3}T + 8.13 \times 10^{-7}T^2$

Table 14. (Continued)

Prior work by:	Function	Remarks	This study
			cal./deg. mole (583° to 1141°K)
			ΔH_{trans} = 753 cal./mole (at 1141°K)
			C_p = 9.45 cal./deg. mole (1141° to 1193°K)
	ΔH_{fus} = 2750 cal./mole (at 1193°K)	Estimated	ΔH_{fus} = 1482 cal./mole (at 1193°K)
	C_p = 8.00 cal./deg. mole (1193° to 3000°K)	Estimated	C_p = 8.21 cal./deg. mole (1193° to 1373°K)
Jennings *et al.* (1960)	S_{298} = 13.61 e.u.	From θ and γ values of La	------

Table 15. Comparison of thermodynamic functions reported in literature to results reported in this investigation for praseodymium metal

Prior work by:	Function	Remarks	This study
Canneri (1934a, 1934b)	ΔH_{fus} = 2650 cal./mole = 2750 cal./mole	Thermal analysis studies on the Pr-Ag and Pr-Cu alloy systems	ΔH_{fus} = 1652 cal./mole (at 1208°K)
Rossi (1934)	$\bar{c}_p$ = 0.0486 cal./deg. gm. (20° to 100°C)	Sample reported 99.5% pure, and m.p. as 950°C	$\bar{c}_p$ = 0.04656 cal./deg. gm. (20° to 100°C)
Cavallaro (1943)	ΔH_{fus} = 3100 cal./mole	Thermal analysis studies on sample reported 99% pure	ΔH_{fus} = 1652 cal./mole (at 1208°K)
Parkinson *et al.* (1951)	S_{298} = 17.49 e.u.	Extrapolated from results of low temperature calorimetric studies	-------
Stull and Sinke (1956)	ΔH_{trans} = 320 cal./mole (at 1071°K)	Estimated	ΔH_{trans} = 760 cal./mole (at 1071°K)
	ΔH_{fus} = 2400 cal./mole (at 1208°K)	Estimated	ΔH_{fus} = 1652 cal./mole (at 1208°K)
	C_p = 8.00 cal./deg. mole (1208° to 3000°K)	Estimated	C_p = 10.27 cal./deg. mole (1208° to 1373°K)

Table 15. (Continued)

Prior work by:	Function	Remarks	This study
Kelley (1960)	$C_p=5.50 + 3.20\text{x}10^{-3}T$ cal./deg. mole (298° to 1071°K)	Estimated	$C_p= 5.76 + 1.65\text{x}10^{-3}T + 2.21\text{x}10^{-6}T^2$ cal./deg. mole (298° to 1071°K)
	$\Delta H_{fus}= 2800$ cal./mole	Estimated	
	$C_p=8.00$ cal./deg. mole (1071° to 1208°K)	Estimated	$C_p= 9.19$ cal./deg. mole (1071° to 1208°K)
McKeown (1958)	$C_p=6.59 + 1.02\text{x}10^{-3}t + 4.63\text{x}10^{-6}t^2$ cal./deg. mole (0° to 798°C)	Calorimetric studies with Bunsen ice calorimeter from 0° to 875°C	$C_p= 6.38 + 2.85\text{x}10^{-3}t + 2.21\text{x}10^{-6}t^2$ cal./deg. mole (0° to 798°C)
	$\Delta H_{trans}=722$ cal./mole		$\Delta H_{trans}= 760$ cal./mole

Table 16. Comparison of thermodynamic functions reported in literature to results reported in this investigation for europium metal

Prior work by:	Function	Remarks	This study
Stull and Sinke (1956) and Kelley (1960)	$S_{298} = 17$ e.u.	Estimated	-------
	$C_p = 5.81 + 1.98 \times 10^{-3} T$ cal./deg. mole (298° to 1100°K)	Estimated	$C_p = 5.87 + 2.05 \times 10^{-3} T$ cal./deg. mole (298° to 503°K)
			$\Delta H_{trans} = 12$ cal./mole (at 503°K)
			$C_p = 8.36 - 5.8 \times 10^{-3} T + 6.52 \times 10^{-6} T^2$ cal./deg. mole (503° to 1090°K)
	$\Delta H_{fus} = 2500$ cal./mole (at 1100°K)	Estimated	$\Delta H_{fus} = 2204$ cal./mole (at 1090°K)
	$C_p = 8.00$ cal./deg. mole (1100° to 1700°K)	Estimated	$C_p = 9.11$ cal./deg. mole (1090° to 1373°K)

Table 17. Comparison of thermodynamic functions reported in literature to results reported in this investigation for ytterbium metal

Prior work by:	Function	Remarks	This study
Stull and Sinke (1956) and Kelley (1960)	$C_p = 5.41 + 1.98 \times 10^{-3}T$ cal./deg. mole (298° to 1071°K)	Estimated	$C_p = 2.66 + 1.55 \times 10^{-2}T - 1.28 \times 10^{-5}T^2$ cal./deg. mole (298° to 553°K)
			$\Delta H_{trans} = 27$ cal./mole (at 553°K)
			$C_p = 2.92 + 9.87 \times 10^{-3}T - 5.27 \times 10^{-6}T^2$ cal./deg. mole (553° to 1033°K)
	$\Delta H_{trans} = 300$ cal./mole (at 1071°K)	Estimated	$\Delta H_{trans} = 418$ cal./mole (at 1033°K)
	$C_p = 7.70$ cal./deg. mole (1071° to 1097°K)	Estimated	$C_p = 8.63$ cal./deg. mole (1033° to 1097°K)
	$\Delta H_{fus} = 2200$ cal./mole (at 1097°K)	Estimated	$\Delta H_{fus} = 1830$ cal./mole (at 1097°K)
	$C_p = 7.50$ cal./deg. mole (1097° to 1800°K)	Estimated	$C_p = 8.79$ cal./deg. mole (1097° to 1373°K)

Table 18. Comparison of thermodynamic functions reported in literature to results reported in this investigation for yttrium metal

Prior work by:	Function	Remarks	This study
Brewer (1950)	S_{298}= 11 e.u.	Estimated	-------
	ΔH_{fus}= 4000 cal./mole (at 1750°K)	Estimated	ΔH_{fus}= 2732 cal./mole (at 1803°K)
	ΔS_{fus}= 2.3 e.u.	Estimated	ΔS_{fus}= 1.515 e.u.
Stull and Sinke (1956) and Kelley (1960)	C_p= 5.72 + 1.00x10^{-3}T	Estimated	C_p= 5.90 + 1.46x10^{-3}T + 1.55x$10^{-7}T^2$ cal./deg. mole (298° to 1758°K)
			ΔH_{trans}= 1189 cal./mole (at 1758°K)
			C_p= 8.37 cal./deg. mole (1758° to 1803°K)
	ΔH_{fus}= 4100 cal./mole (at 1773°K)	Estimated	ΔH_{fus}= 2732 cal./mole (at 1803°K)
	C_p= 8.00 cal./deg. mole (1773° to 3000°K)	Estimated	C_p= 10.30 cal./deg. mole (1803° to 1950°K)
Jennings *et al.* (1960)	S_{298}= 10.63 e.u.	Obtained from low temperature calorimetric studies	------
	C_p= 6.34 cal./deg. mole (at 298°K)		C_p= 6.348 cal./deg. mole (at 298°K)

Table 18. (Continued)

Prior work by:	Function	Remarks	This study
Simmons *et al.* (1958)	$\Delta H\Big]_{0}^{996.2°C} = 89.4$ cal./gm.	Calorimetric studies from 0° to 1000°C	$\Delta H\Big]_{0}^{996.2°C} = 79.89$ cal./gm. (calculated) $\Delta H\Big]_{0}^{998.9°C} = 80.45$ cal./gm. (observed)

heat contents. As previously noted, it appeared that the temperature measurement introduced the greatest error in the method. If a reliable high temperature thermocouple were available to be substituted for the optical pyrometer, more precise results would have been obtained.

The data were treated using a least-squares method to fit them to empirical equations in the temperature ranges studied. This was done in part using an IBM computer. The greatest error of this method occurred between 0° and 100°C, as the curve is force fitted through the origin and the fit at 100°C is established by the data at higher temperatures. The heats of transition and of fusion were obtained by computing the enthalpies at the transition temperature utilizing the enthalpy equations which defined the heat contents above and below the transition temperature. The errors of the heats of transition were computed from the average deviations of the calculated and measured values of the data on either side of the transition.

Small breaks, as yet unexplained, were observed in the enthalpy curves for europium and ytterbium at 503° and 553°K respectively. From magnetic susceptibility work by Lock (1957), ytterbium metal at room temperature is in the $^1S_0$ state with only one atom in 260 estimated to be in the $^2F_{7/2}$ state. Thus ytterbium behaves as a divalent ion in the metal with fourteen electrons in the 4f shell and only two electrons in the conduction band. The behavior of europium in the metallic state is quite complex as shown by the conflicting data reported in the magnetic studies performed by La Blanchetais and Trombe (1956), Bozorth and Van Vleck (1960) and Arajs and Colvin (1961) in which these workers proposed states from Eu^{+1} to Eu^{+3} in the temperature region of 0° to 1500°K. Curry (1958) studied the resistivity of europium and ytterbium metals and found two anomalies in the ytterbium metal above room temperature, one at 450° and one at 600°K. The high temperature anomaly was the larger of the two, but is 43° above the anomaly found in this study. However, she reported no strange behavior in europium metal above room temperature. It may be possible that the breaks in one or both of the studies are the result of 4f electron promotion into the conduction band creating some trivalent ions in the metals. If there were much promotion in europium, the heat capacity measurements should have reflected it; since the effect of the anomaly was extremely small, very little promotion to the trivalent state could have occurred.

Spedding et al. (1961) in a study of the high temperature crystallography of thin metal wire samples of the rare earths, reported a fcc to hcp transition for ytterbium above 583° if impurities were present. They were unable to observe the transition for pure samples of ytterbium; however, the presence of some impurities seemed to cause the transition to occur in a reasonable time. From the results of analysis performed on the ytterbium sample after its study to 1100°C, it seems quite unlikely that sufficient impurities were present for such a transformation to have occurred. The entropy for the transition of hcp lanthanum to fcc lanthanum is considerably greater than the entropy associated with the anomalies in ytterbium and europium (see Table 13). Thus if a transition occurred, it was probably an electronic transition, or, a combination of structure and electronic transitions. It should be observed that the breaks which occur in the heat capacity curves for europium, Figure 15, and ytterbium, Figure 17, were introduced through the empirical formulas used to fit the enthalpy data on either side of the anomalies, and likely are not as large as indicated.

A plot of the entropies of transition for the low temperature form of the rare earth metals to the body-centered cubic modification of the elements is presented in Figure 20, and no simple correlation with the atomic number or 4f electrons is apparent with the temperature of the transformations or the magnitudes of the entropies or enthalpies of the transformations. However, the entropy of transition for the divalent ytterbium is approximately two-thirds the entropy of transition for the trivalent metals.

As was explained in the results for lanthanum metal, reproducible data could be obtained for the heat content of

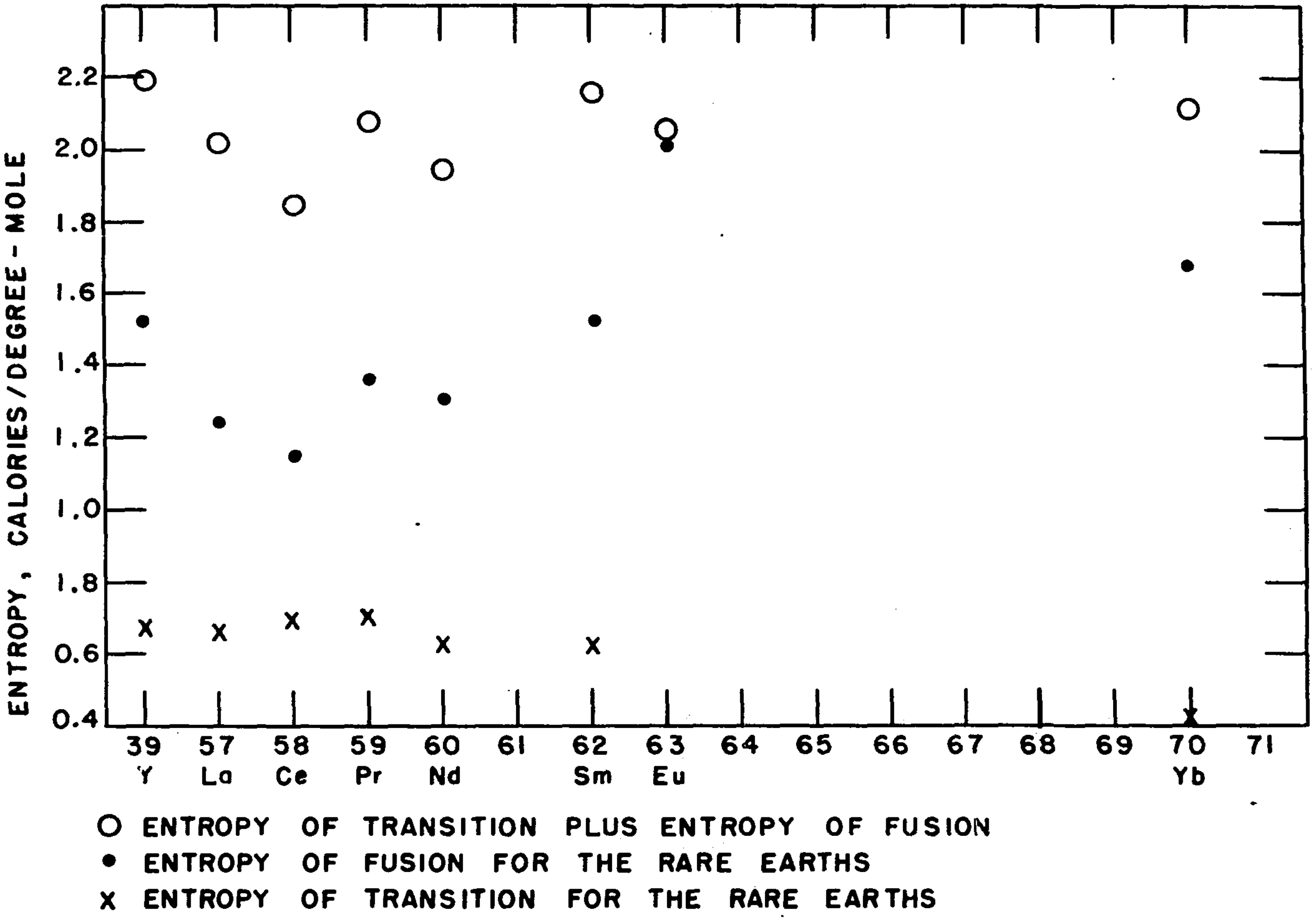

Figure 20. A comparison of the entropies of transitions and fusions of the rare earth metals

the metal above the hcp-fcc transition only by melting and annealing the metal after each drop. No quantitative method for the determination of the amount of fcc lanthanum quenched in the room temperature form was determined. It is felt that the heat of fusion for lanthanum is more reliable than the heat of transition as it is probable the relative amount of fcc modification quenched out was nearly the same from drops made in the bcc region as from drops made in the liquid region as the data were both reproducible and fit a straight line as well as or better than data for some of the other metals in these regions. If a high energy form of the metal is quenched, low values for the associated thermodynamic functions will result.

A plot of the entropies of fusion and of the combined entropies of transition and fusion of the rare earths is also made in Figure 20. This combined entropy, i.e., from a close-packed form of the metal to the liquid state, can be seen to be approximately 2 e.u. Richard's rule predicts a value of 2 e.u. for the heat of fusion for a close-packed metal upon melting. The close-packed structure of the light rare earths with ABAC... stacking has six nearest neighbors and six slightly more distant neighbors, whereas normal close-packing as in the heavy rare earth metals, has the layers arranged ABAB... with twelve equidistant neighbors. One would therefore expect a change for the entropy of fusion of 2 e.u.

for the rare earths except for europium which is body-centered cubic. However, it was found that europium also had an entropy of fusion of 2 e.u. Kelley (1960) lists the following values for the entropies of transition and fusion of the alkaline earth metals: beryllium - hcp-liq., 1.80 e.u.; magnesium - hcp-liq., 2.32 e.u.; calcium - fcc-bcc, 0.38 e.u., bcc-liq., 1.84 e.u., total, 2.22 e.u.; strontium - fcc-bcc, 0.23 e.u., bcc-liq., 2.30 e.u., total, 2.53 e.u.; and, barium - bcc-liq., 2.10 e.u.

The heat capacity at constant pressure given in Equation 3, was based on a qualitative treatment in which the heat capacity was arbitrarily separated into four components - the lattice heat capacity at constant volume, an electronic contribution from the 4f electrons, an electronic contribution from the conduction electrons and a dilation term which is the difference of the lattice heat capacities at constant pressure and at constant volume. If the atoms of the lattice are treated as harmonic oscillators, the lattice contribution to the heat capacity approaches the upper limit of Debye's equation at high temperature, or 3R calories per mole per degree. However, departures are to be expected from this value due to anharmonic motion of the atoms which would increase as the temperature increases.

At low temperatures, the Debye equation becomes proportional to T^3, and the electronic term due to the conduction electrons, which is linear with temperature, is the more significant contribution to the heat capacity. From low temperature heat capacity measurements, the temperature coefficient (γ) for the electronic term of the conduction electrons has been determined for lanthanum by Berman _et al_. (1958) as $24.1\text{x}10^{-4}$ calories per degree^2 per mole, and by Jennings _et al_. (1960) as $23.9\text{x}10^{-4}$ calories per degree^2 per mole. Jennings _et al_. (1960) reported the temperature coefficient γ for yttrium to be $20.3\text{x}10^{-4}$ calories per degree^2 per mole. From preliminary experiments on ytterbium, Gerstein[1] estimated the γ coefficient to be about $12\text{x}10^{-4}$ calories per degree^{2}per mole. If the temperature coefficients for praseodymium and europium are nearly the same as those of lanthanum and ytterbium, the conduction electronic term of the metals studied would contribute to the heat capacity at 300° and 1000°K the following amount:

	300°K	1000°K	
(1) lanthanum	0.72	2.40	calories/degree-mole
(2) praseodymium	0.72	2.40	calories/degree-mole
(3) europium	0.36	1.20	calories/degree-mole
(4) ytterbium	0.36	1.20	calories/degree-mole
(5) yttrium	0.61	2.03	calories/degree-mole

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[1] Gerstein (1961). The temperature coefficient, γ , of ytterbium. Private communication.

Lanthanum and yttrium have no electrons in an unfilled inner shell and therefore have no inner electronic contribution to the heat capacity. Praseodymium, with three electrons in the conduction band, has two electrons in the incomplete 4f shell. From magnetic susceptibility data, it has been shown that these inner electrons give rise to a $^3H_4$ state which roughly follows the Russell-Saunders coupling scheme. Van Vleck (1932) has shown that the higher J values of the ^3H state should give rise to low lying excited states; in the temperature range studied, some of the ions may be excited to these states resulting in a contribution to the heat capacity. All of these states are split by the crystal fields of solid compounds, and if the splitting is large enough in the metal to change the population of states with changing temperature, such a population change would also be reflected in the heat capacity curve. Finally, if in the metal the "exchange term" between the conduction electrons and the ions in the Hamiltonian disturbs the low lying levels in such a way that a population change is caused with changing temperature, this should be reflected in the heat capacity, too.

Approximate calculations can be made for the thermal contribution of the excited states arising from the higher J values following the method outlined in Van Vleck. However, until more is known about the crystal fields and the magnitude of the exchange integral, detailed calculations arising from these effects are not feasible. The crystal field effect would be a flattening of the bumps produced by the Schottky (1922) effect, arising from the higher J value contributions.

If ytterbium and europium are in the pure divalent state with two conduction electrons, the 4f shell will be one-half or completely full. The inner electrons would then give rise to an $^8S_{7/2}$ state for europium, and a $^1S_0$ state for ytterbium. It would take considerable energy to excite the seven f electrons of europium to higher states, and in the temperature range measured, these states would not be populated. In addition, the S states are not split in a crystal field and therefore would not contribute to the heat capacity. On the other hand, if one of the 4f electrons is promoted to a higher subshell, the lowest state in europium would be a $^7F_0$ state and low lying levels of higher J values would be expected to be present. These levels would be split by crystal fields and heat capacity anomalies would be expected as the excited states become populated. The fact that no marked anomalies were observed indicated that a very small percentage of the 4f electrons through out the crystal were promoted, and the heat capacity data confirmed the data from density measurements and other data that europium is primarily in the divalent form.

The same is true for ytterbium since the promotion of a 4f electron would leave the remaining thirteen 4f electrons in a $^2F_{7/2}$ state, and this transition should be reflected in the heat capacity data. The $^2F_{5/2}$ state would be considerably above the ground state and in the temperature range studied, it would not be expected that this higher state would be appreciably populated. The fact that no appreciable anomalies occurred in the heat capacity to indicate considerable 4f electron promotion confirms density measurements that ytterbium is predominantly divalent.

It should be emphasized that the heat capacity is not measured but is the result of taking the slope of the observed enthalpy data and thus extremely sensitive to small experimental errors. The apparent anomalous behavior of the heat capacity curves for ytterbium in bending down at higher temperatures, and the anomalous thermal coefficient of expansion data observed by Spedding _et al_. (1961), may indicate the promotion of 4f electrons is taking place at higher temperatures, but it certainly must be small since the data did not indicate a large change.

For a rare earth metal with three conduction electrons, the average energy can be computed from a Boltzman distribution law. This type of calculation was programmed in Fortransit language and results computed for 4f electronic contribution to the heat capacity in which only the transitions between J values of the trivalent ions were considered, and crystal splitting and exchange interactions were neglected. The results at 300° and 1000°K were computed as:

	300°K	1000°K	
(1) praseodymium	0.01	1.10	calories/degree-mole
(2) europium	2.02	1.95	calories/degree-mole
(3) ytterbium	0.00	0.00	calories/degree-mole

The difference between the lattice heat capacity at constant pressure and at constant volume, is given by:

$$C_p - C_v = -T\left(\frac{\partial V}{\partial T}\right)_p^2 \left(\frac{\partial P}{\partial V}\right)_T = \frac{\alpha_v^2 TV}{K}, \qquad (111)$$

where α_v is the volume expansion coefficient given by $(1/V)(\partial V/\partial T)_p$ and K is the compressibility given by $-(1/V)(\partial V/\partial P)_T$. This expression may be rewritten as:

$$C_p - C_v = C_v \Gamma \alpha_v T, \qquad (112)$$

where Γ is the Gruneisen constant, equal to $\alpha_v V/KC_v$. This coefficient has been found to be nearly independent of temperature. Thus, one may calculate the dilatation correction at one temperature where the heat capacity of the lattice at constant pressure, and coefficient of volume expansion and the compressibility are known, obtain Γ, and compute the dilatation term at any other temperature for which the heat capacity of the lattice and the volume expansion coefficient are known. Another useful method for obtaining this information is through the use of the Nernst-Lindemann equation:

$$C_p - C_v = AC_p^2T \ , \qquad (113)$$

where $A = V\alpha_v^2/KC_p^2$, which remains approximately constant as the temperature changes.

The dilatation terms for the rare earth metals as trivalent ions were computed from the compressibilities given by Bridgman (1953, 1954 and 1955) and the volume expansion given by Spedding et al. (1961) utilizing the above equations.

	300°K	1000°K	
(1) lanthanum	0.04	0.13	calories/degree-mole
(2) praseodymium	0.02	0.07	calories/degree-mole
(3) europium	0.27	1.85	calories/degree-mole
(4) ytterbium	0.15	0.58	calories/degree-mole
(5) yttrium	0.07	0.22	calories/degree-mole

If one considers the total lattice, electronic (due to the inner and to the outer electrons) and dilatation contributions to the heat capacity and neglects the crystal field splitting and exchange contributions, the following values for the trivalent model of the rare earth metals can be compared to the heat capacities obtained from the observed enthalpies.

	C_p obs. 300°K	C_p calc. 300°K	C_p obs. 1000°K	C_p calc. 1000°K
(1) lanthanum	6.26	6.72	7.90	8.49
(2) praseodymium	6.46	6.71	9.62	9.53
(3) europium	6.48	8.61	9.08	10.96

(4) ytterbium[1]	6.17	6.47	7.53	7.74
(5) yttrium	6.35	6.64	7.51	8.21

For europium metal as a trivalent ion, the Schottky effect was calculated as 2.02 and 1.95 calories/degree-mole at 300° and 1000°K. From a comparison of the calculated values to the observed values, it can be seen that they differ by an amount as large as the Schottky effect and although the agreement would not be exact, the approximation of the linear term and a small contribution due to some promotion to excited states could explain the difference.

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[1] This calculation does not distinguish the difference between the di- and trivalent states for ytterbium as the Schottky effect is 0.0 for the temperature ranges calculated, and other effects resulting in a contribution to the heat capacity are neglected.

SUMMARY

This study has described the design, method of use and calibration of a modified Bunsen ice calorimeter and furnace. The apparatus operated in a vacuum and was used to successfully measure heat contents from 1100° to 1700°C. The calorimeter was calibrated with α-Al_2O_3 from 1100° to 1700°C, and the results were compared to the data observed by other workers in this temperature range.

The thermodynamic properties of the following rare earth metals were determined and described from a study of their enthalpies as a function of temperature.

(1) lanthanum 0° to 1100°C
(2) praseodymium 0° to 1100°C
(3) europium 0° to 1100°C
(4) ytterbium 0° to 1100°C
(5) yttrium 0° to 1675°C

The heats of transformation and of fusion were calculated from the enthalpy curves used to describe the data.

Anomalies in europium and in ytterbium were observed in the enthalpy data and were attributed to electronic states of the 4f electrons which are present in a predominantly divalent metal containing some trivalent ions.

Lanthanum was found to quench some fcc modification of the metal in the hcp room temperature form in studies above the hcp-fcc transition. A procedure is described to obtain reproducible quantities of the quenched fcc modification.

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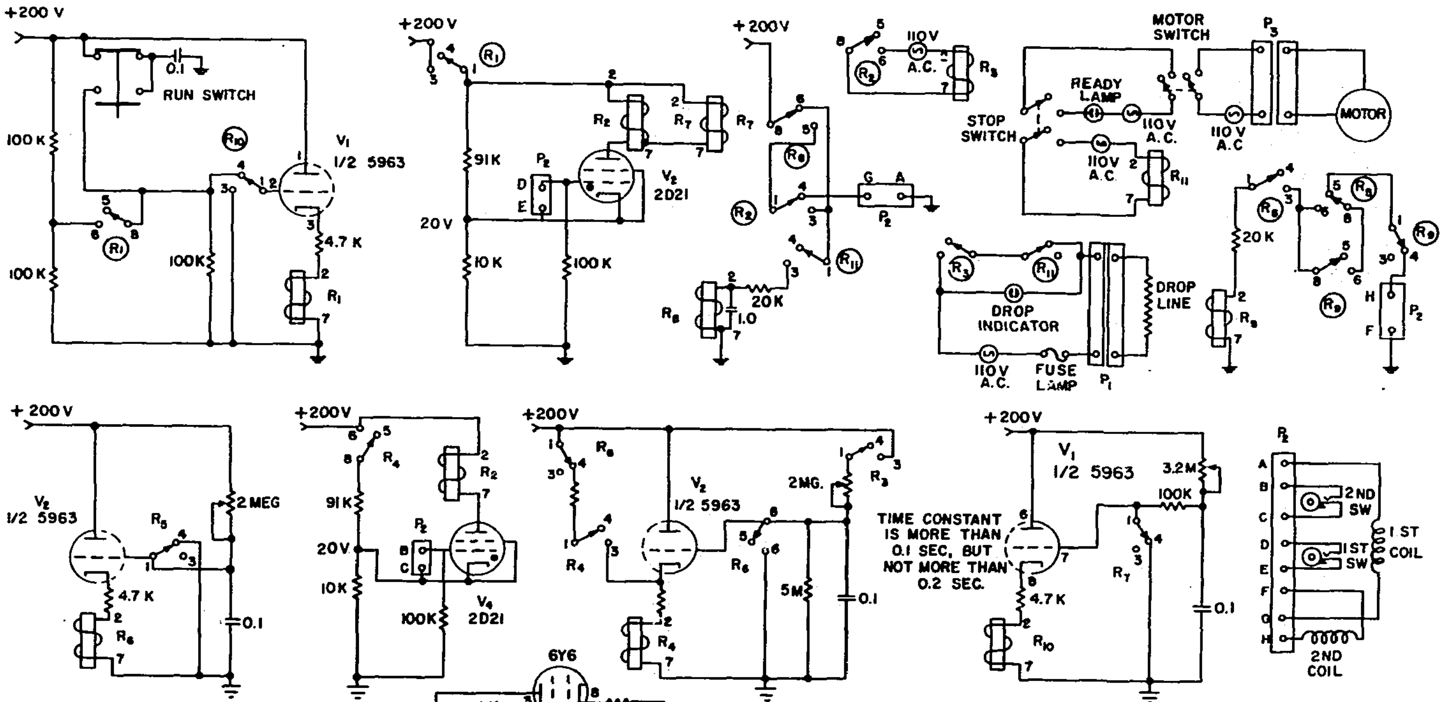
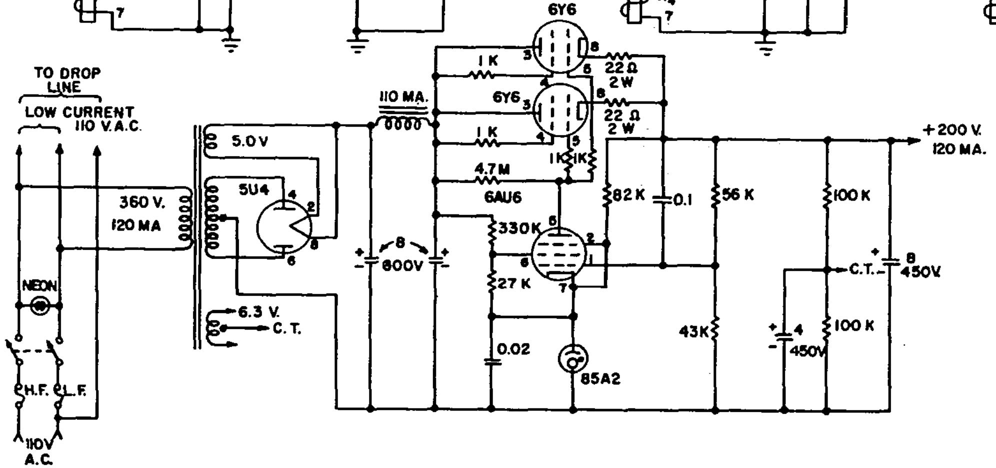
APPENDIX

The circuit diagram (Figure 21) of the dropping mechanism for the high temperature vacuum calorimeter was designed by Mr. J. Goss of the Electronics Section of the Ames Laboratory.

Figure 21. Circuit diagram of the dropping mechanism for the high temperature vacuum calorimeter





NOTE

ALL RESISTANCES IN OHMS, 1/2 WATT
ALL CAPACITANCES IN MICROFARADS
UNLESS SPECIFIED.