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MASTER

# THE HIGH TEMPERATURE HEAT CONTENTS AND RELATED THERMODYNAMIC PROPERTIES OF LANTHANUM, PRASEODYMIUM, EUROPIUM, YTTERBIUM AND YTTRIUM[1]

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The high temperature enthalpies of five rare-earth metals were measured from 0° to 1100°C using a Bunsen ice calorimeter. The enthalpy of yttrium metal was studied from 1100° to 1675°C using a modified high temperature vacuum Bunsen calorimeter. The data were fitted to empirical equations from which the heat of transition and fusion, the heat capacity, and the related thermodynamic quantities were calculated. These results confirmed indications from other properties that europium and ytterbium metals are primarily in the divalent state. Small anomalies observed in europium and ytterbium were attributed to transitions between electronic states when some trivalent ions occur in these metals. The entropy of the fcc-bcc transition for ytterbium was found to be approximately two-thirds that of the other rare-earth metals for which a close-packed to body-centered cubic transformation has been observed.

## INTRODUCTION

Thermal analysis studies[2] of the rare-earth metals detected a solid state transformation in some rare-earth metals near the melting point.

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(1) Contribution No. 1058. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission and the Department of Chemistry. This paper is based in part on a Ph.D. thesis presented to Iowa State University of Science and Technology, July, 1961, by J. R. Berg.

(2) F. H. Spedding and A. H. Daane, "Progress in Nuclear Energy," ser. 5, Vol. 1, H. M. Finnston and J. P. Howe, eds., Pergamon Press, London, 1956, pp. 413-31.

# DISCLAIMER

The large heat associated with this change had erroneously led some early investigators to mistake the transition temperature for the melting point of these metals. High temperature x-ray crystallography studies by Spedding, Hanak and Daane[3] showed that most of the light rare-earth metals and some of the heavy rare-earth metals transformed from a close-packed room temperature form to a body-centered cubic modification at higher temperatures. The study of the high temperature heat contents of the rare-earth metals was begun by Spedding, McKeown and Daane[4] who reported the heats of transition nearly twice as large as previously predicted while the heats of fusion were smaller.[5] This investigation is a continuation of the program to define the high temperature thermodynamic properties of the rare-earth metals.

## Equipment and Materials

Calorimeters. - The instrument used in the studies from 0° to 1100°C was the same as described previously.[4] A new high temperature vacuum calorimeter was designed, constructed and calibrated for studies above 1100°C, and is to be described elsewhere.[6]

Materials. - The rare earths were separated and purified by ion-exchange techniques described by Spedding and Powell.[7] Lanthanum and praseodymium metals were prepared by the metallothermic reduction of their anhydrous fluorides with calcium metal as described by Spedding

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(3) F. H. Spedding, J. J. Hanak and A. H. Daane, J. Less-Common Metals, 3, 110 (1961).

(4) F. H. Spedding, J. J. McKeown and A. H. Daane, This Journal, 64, 289 (1960).

(5) D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements," American Chemical Society, Washington, D.C., pp. 233 (1956).

(6) J. R. Berg, J. Weber, Jr. and A. H. Daane, "High Temperature Vacuum Calorimeter," submitted to Rev. Sci. Instr.

(7) F. H. Spedding and J. E. Powell, J. Metals, 6, 1131 (1954).

and Daane.[2,8] The europium and ytterbium metals were prepared by the reduction of the sintered oxides with lanthanum metal as has been described by Daane, Dennison and Spedding[9] and by Spedding, Hanak and Daane.[3] The yttrium was prepared by the reduction of the anhydrous fluoride with calcium and subsequent distillation of the yttrium metal as described by Habermann.[10]

The four lower melting metals were cast into 1/2-inch rods from which 3/4-inch long samples were prepared. The samples were sealed under helium in tantalum crucibles prepared from 5-mil. sheet. These crucibles often ruptured along the side seam from fatigue of the tantalum caused by the expansion and contraction of the samples. In later investigations, the crucibles were prepared from 1/2-inch i.d. tantalum tubing of 7-mil. wall thickness. The enclosed samples were then sealed in platinum crucibles under an atmosphere of helium.

The yttrium metal, obtained as crystals from the distillation process, was pressed into a 1/2-inch diameter rod. For studies to 1100°C, the yttrium was jacketed as described for the other metals; for the studies above 1100°C, it was sealed under a reduced pressure of helium in two concentric tantalum crucibles. The weights and temperature ranges of the metals studied were: lanthanum, 13.3877g (0° to 1100°C);

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(8) F. H. Spedding and A. H. Daane, J. Metals, 6, 504 (1954).

(9) A. H. Daane, D. H. Dennison and F. H. Spedding, J. Am. Chem. Soc., 75, 2272 (1953).

(10) C. E. Habermann, "Purification of Yttrium Metal by Distillation," unpublished M.S. thesis, Library, Iowa State University of Science and Technology, Ames, Iowa.

praseodymium, 21.3845g (0° to 1100°C); europium, 10.9970g (0C to 1100°C); ytterbium, 18.0404g (0° to 814°C) and 17.3980g (800° to 1100°C); and yttrium, 9.5855g (0° to 1100°C) and 7.4528g (1100° to 1675°C). Table I indicates the result of chemical analyses performed on the samples.

## Procedure

For the measurements from 0° to 1100°C, the enclosed sample was suspended in a platinum wound resistance furnace, heated to equilibrium, and dropped into the calorimeter as described by Spedding, McKeown and Daane.[4] The temperature was measured with a platinum, platinum-13% rhodium thermocouple. In the high temperature apparatus, the sample was suspended on a fuse wire, heated to equilibrium by a tantalum tube resistance furnace in a vacuum and dropped into the calorimeter by fusing the wire. This apparatus and the procedure followed in its use are to be described elsewhere.[6] The temperature was measured with an optical pyrometer.

## Results

The heat content of lanthanum, praseodymium, europium, ytterbium and yttrium was determined from 0° to 1100°C at 100-degree intervals except near the transition temperatures and melting points where measurements were made over shorter temperature ranges. At least three sample "drops" were made at each temperature with one exception for the ytterbium sample. The yttrium sample was studied from 1100° to 1434°C with at least three "drops" made at each temperature. Above the later temperature, measurements were made at shorter temperature intervals and only one observation was made at each point in an effort to reduce

## TABLE I

## ANALYSIS OF SAMPLES

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

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[a] The symbol < means the lowest spectrographic limit detectable; if element is present, the quantity is less than the figure given.

[b] Element detected.

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

TABLE I. Continued

| Sample | Impurities | | | |
|---|---|---|---|---|
| | (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 | |

to a minimum the attack of the tantalum by the yttrium. The heat content of the sample was determined by subtracting the heat content of the empty crucibles (blank) from the heat content of the enclosed sample. The data were fitted to empirical equations utilizing a least-squares treatment.

The study of lanthanum metal by Jaeger, Bottema and Rosenbohm[11, 12] indicated that an intermediate phase of the metal could be quenched in the room temperature form. In this present study, it was found that immediately above the hcp-fcc transition temperature of 310°C the heat content measurements were not reproducible. Successively greater amounts of the fcc modification were quenched as the amount of heat liberated from successive drops became smaller after each drop. It was found that by annealing the sample approximately 10° to 20° above the melting point in an auxiliary

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(11) F. M. Jaeger, J. A. Bottema and E. Rosenbohm, Proc. Acad. Sci., Amsterdam, 39, 921 (1936).

(12) F. M. Jaeger, J. A. Bottema and E. Rosenbohm, Rec. trav. chim., 57, 1137 (1938).

furnace for one-half to one hour 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 annealed in this manner and the metal therefore contained an undetermined but apparently uniform amount of fcc modification quenched in the sample in the studies conducted above the transformation temperature. This unknown amount of the high energy form results in low values for the thermodynamic functions reported above this transformation.

The empirical equations to which the data for lanthanum were fitted are:

$$\Delta H]_0^t = 6.188t + 1.304\times10^{-3}t^2 \text{ calories/mole} \qquad (1)$$

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

$$\Delta H]_0^t = 5.810t+1.139\times10^{-3}t^2+2.709\times10^{-7}t^3+192.1 \text{ calories/mole} \qquad (2)$$

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

$$\Delta H]_0^t = 9.450t - 1178.8 \text{ calories/mole} \qquad (3)$$

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

$$\Delta H]_0^t = 8.214t + 1440.0 \text{ calories/mole} \qquad (4)$$

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

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

$$\Delta H]_{298.15}^T = 5.475T + 1.304\times10^{-3}T^2 - 1748.5 \text{ calories/mole} \qquad (5)$$

(298.15° to 583.15°K)

$$\Delta H]_{298.15}^{T} = 5.248T + 9.175\times10^{-4}T^{2} + 2.709\times10^{-7}T^{3} - 1470.9 \text{ calories/mole } (583.15° \text{ to } 1141.15°K) \quad (6)$$

$$\Delta H]_{298.15}^{T} = 9.450T - 3915.7 \text{ calories/mole } (1141.15° \text{ to } 1193.15°K) \quad (7)$$

$$\Delta H]_{298.15}^{T} = 8.214T - 959.2 \text{ calories/mole } (1193.15° \text{ to } 1373.15°K) \quad (8)$$

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

$$C_p = 5.475 + 2.608\times10^{-3}T \text{ calories/degree-mole } (298.15° \text{ to } 583.15°K) \quad (9)$$

$$C_p = 5.248 + 1.835\times10^{-3}T + 8.128\times10^{-7}T^{2} \text{ calories/degree-mole } (583.15° \text{ to } 1141.15°K) \quad (10)$$

$$C_p = 9.450 \text{ calories/degree-mole } (1141.15° \text{ to } 1193.15°K) \quad (11)$$

$$C_p = 8.214 \text{ calories/degree-mole } (1193.15° \text{ to } 1373.15°K) \quad (12)$$

The observed enthalpies, reproducibilities, calculated enthalpies and deviations are listed for lanthanum in Table II. The calculated thermodynamic functions are given in Table III; the entropy at 298.15°K was based on values reported by Jennings, Miller and Spedding.[13] The observed enthalpies are plotted in Figure 1 for the rare-earth metals studied. The heats of transitions and of melting were calculated as 67±6, 753±4 and 1482±2 calories per mole. The errors of these enthalpies were calculated from the average deviation of the observed values from the calculated values for the empirical equations used.

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(13) L. Jennings, R. Miller and F. H. Spedding, J. Chem. Phys., 33, 1849 (1960).

## TABLE II

## 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 |

## TABLE III

## THERMODYNAMIC PROPERTIES OF LANTHANUM METAL

## (CALORIES PER DEGREE PER MOLE)

| T°K | $C_p$ | $S^\circ_T - S^\circ_o$ | $\frac{H^\circ_T - H^\circ_{298.15}}{T}$ | $-\frac{(F^\circ_T - H^\circ_{298.15})}{T}$ |
|---|---|---|---|---|
| 298.15 | 6.25 | 13.61 | 0.00 | 13.61 |
| 300 | 6.26 | 13.65 | 0.04 | 13.61 |
| 350 | 6.39 | 14.62 | 0.94 | 13.68 |
| 400 | 6.52 | 15.48 | 1.63 | 13.85 |
| 450 | 6.65 | 16.26 | 2.18 | 14.08 |
| 500 | 6.78 | 16.96 | 2.63 | 14.33 |
| 550 | 6.91 | 17.62 | 3.01 | 14.61 |
| 583.15 | 7.00 | 18.02 | 3.24 | 14.78 |
| 583.15 | 6.59 | 18.14 | 3.35 | 14.79 |
| 600 | 6.64 | 18.33 | 3.44 | 14.89 |
| 650 | 6.78 | 18.86 | 3.69 | 15.17 |
| 700 | 6.93 | 19.37 | 3.92 | 15.45 |
| 750 | 7.08 | 19.86 | 4.13 | 15.73 |
| 800 | 7.24 | 20.32 | 4.32 | 16.00 |
| 850 | 7.39 | 20.76 | 4.49 | 16.27 |
| 900 | 7.56 | 21.19 | 4.66 | 16.53 |
| 950 | 7.72 | 21.60 | 4.82 | 16.78 |
| 1000 | 7.90 | 22.00 | 4.97 | 17.03 |
| 1050 | 8.07 | 22.39 | 5.11 | 17.28 |
| 1100 | 8.25 | 22.77 | 5.25 | 17.52 |

TABLE III. Continued

| T°K | $C_p$ | $S^\circ_T - S^\circ_0$ | $\frac{H^\circ_T - H^\circ_{298.15}}{T}$ | $-\frac{(F^\circ_T - H^\circ_{298.15})}{T}$ |
|---|---|---|---|---|
| 1141.15 | 8.40 | 23.08 | 5.36 | 17.72 |
| 1141.15 | 9.45 | 23.74 | 6.02 | 17.72 |
| 1150 | 9.45 | 23.81 | 6.05 | 17.76 |
| 1193.15 | 9.45 | 24.16 | 6.17 | 17.99 |
| 1193.15 | 8.21 | 25.40 | 7.41 | 17.99 |
| 1200 | 8.21 | 25.44 | 7.41 | 18.03 |
| 1250 | 8.21 | 25.78 | 7.45 | 18.33 |
| 1300 | 8.21 | 26.10 | 7.47 | 18.63 |
| 1350 | 8.21 | 26.41 | 7.50 | 18.91 |
| 1373.15 | 8.21 | 26.55 | 7.51 | 19.04 |

The empirical equations to which the data were fitted for praseodymium metal are:

$$\Delta H]_0^t = 6.381t + 1.428\times10^{-3}t^2 + 7.359\times10^{-7}t^3 \text{ calories/mole} \quad (13)$$

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

$$\Delta H]_0^t = 9.189t - 198.0 \text{ calories/mole} \quad (14)$$

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

$$\Delta H]_0^t = 10.272t + 441.4 \text{ calories/mole} \quad (15)$$

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

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

$$\Delta H]_{298.15}^{T} = 5.765T+8.255\times10^{-4}T^{2}+7.359\times10^{-7}T^{3}-1811.7 \quad (16)$$
calories/mole (298.15° to 1071.15°K)

$$\Delta H]_{298.15}^{T} = 9.189T - 2868.3 \text{ calories/mole} \quad (17)$$
(1071.15° to 1208.15°K)

$$\Delta H]_{298.15}^{T} = 10.272T - 2524.7 \text{ calories/mole} \quad (18)$$
(1208.15° to 1373.15°K)

The heat capacities corresponding to these temperature ranges are:

$$C_p = 5.765+1.651\times10^{-3}T+2.208\times10^{-6}T^{2} \text{ calories/degree-mole} \quad (19)$$
(298.15° to 1071.15°K)

$$C_p = 9.189 \text{ calories/degree-mole} \quad (20)$$
(10171.15° to 1208.15°K)

$$C_p = 10.272 \text{ calories/degree-mole} \quad (21)$$
(1208.15° to 1373.15°K)

The observed enthalpies, reproducibilities, calculated enthalpies and deviations of the observed values from the calculated values are given in Table IV. The calculated thermodynamic functions are listed in Table V; the entropy at 298.15°K was taken from work by Parkinson, Simon and Spedding.[14] The heats of transition and fusion were computed to be 760±10 and 1652±3 calories per mole.

An anomalous break was observed in the enthalpy of europium at 230°C (503.15°K). Empirical equations were fitted to the data above and below the break as well as in the liquid region. If an empirical

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(14) D. H. Parkinson, F. E. Simon and F. H. Spedding, Proc. Phys. Soc. (London), A207, 137 (1951).

## TABLE IV

## 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 | --- |

equation is fitted to the data over the solid region, the deviation of the observed values from the calculated values will exceed the limit of error of the method. The empirical equations fitted to the europium data are:

## TABLE V

## THERMODYNAMIC PROPERTIES OF PRAESODYMIUM METAL

## (CALORIES PER DEGREE PER MOLE)

| T°K | $C_p$ | $S^\circ_T - S^\circ_o$ | $\frac{H^\circ_T - H^\circ_{298.15}}{T}$ | $-\left(\frac{F^\circ_T - H^\circ_{298.15}}{T}\right)$ |
|---|---|---|---|---|
| 298.15 | 6.45 | 17.45 | 0.00 | 17.45 |
| 300 | 6.46 | 17.49 | 0.04 | 17.45 |
| 350 | 6.61 | 18.50 | 0.97 | 17.53 |
| 400 | 6.78 | 19.39 | 1.68 | 17.71 |
| 450 | 6.96 | 20.20 | 2.26 | 17.94 |
| 500 | 7.14 | 20.94 | 2.74 | 18.20 |
| 550 | 7.34 | 21.63 | 3.15 | 18.48 |
| 600 | 7.55 | 22.28 | 3.51 | 18.77 |
| 650 | 7.77 | 22.89 | 3.82 | 19.07 |
| 700 | 8.00 | 23.48 | 4.12 | 19.36 |
| 750 | 8.25 | 24.04 | 4.38 | 19.66 |
| 800 | 8.50 | 24.58 | 4.63 | 19.95 |
| 850 | 8.76 | 25.10 | 4.87 | 20.23 |
| 900 | 9.04 | 25.61 | 5.09 | 20.52 |
| 950 | 9.33 | 26.11 | 5.31 | 20.80 |
| 1000 | 9.62 | 26.59 | 5.51 | 21.08 |
| 1050 | 9.93 | 27.07 | 5.72 | 21.35 |
| 1071.15 | 10.07 | 27.27 | 5.80 | 21.47 |
| 1071.15 | 9.19 | 27.98 | 6.51 | 21.47 |
| 1100 | 9.19 | 28.22 | 6.58 | 21.64 |
| 1150 | 9.19 | 28.63 | 6.70 | 21.93 |
| 1200 | 9.19 | 29.02 | 6.80 | 22.22 |

TABLE V. Continued

| T°K | $C_p$ | $S^\circ_T - S^\circ_0$ | $\frac{H^\circ_T - H^\circ_{298.15}}{T}$ | $-\left(\frac{F^\circ_T - H^\circ_{298.15}}{T}\right)$ |
|---|---|---|---|---|
| 1208.15 | 9.19 | 29.08 | 6.81 | 22.27 |
| 1208.15 | 10.27 | 30.45 | 8.18 | 22.27 |
| 1250 | 10.27 | 30.80 | 8.25 | 22.55 |
| 1300 | 10.27 | 31.20 | 8.33 | 22.87 |
| 1350 | 10.27 | 31.59 | 8.40 | 23.19 |
| 1373.15 | 10.27 | 31.76 | 8.43 | 23.33 |

$$\Delta H]_0^t = 6.426t + 1.025\times10^{-3}t^2 \text{ calories/mole} \qquad (22)$$

(0° to 230°C, estimated deviation, ±0.33%, for bcc Eu below the anomalous break)

$$\Delta H]_0^t = 7.261t - 1.119\times10^{-3}t^2 + 2.174\times10^{-6}t^3 - 92.6 \text{ calories/mole} \qquad (23)$$

(230° to 817°C, average deviation of observed values from calculated values, ±0.15%, for bcc Eu above the anomalous break)

$$\Delta H]_0^t = 9.113t + 1036.3 \text{ calories/mole} \qquad (24)$$

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

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

$$\Delta H]_{298.15}^T = 5.866T + 1.025\times10^{-3}T^2 - 1840.2 \text{ calories/mole} \qquad (25)$$

(298.15° to 503.15°K)

$$\Delta H]_{298.15}^T = 8.359T - 2.900\times10^{-3}T^2 + 2.174\times10^{-6}T^3 - 2364.9 \qquad (26)$$

calories/mole (503.15° to 1090.15°K)

$$\Delta H]_{298.15}^{T} = 9.113T-1614.3 \text{ calories/mole} \qquad (27)$$
(1090.15° to 1373.15°K)

For the heat capacity,

$$C_p = 5.866 + 2.050\text{x}10^{-3}T \text{ calories/degree-mole} \qquad (28)$$
(298.15° to 503.15°K)

$$C_p = 8.359 - 5.800\text{x}10^{-3}T + 6.521\text{x}10^{-6}T^2 \text{ calories/degree-mole} \qquad (29)$$
(503.15° to 1090.15°K)

$$C_p = 9.113 \text{ calories/degree-mole} \qquad (30)$$
(1090.15° to 1373.15°K)

In obtaining the heat capacity by differentiating the enthalpy function, the mathematical process exaggerates the small changes in slope near the anomaly, and indicates heat capacity differences that are undoubtedly much larger than actually exist. The observed enthalpies, reproducibilities, calculated enthalpies and deviations of observed values from calculated values are listed in Table VI. The calculated thermodynamic functions are listed in Table VII; the free energy function was not reported in the usual manner as low temperature studies of the thermodynamic functions have not been reported for europium metal. The heat of the anomalous transition was computed to be 12 calories per mole based on the empirical equations used to fit the data. The heat of fusion was computed to be 2204±18 calories per mole.

An anomalous break also occurred in the study of the ytterbium enthalpy at 280°C (553.15°K). Empirical equations were used to express the data above and below this break as well as above the high temperature transition and in the liquid range. As in the case of europium, an empirical equation fitted to the data in the fcc region of ytterbium produced

## TABLE VI

## 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 |

## TABLE VII

## THERMODYNAMIC PROPERTIES OF EUROPIUM METAL

## (CALORIES PER DEGREE PER MOLE)

| T °K | $C_p$ | $S^\circ_T - S^\circ_{298.15}$ | $\frac{H^\circ_T - H^\circ_{298.15}}{T}$ |
|---|---|---|---|
| 298.15 | 6.48 | 0.00 | 0.00 |
| 300 | 6.48 | 0.04 | 0.04 |
| 350 | 6.58 | 1.05 | 0.97 |
| 400 | 6.69 | 1.93 | 1.68 |
| 450 | 6.79 | 2.73 | 2.24 |
| 500 | 6.89 | 3.45 | 2.70 |
| 503.15 | 6.90 | 3.49 | 2.72 |
| 503.15 | 7.09 | 3.52 | 2.75 |
| 550 | 7.14 | 4.15 | 3.12 |
| 600 | 7.23 | 4.77 | 3.46 |
| 650 | 7.34 | 5.36 | 3.75 |
| 700 | 7.49 | 5.91 | 4.02 |
| 750 | 7.68 | 6.43 | 4.25 |
| 800 | 7.89 | 6.93 | 4.47 |
| 850 | 8.14 | 7.42 | 4.68 |
| 900 | 8.42 | 7.89 | 4.88 |
| 950 | 8.73 | 8.35 | 5.08 |
| 1000 | 9.08 | 8.81 | 5.27 |
| 1050 | 9.46 | 9.26 | 5.46 |
| 1090.15 | 9.78 | 9.62 | 5.61 |

TABLE VII. Continued

| T°K | $C_p$ | $S^\circ_T - S^\circ_{298.15}$ | $\frac{H^\circ_T - H^\circ_{298.15}}{T}$ |
|---|---|---|---|
| 1090.15 | 9.11 | 11.64 | 7.63 |
| 1100 | 9.11 | 11.73 | 7.65 |
| 1150 | 9.11 | 12.13 | 7.71 |
| 1200 | 9.11 | 12.52 | 7.77 |
| 1250 | 9.11 | 12.89 | 7.82 |
| 1300 | 9.11 | 13.25 | 7.87 |
| 1350 | 9.11 | 13.59 | 7.92 |
| 1373.15 | 9.11 | 13.75 | 7.94 |

deviations of the observed data compared to the calculated data which exceeded the limits of error of the method. The empirical equations fitted to the ytterbium data are:

$$\Delta H]_0^t = 5.950t + 4.276\text{x}10^{-3}t^2 - 4.257\text{x}10^{-6}t^3 \text{ calories/mole} \quad (31)$$

(0° to 280°C, average deviation of observed values from calculated values, ±0.29%, for fcc Yb below the anomalous break)

$$\Delta H]_0^t = 5.224t + 3.497\text{x}10^{-3}t^2 - 1.755\text{x}10^{-6}t^3 + 236.7 \quad (32)$$

calories/mole (280° to 760°C, average deviation of observed values from calculated values, ±0.05%, for fcc Yb above the anomalous break)

$$\Delta H]_0^t = 8.630t - 684.2 \text{ calories/mole} \quad (33)$$

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

$\Delta H]_{0}^{t} = 8.794t + 1010.7$ calories/mole (34)
(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 enthalpy functions can be expressed:

$\Delta H]_{298.15}^{T} = 2.662T + 7.764\times10^{-3}T^{2} - 4.257\times10^{-6}T^{3} - 1370.9$ calories/mole (298.15° to 553.15°K) (35)

$\Delta H]_{298.15}^{T} = 2.921T + 4.936\times10^{-3}T^{2} - 1.755\times10^{-6}T^{3} - 1045.0$ calories/mole (553.15° to 1033.15°K) (36)

$\Delta H]_{298.15}^{T} = 8.630T - 3192.8$ calories/mole (37)
(1033.15° to 1097.15°K)

$\Delta H]_{298.15}^{T} = 8.794T - 1452.9$ calories/mole (38)
(1097.15° to 1373.15°K)

For the heat capacity, differentiation of the enthalpies gives:

$C_p = 2.662 + 1.553\times10^{-2}T - 1.277\times10^{-5}T^{2}$ calories/degree-mole (39)
(298.15° to 553.15°K)

$C_p = 2.921 + 9.871\times10^{-3}T - 5.266\times10^{-6}T^{2}$ calories/degree-mole (40)
(553.15° to 1033.15°K)

$C_p = 8.630$ calories/degree-mole (41)
(1033.15° to 1097.15°K)

$C_p = 8.794$ calories/degree-mole (42)
(1097.15° to 1373.15°K)

Again, the mathematical operation of calculating the heat capacity has undoubtedly exaggerated the differences that actually exist in the region of the anomaly. The observed enthalpies, reproducibilities, calculated enthalpies and deviations of the observed enthalpies from the calculated values are given in Table VIII. The calculated thermodynamic functions

## TABLE VIII

## 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 |

are given in Table IX; as the low temperature thermodynamic studies are not yet completed, the free energy function was not reported in the usual manner. The enthalpy associated with the anomalous break was computed to be 27±6 calories per mole; the enthalpies of transition and fusion were computed to be 418±3 and 1830±8 calories per mole.

The observed enthalpies for yttrium metal were fitted to empirical equations. These are:

$$\Delta H]_{0}^{t} = 6.310t + 7.733\times10^{-4}t^{2}+5.164\times10^{-8}t^{3} \text{ calories/mole} \quad (43)$$

(0° to 1485°C, average deviation of observed values from calculated values, ±0.29%, for hcp Y)

$$\Delta H]_{0}^{t} = 8.371t + 1.1 \text{ calories/mole} \quad (44)$$

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

$$\Delta H]_{0}^{t} = 10.303t - 222.2 \text{ calories/mole} \quad (45)$$

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

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

$$\Delta H]_{298.15}^{T} = 5.899T+7.309\times10^{-4}T^{2} + 5.164\times10^{-8}T^{3}-1825 \quad (46)$$

calories/mole (298.15° to 1758.15°K)

$$\Delta H]_{298.15}^{T} = 8.371T - 2443.7 \text{ calories/mole} \quad (47)$$

(1758.15° to 1803.15°K)

$$\Delta H]_{298.15}^{T} = 10.303T - 3194.6 \text{ calories/mole} \quad (48)$$

(1803.15° to 1950.15°K)

The heat capacities are expressed by:

$$C_{p} = 5.899 + 1.462\times10^{-3}T + 1.549\times10^{-7}T^{2} \text{ calories/degree-mole} \quad (49)$$

(298.15° to 1758.15°K)

## TABLE IX

## THERMODYNAMIC PROPERTIES OF YTTERBIUM METAL

## (CALORIES PER DEGREE PER MOLE)

| T°K | $C_p$ | $S^\circ_T - S^\circ_{298.15}$ | $\frac{H^\circ_T - H^\circ_{298.15}}{T}$ |
|---|---|---|---|
| 298.15 | 6.16 | 0.00 | 0.00 |
| 300 | 6.17 | 0.04 | 0.04 |
| 350 | 6.53 | 1.02 | 0.94 |
| 400 | 6.83 | 1.91 | 1.66 |
| 450 | 7.06 | 2.73 | 2.25 |
| 500 | 7.23 | 3.48 | 2.74 |
| 550 | 7.34 | 4.18 | 3.15 |
| 553.15 | 7.34 | 4.22 | 3.18 |
| 553.15 | 6.77 | 4.27 | 3.23 |
| 600 | 6.95 | 4.83 | 3.51 |
| 650 | 7.11 | 5.39 | 3.78 |
| 700 | 7.25 | 5.92 | 4.02 |
| 750 | 7.36 | 6.42 | 4.24 |
| 800 | 7.45 | 6.90 | 4.44 |
| 850 | 7.51 | 7.36 | 4.62 |
| 900 | 7.54 | 7.79 | 4.78 |
| 950 | 7.55 | 8.19 | 4.93 |
| 1000 | 7.53 | 8.58 | 5.06 |
| 1033.15 | 7.50 | 8.83 | 5.14 |
| 1033.15 | 8.63 | 9.23 | 5.54 |
| 1050 | 8.63 | 9.37 | 5.59 |
| 1097.15 | 8.63 | 9.75 | 5.72 |
| 1097.15 | 8.79 | 11.42 | 7.39 |

TABLE IX. Continued

| T°K | $C_p$ | $S^\circ_T - S^\circ_{298.15}$ | $\frac{H^\circ_T - H^\circ_{298.15}}{T}$ |
|---|---|---|---|
| 1100 | 8.79 | 11.44 | 7.39 |
| 1150 | 8.79 | 11.83 | 7.45 |
| 1200 | 8.79 | 12.21 | 7.51 |
| 1250 | 8.79 | 12.56 | 7.56 |
| 1300 | 8.79 | 12.91 | 7.61 |
| 1350 | 8.79 | 13.24 | 7.65 |
| 1373.15 | 8.79 | 13.39 | 7.67 |

$C_p$ = 8.371 calories/degree-mole (50)
(1758.15° to 1803.15°K)

$C_p$ = 10.303 calories/degree-mole (51)
(1803.15° to 1950.15°K)

The observed enthalpies, reproducibilities, calculated enthalpies and deviations of the observed enthalpy values from the calculated are listed in Table X. The thermodynamic functions computed from the empirical equations are listed for yttrium metal in Table XI. The value for the entropy at 298.15° was taken from data reported by Jennings, Miller and Spedding.[13] The enthalpies of transition and fusion were computed from the empirical equations and found to be 1189±46 and 2732±25 calories per mole.

## TABLE X

## 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 X. 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 |

## Discussion

A transformation (hcp-fcc) in lanthanum metal was observed in dilatometric studies by Barson, Legvold and Spedding[15] at 310°C, and confirmed in this study. From thermal analysis studies, Spedding and Daane[8] reported the transformation (fcc-bcc) and melting temperatures for the metal as 868° and 920°C; these temperatures were found to be in agreement with the observations of this study. Some premelting occurred about 15° below the melting point, and had been observed in other studies.

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(15) F. Barson, S. Legvold and F. H. Spedding, Phys. Rev., <u>105</u>, 418 (1957).

## TABLE XI

## THERMODYNAMIC PROPERTIES OF YTTRIUM METAL

## (CALORIES PER DEGREE PER MOLE)

| T °K | $C_p$ | $S^\circ_T - S^\circ_o$ | $\frac{H^\circ_T - H^\circ_{298.15}}{T}$ | $-\left(\frac{F^\circ_T - H^\circ_{298.15}}{T}\right)$ |
|---|---|---|---|---|
| 298.15 | 6.35 | 10.63 | 0.00 | 10.63 |
| 300 | 6.35 | 10.67 | 0.04 | 10.63 |
| 350 | 6.43 | 11.65 | 0.94 | 10.71 |
| 400 | 6.51 | 12.52 | 1.64 | 10.88 |
| 450 | 6.59 | 13.29 | 2.18 | 11.11 |
| 500 | 6.67 | 13.99 | 2.63 | 11.36 |
| 550 | 6.75 | 14.63 | 3.00 | 11.63 |
| 600 | 6.83 | 15.21 | 3.31 | 11.90 |
| 650 | 6.91 | 15.77 | 3.59 | 12.18 |
| 700 | 7.00 | 16.28 | 3.83 | 12.45 |
| 750 | 7.08 | 16.77 | 4.04 | 12.73 |
| 800 | 7.17 | 17.23 | 4.24 | 12.99 |
| 850 | 7.25 | 17.66 | 4.40 | 13.26 |
| 900 | 7.34 | 18.08 | 4.57 | 13.51 |
| 950 | 7.43 | 18.48 | 4.72 | 13.76 |
| 1000 | 7.52 | 18.87 | 4.86 | 14.01 |
| 1050 | 7.60 | 19.23 | 4.98 | 14.25 |
| 1100 | 7.69 | 19.59 | 5.11 | 14.48 |
| 1150 | 7.78 | 19.93 | 5.22 | 14.71 |
| 1200 | 7.88 | 20.27 | 5.33 | 14.94 |
| 1250 | 7.97 | 20.59 | 5.43 | 15.16 |
| 1300 | 8.06 | 20.90 | 5.53 | 15.37 |
| 1350 | 8.15 | 21.21 | 5.63 | 15.58 |

TABLE XI. Continued

| T°K | $C_p$ | $S^\circ_T - S^\circ_o$ | $\frac{H^\circ_T - H^\circ_{298.15}}{T}$ | $-\left(\frac{F^\circ_T - H^\circ_{298.15}}{T}\right)$ |
|---|---|---|---|---|
| 1400 | 8.25 | 21.51 | 5.72 | 15.79 |
| 1450 | 8.34 | 21.80 | 5.81 | 15.99 |
| 1500 | 8.44 | 22.08 | 5.89 | 16.19 |
| 1550 | 8.54 | 22.36 | 5.98 | 16.38 |
| 1600 | 8.63 | 22.64 | 6.06 | 16.58 |
| 1650 | 8.73 | 22.90 | 6.14 | 16.76 |
| 1700 | 8.83 | 23.17 | 6.22 | 16.95 |
| 1750 | 8.93 | 23.42 | 6.29 | 17.13 |
| 1758.15 | 8.95 | 23.46 | 6.30 | 17.16 |
| 1758.15 | 8.37 | 24.14 | 6.98 | 17.16 |
| 1800 | 8.37 | 24.28 | 7.01 | 17.27 |
| 1803.15 | 8.37 | 24.29 | 7.02 | 17.27 |
| 1803.15 | 10.30 | 25.80 | 8.53 | 17.27 |
| 1850 | 10.30 | 25.96 | 8.58 | 17.38 |
| 1900 | 10.30 | 26.11 | 8.62 | 17.49 |
| 1950 | 10.30 | 26.26 | 8.66 | 17.60 |

Praseodymium metal was observed to transform[8] (hcp-fcc) at 798° and melt at 935°C; these temperatures were also observed in this study.

Europium metal has been reported to melt at 826±10°C[16]; however, from this study, it was found to melt at 817±5°C. The melting points of

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(16) F. H. Spedding, J. J. Hanak and A. H. Daane, Trans. AIME, 212, 379 (1958).

the rare-earth metals are very sensitive to non-metallic impurities, and some of the differences observed in the reported temperatures may be due to varying amounts of these impurities.

The fcc-bcc transformation of ytterbium metal reported from high temperature x-ray studies is 732°C;[3] this study found the transformation at 760±5°C which is 32° lower than that reported from thermal analysis.[8] The melting point of 824°C, however, agreed with the value reported in the thermal analysis studies.[8]

Yttrium metal was reported to transform (hcp-bcc) at 1459°C by Habermann[10] and at 1490°C by Eash.[17] This transformation was observed in this study at 1485±8°C. The melting point of 1530±8°C observed in this study is higher than the reported melting points of 1510°C[10] and 1515-1517°C.[17] The high titanium and tantalum content of the metal at the conclusion of the runs may explain the large deviations of this study.

Hillebrand[18] reported a mean specific heat of 0.04485 calories per degree per gram for lanthanum between 0° and 100° compared to the value of 0.04526 calories per degree per gram observed between 0° and 99.0°C in this study. Jaeger, Bottema and Rosenbohm[11, 12] reported the quenching of an intermediate phase of lanthanum between 420° and 665°C in the room temperature form, making an interpretation of their results difficult in this region. They reported a mean specific heat of 0.04964 and 0.05048 calories per degree per gram between 20° and 300°,

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(17) D. T. Eash, "Yttrium-Thorium Alloy System," unpublished Ph.D. thesis, Library, Iowa State University of Science and Technology, Ames, Iowa.

(18) W. F. Hillebrand, Pogg. Ann., <u>158</u>, 71 (1876).

and 20° and 420°C. The same quantity calculated from this study is 0.04755 and 0.04911 calories per degree per gram for the same temperature ranges. These same authors estimated the heat capacity between 672° and 701°C to be between 8 and 11 calories per degree per mole, and between 711° and 750°C to be between 10 and 12 calories per degree per mole; the heat capacity in this study was found to be 7.708 calories per degree per mole at 672°C, and 7.976 calories per degree per mole at 750°C. Cavallaro,[19] from a thermal analysis study, determined a heat of fusion of 5000 calories per mole for lanthanum. Brewer[20] estimated the heat of fusion to be 2300 calories per mole. Stull and Sinke[5] estimated 2700 calories per mole, and Kelley[21] estimated 2750 calories per mole, also for the heat of fusion. The heat of fusion from this study was found to be 1482 calories per mole.

From studies of praseodymium alloy systems, Canneri[22,23] reported the heat of fusion of praseodymium to be 2650 and 2750 calories per mole;

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(19) U. Cavallaro, Atti accad. Italia, Rend., 4, 520 (1943).

(20) L. Brewer, "The Chemistry and Metallurgy of Miscellaneous Materials," L. L. Quill, Ed., McGraw-Hill Book Co., Inc., New York, N. Y. pp. 13-39 (1950).

(21) K. K. Kelley, U. S. Bur. Mines, Bull., 584 (1960).

(22) G. Canneri, Metallurgia ital., 26, 794 (1934).

(23) G. Canneri, Ibid., 26, 869 (1934).

Cavallaro[19] determined a heat of fusion of 3100 calories per mole from thermal analysis studies; and, the estimated values for the heat of fusion reported for praseodymium by Stull and Sinke[5] and Kelley[21] are 2400 and 2800 calories per mole, respectively. The heat of fusion calculated from this study is 1652 calories per mole. Rossi[24] determined a mean specific heat of 0.0486 calories per degree per gram between 20° and 100°C; in this same temperature range, the mean specific heat was calculated to be 0.04656 calories per degree per gram from this study. Stull and Sinke[5] and Kelley[21] reported an estimated heat of transition for praseodymium of 320 calories per mole; from this study, the heat of transition was found to be 760 calories per mole.

Stull and Sinke[5] estimated the heat of fusion of europium to be 2500 calories per mole; this value is also given by Kelley;[21] from this study, the heat of fusion of europium was calculated to be 2204 calories per mole.

Stull and Sinke[5] estimated the heat of transition for ytterbium to be 300 calories per mole, and the heat of fusion to be 2200 calories per mole; these values are also quoted by Kelley.[21] The heat of transition in this study was determined to be 418 calories per mole, and the heat of fusion to be 1830 calories per mole.

Brewer[20] estimated the heat of fusion of yttrium to be 4000 calories per mole; Stull and Sinke[5] estimated the heat of fusion to be 4100 calories per mole and this same value is quoted by Kelley.[21] In this study, the

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(24) A. Rossi, Gazz. chim. ital., 64, 748 (1934).

heat of fusion was found to be 2732 calories per mole. Simmons and other workers[25] reported the enthalpy between 0° and 1000°C to be 89.4 calories per gram; the enthalpy observed in this study between 0° and 998.9°C was found to be 80.45 calories per gram. Jennings, Miller and Spedding[13] reported the heat capacity of yttrium at 298.15°C to be 6.34 calories per degree per mole compared to the value of 6.348 calories per degree per mole reported in this study.

The purity of the metals used in this work was greater than that used by others who have studied the high temperature thermodynamic properties of the metals; it therefore seems reasonable to expect that the results reported here are more accurate.

We do not fully understand the small breaks observed in the enthalpy studies of europium and ytterbium at 503° and 553°K, respectively. From the magnetic susceptibility work of Lock,[26] ytterbium metal at room temperature was shown to be in the $^1S_0$ state with only one atom in 260 estimated to be in the $^2F_{7/2}$ state. Ytterbium is thus primarily divalent with a filled 4f shell and two conduction electrons. The behavior of europium in the metallic state has been subject to much discussion. From density measurements, it would appear to be divalent, but Bozorth and Van Vleck[27] propose a trivalent model at very low temperatures to

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(25) C. R. Simmons, C. B. Magee, E. S. Funston, J. A. McGurty and V. P. Calkins, "The Chemistry and Metallurgy of Yttrium," U. S. Atomic Energy Commission Report APEX-475, General Electric Co., Aircraft Nuclear Propulsion Dept., Cincinnati (Classified) (1958).

(26) J. M. Lock, Proc. Phys. Soc. (London), B70, 476 (1957).

(27) R. M. Bozorth and J. H. Van Vleck, Phys. Rev., 118, 1493 (1960).

explain their magnetic susceptibility measurements; at higher temperatures, their results agree with those expected from a divalent model. From electrical resistivity measurements, Curry[28] found anomalies in ytterbium metal at 450° and 600°K, with the latter the larger of the two.

If ytterbium and europium are in the pure divalent state with two conduction electrons, the 4f shell will be half or completely filled, respectively. The inner electrons would then give rise to an $^8S_{7/2}$ state for europium, and an $^1S_0$ state for ytterbium. It would take considerable energy to excite the f electrons to higher energy 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. 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. The 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 throughout the crystal were promoted, and the data confirm density values and other properties that europium is primarily divalent.

The same is true for ytterbium since the promotion of a 4f electron would leave the remaining thirteen 4f electrons in $^2F_{7/2}$ state. However,

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(28) M. Curry, "Electrical Resistivity of Sm, Eu, Tm, Yb and Lu," unpublished M.S. thesis, Library, Iowa State University of Science and Technology, Ames, Iowa.

the next highest J level for a trivalent ytterbium ion is the $^2F_{5/2}$ state which is considerably above the ground state and in the temperature range measured would not be appreciably populated.

The breaks observed in these two metals may therefore have resulted from the promotion of a 4f electron to the conduction band at a fraction of the lattice sites. Since the heat effects are small, it is evident that any such promotion must have occurred to relatively few ions, leaving a predominately divalent model of the metals. Until further evidence can confirm this, it remains as conjecture.

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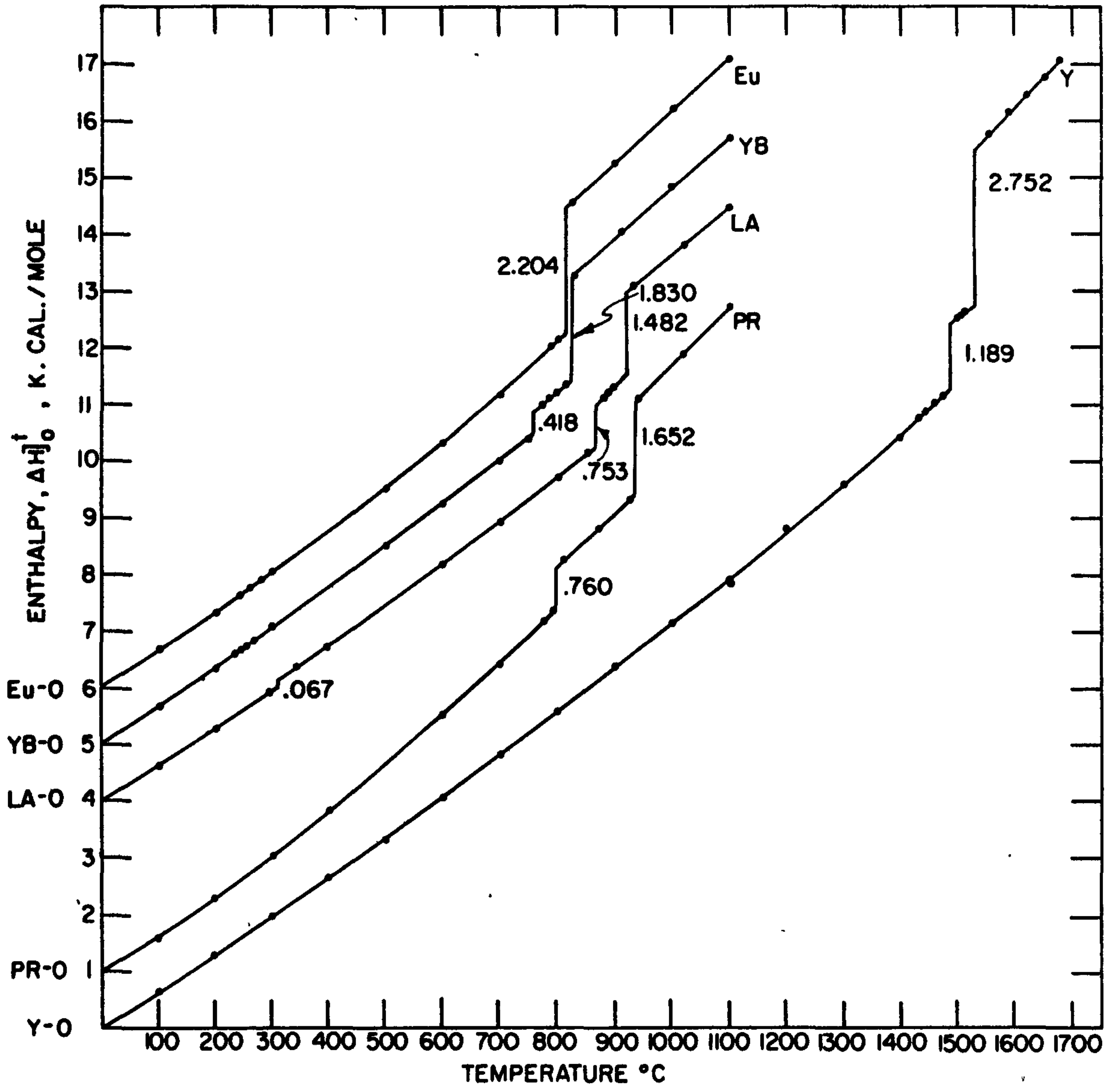

OBSERVED HEAT CONTENTS OF FIVE RARE-EARTH METALS

Figure 1. The enthalpies of lanthanum, praseodymium, europium, ytterbium and yttrium, showing breaks at the solid state transformations where applicable, and at the melting points. Enthalpies are in kilocalories per mole, temperature in degrees centigrade.