# HIGH-TEMPERATURE HEAT CONTENTS AND ENTROPIES OF THE SESQUIOXIDES OF ERBIUM, HOLMIUM, THULIUM, AND YTTERBIUM

By L. B. Pankratz and E. G. King

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# HIGH-TEMPERATURE HEAT CONTENTS AND ENTROPIES OF THE SESQUIOXIDES OF ERBIUM, HOLMIUM, THULIUM, AND YTTERBIUM

by

L. B. Pankratz[1] and E. G. King[2]

## ABSTRACT

The heat contents of the sesquioxides of erbium, holmium, thulium, and ytterbium ($Er_2O_3$, $Ho_2O_3$, $Tm_2O_3$, and $Yb_2O_3$) in the cubic crystalline form were measured over the temperature range from 298° to 1,800° K. The erbium and holmium sesquioxides gave regular heat content-temperature curves. Thulium sesquioxide had a minor thermal anomaly near 1,680° K, with a heat absorption of 310 cal/mole; similarly, ytterbium sesquioxide had a minor anomaly near 1,365° K, with a heat absorption of 150 cal/mole.

The heat content results are presented in both tabular form (at 100° intervals) and in algebraic form. Entropy increments, corresponding to the tabulated heat content results, also are listed.

## INTRODUCTION

This is the third Bureau of Mines report giving results of high-temperature heat content measurements of rare-earth oxides. Previous measurements were of cerium dioxide[3] and the sesquioxides of europium, gadolinium, and neodymium, and samarium.[4] This report gives the experimentally determined heat content values of the sesquioxides of erbium, holmium, thulium, and ytterbium over the range from 298° to 1,800° K. Smooth values of the heat contents and corresponding entropy increments are given in tabular form, and equations were derived to represent the heat content values.

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[2]Supervisory chemist, Berkeley Thermodynamics Laboratory, Bureau of Mines, Berkeley, Calif.
[3]King, E. G., and A. U. Christensen. High-Temperature Heat Contents and Entropies of Cerium Dioxide and Columbium Dioxide. BuMines Rept. of Inv. 5789, 1961, 6 pp.
[4]Pankratz, L. B., E. G. King, and K. K. Kelley. High-Temperature Heat Contents and Entropies of Sesquioxides of Europium, Gadolinium, Neodymium, Samarium, and Yttrium. BuMines Rept. of Inv. 6033, 1962, 18 pp.

Work on manuscript completed July 1962.

No previous data exist for the sesquioxides of holmium and thulium. The only previous data for the sesquioxides of erbium and ytterbium are measurements made in 1880 between 273° and 373° K. Kelley's[5] treatment of these data gives an average heat capacity of 24.86 cal/deg mole for $Er_2O_3$ and 25.5 cal/deg mole for $Yb_2O_3$. The lack of heat-capacity values below 298° K makes possible only a crude comparison. The old value for $Er_2O_3$ is 4 percent lower and that for $Yb_2O_3$ is 9 percent lower than the measurements reported in this paper.

## MATERIALS

The four sesquioxides used in this work were commercial products having a claimed purity of 99.9 percent. X-ray diffraction showed them to be the cubic crystalline variety. Before use in the measurements, the substances were heated to at least 1,470° K and then pressed into pellets. The pellets were reheated and crushed for filling the sample capsules. At the close of the measurements each substance was again examined by X-ray diffraction; no change in pattern was observed.

## MEASUREMENTS AND RESULTS

The measurements were made with previously described apparatus.[6] The results are expressed in defined calories (1 calorie = 4.1840 absolute joules) per mole. Molecular weights conform with the 1961 Table of Atomic Weights[7] and are as follows: $Er_2O_3$, 382.52; $Ho_2O_3$, 377.86; $Tm_2O_3$, 385.87; and $Yb_2O_3$, 394.08. The masses of the samples measured (corrected to vacuum) were: $Er_2O_3$, 16.2631 g; $Ho_2O_3$, 15.1308 g; $Tm_2O_3$, 17.9038 g; and $Yb_2O_3$, 20.0342 g. The precision uncertainty of the heat content measurements was 0.1 percent or less for all substances.

During the measurements the samples were held in platinum-rhodium capsules (the heat contents of which were determined separately). After filling, the capsules and contents were heated to at least 1,350° K and then sealed gastight by platinum welding.

### Erbium Sesquioxide

The measured heat content values for erbium oxide are listed in table 1 and are plotted against temperature in figure 1.

Table 2 contains smooth values of the heat content of erbium oxide above 298.15° K and the corresponding entropy increments. The entropy increments were calculated from the heat content results by the method of Kelley.[8]

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[5]Kelley, K. K. Contributions to the Data on Theoretical Metallurgy. XIII. High-Temperature Heat-Content, Heat-Capacity, and Entropy Data for the Elements and Inorganic Compounds. BuMines Bull. 584, 1960, 232 pp.
[6]Kelley, K. K., B. F. Naylor, and C. H. Shomate. The Thermodynamic Properties of Manganese. BuMines Tech. Paper 686, 1946, 34 pp.
[7]Chemical and Engineering News. IUPAC Revises Atomic Weight Values. V. 39, Nov. 20, 1961, pp. 42-43.
[8]Work cited in footnote 5.

TABLE 1. - Heat content of $Er_2O_3$ (measured values)

| T, °K | $H_T - H_{298.15}$, cal/mole | T, °K | $H_T - H_{298.15}$, cal/mole |
|---|---|---|---|
| 399.0... | 2,680 | 1,098.2... | 23,740 |
| 503.5... | 5,650 | 1,201.4... | 26,990 |
| 607.6... | 8,700 | 1,291.4... | 29,820 |
| 704.9... | 11,610 | 1,400.9... | 33,360 |
| 793.1... | 14,280 | 1,499.1... | 36,560 |
| 874.6... | 16,750 | 1,600.6... | 39,900 |
| 998.1... | 20,620 | 1,695.8... | 43,070 |
| 1,097.0... | 23,680 | 1,797.3... | 46,350 |

TABLE 2. - Heat content and entropy increments for $Er_2O_3$ (smooth values)

| T, °K | $H_T - H_{298.15}$, cal/mole | $S_T - S_{298.15}$, cal/deg mole | T, °K | $H_T - H_{298.15}$, cal/mole | $S_T - S_{298.15}$, cal/deg mole |
|---|---|---|---|---|---|
| 400.. | 2,710 | 7.80 | 1,300.. | 30,140 | 43.27 |
| 500.. | 5,540 | 14.11 | 1,400.. | 33,360 | 45.66 |
| 600.. | 8,470 | 19.45 | 1,500.. | 36,600 | 47.89 |
| 700.. | 11,460 | 24.06 | 1,600.. | 39,860 | 50.00 |
| 800.. | 14,490 | 28.11 | 1,700.. | 43,140 | 51.99 |
| 900.. | 17,560 | 31.72 | 1,800.. | 46,440 | 53.87 |
| 1,000.. | 20,660 | 34.99 | 1,900.. | 49,750 | 55.66 |
| 1,100.. | 23,790 | 37.97 | 2,000.. | 53,070 | 57.36 |
| 1,200.. | 26,950 | 40.72 | | | |

The heat content values in table 2 are represented by the following equation. The average deviation of the equation from the smooth heat content data and the temperature range of validity are shown in parentheses. The equation was derived by the method of Shomate,[9] which permits simultaneous use of all the heat content data, rather than selected values. All similar equations in this paper were derived in this manner.

$$Er_2O_3\text{(cubic)}: \quad H_T - H_{298.15} = 29.66T + 1.00 \times 10^{-3}T^2 + 4.50 \times 10^5T^{-1} - 10{,}441;$$

$$(0.1 \text{ pct}; 298° - 2{,}000° \text{ K}).$$

The corresponding heat capacity equation is

$$C_p = 29.66 + 2.00 \times 10^{-3}T - 4.50 \times 10^5T^{-2}.$$

[9] Shomate, C. H. High-Temperature Heat Contents of Magnesium Nitrate, Calcium Nitrate, and Barium Nitrate. J. Am. Chem. Soc., v. 66, 1944, pp. 928-929.

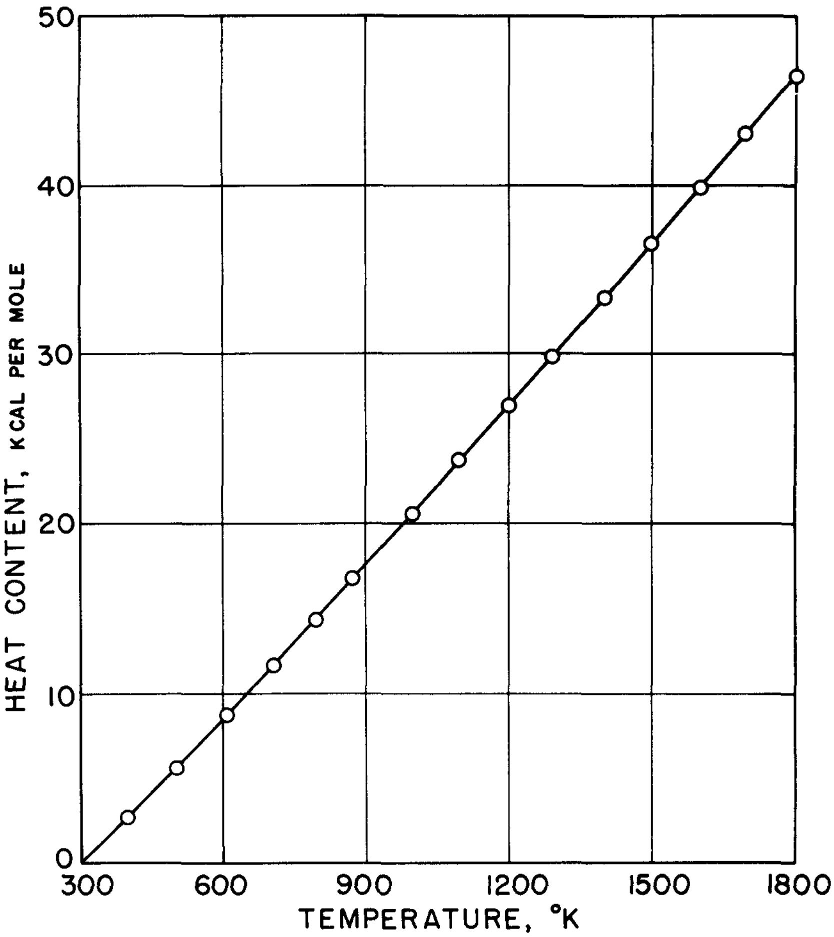


FIGURE 1. - Heat Content of $Er_2O_3$.

## Holmium Sesquioxide

Table 3 contains the measured heat content values for holmium oxide.

TABLE 3. - Heat content of $Ho_2O_3$ (measured values)

| T, ° K | $H_T - H_{298.15}$, cal/mole |
|---|---|
| 399.7.. | 2,800 |
| 500.7.. | 5,750 |
| 504.3.. | 5,840 |
| 599.9.. | 8,650 |
| 602.7.. | 8,740 |
| 694.5.. | 11,530 |
| 786.2.. | 14,340 |
| 904.2.. | 17,980 |
| 1,006.7.. | 21,150 |
| 1,091.3.. | 23,780 |
| 1,200.1.. | 27,180 |
| 1,301.0.. | 30,470 |
| 1,401.3.. | 33,650 |
| 1,499.2.. | 36,880 |
| 1,598.2.. | 40,160 |
| 1,700.6.. | 43,590 |
| 1,798.6.. | 46,840 |

Smooth values of the heat content of holmium oxide above 298.15° K and the corresponding entropy increments are in table 4.

The heat content values in table 4 are represented by the following equation:

$$Ho_2O_3 \text{ (cubic)}: H_T - H_{298.15} = 28.93T + 1.30 \times 10^{-3}T^2 + 2.40 \times 10^5T^{-1} - 9,546;$$

$$(0.2 \text{ pct}; 298° - 2,000° \text{ K}).$$

The corresponding heat capacity equation is

$$C_p = 28.93 + 2.60 \times 10^{-3}T - 2.40 \times 10^5T^{-2}.$$

TABLE 4. - Heat content and entropy increments for $Ho_2O_3$ (smooth values)

| T, ° K | $H_T - H_{298.15}$, cal/mole | $S_T - S_{298.15}$, cal/deg mole | T, ° K | $H_T - H_{298.15}$, cal/mole | $S_T - S_{298.15}$, cal/deg mole |
|---|---|---|---|---|---|
| 400.. | 2,820 | 8.13 | 1,300.. | 30,420 | 43.90 |
| 500.. | 5,710 | 14.57 | 1,400.. | 33,640 | 46.29 |
| 600.. | 8,680 | 19.98 | 1,500.. | 36,900 | 48.54 |
| 700.. | 11,700 | 24.64 | 1,600.. | 40,200 | 50.67 |
| 800.. | 14,760 | 28.72 | 1,700.. | 43,540 | 52.69 |
| 900.. | 17,840 | 32.35 | 1,800.. | 46,920 | 54.63 |
| 1,000.. | 20,940 | 35.62 | 1,900.. | 50,330 | 56.47 |
| 1,100.. | 24,070 | 38.60 | 2,000.. | 53,770 | 58.23 |
| 1,200.. | 27,230 | 41.35 | | | |

## Thulium Sesquioxide

The measured heat content data for thulium oxide are listed in table 5 and plotted in figure 2. This substance had a minor thermal anomaly near 1,680° K (indicated by the vertical arrow in figure 2), the heat absorption being 310 cal/mole. All other results were regular.

TABLE 5. - Heat content of $Tm_2O_3$ (measured values)

| T, ° K | $H_T - H_{298.15}$, cal/mole | T, ° K | $H_T - H_{298.15}$, cal/mole |
|---|---|---|---|
| 396.6... | 2,780 | 1,399.7... | 33,980 |
| 501.0... | 5,880 | 1,499.6... | 37,230 |
| 597.5... | 8,770 | 1,550.9... | 38,840 |
| 697.1... | 11,830 | 1,630.6... | 41,340 |
| 789.1... | 14,700 | 1,665.9... | 42,600 |
| 898.9... | 18,150 | 1,681.0... | 43,240 |
| 993.4... | 21,110 | 1,699.8... | 43,970 |
| 1,096.8... | 24,340 | 1,730.8... | 44,930 |
| 1,198.9... | 27,620 | 1,800.7... | 47,110 |
| 1,301.9... | 30,830 | | |

Table 6 contains smooth values of the heat content and entropy increments above 298.15° K.

TABLE 6. - Heat content and entropy increments for $Tm_2O_3$ (smooth values)

| T, ° K | $H_T - H_{298.15}$, cal/mole | $S_T - S_{298.15}$, cal/deg mole | T, ° K | $H_T - H_{298.15}$, cal/mole | $S_T - S_{298.15}$, cal/deg mole |
|---|---|---|---|---|---|
| 400.. | 2,890 | 8.32 | 1,400.. | 34,000 | 46.95 |
| 500.. | 5,840 | 14.90 | 1,500.. | 37,200 | 49.15 |
| 600.. | 8,860 | 20.41 | 1,600.. | 40,400 | 51.22 |
| 700.. | 11,930 | 25.14 | 1,680.. | 42,960 (α) | 52.78 (α) |
| 800.. | 15,040 | 29.29 | 1,680.. | 43,270 (β) | 52.96 (β) |
| 900.. | 18,170 | 32.97 | 1,700.. | 43,910 | 53.34 |
| 1,000.. | 21,310 | 36.28 | 1,800.. | 47,110 | 55.17 |
| 1,100.. | 24,460 | 39.28 | 1,900.. | 50,310 | 56.90 |
| 1,200.. | 27,630 | 42.04 | 2,000.. | 53,510 | 58.54 |
| 1,300.. | 30,180 | 44.58 | | | |

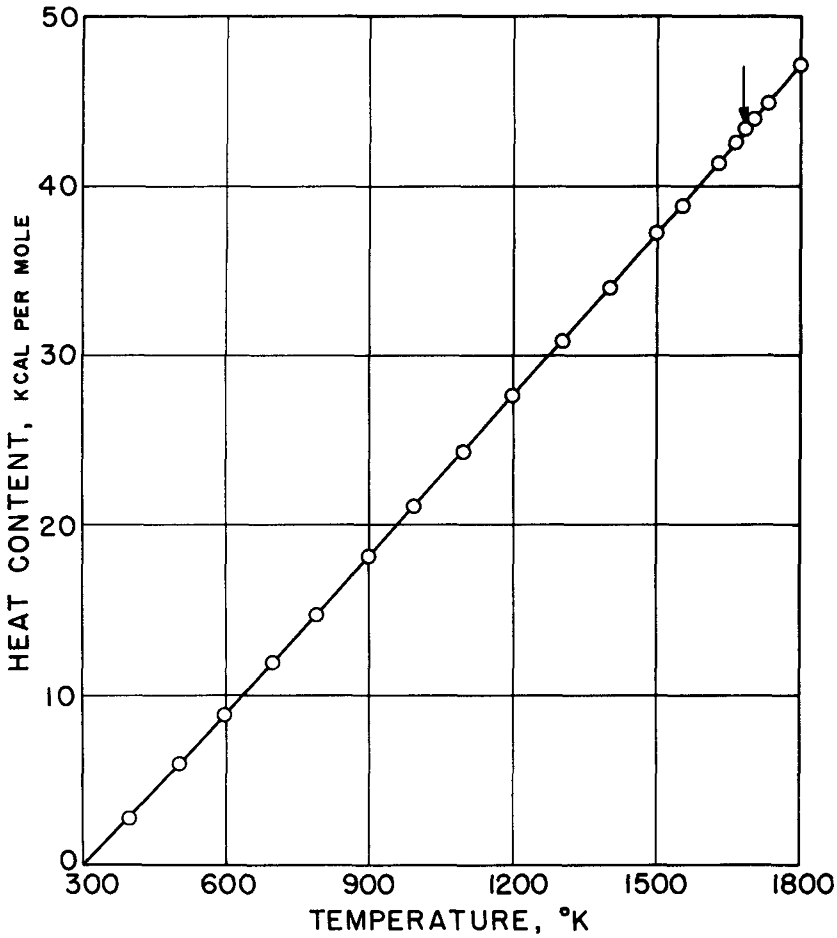

FIGURE 2. - Heat Content of $Tm_2O_3$.

The heat content results in table 6 are represented by the following equations:

$Tm_2O_3$ (cubic):

($\alpha$): $H_T - H_{298.15} = 31.00T + 0.39 \times 10^{-3}T^{2} + 3.42 \times 10^{5}T^{-1} - 10{,}424$;

(0.1 pct; 298° - 1,680° K);

($\beta$): $H_T - H_{298.15} = 32.00T - 10{,}490$;

(0.1 pct; 1,680° - 2,000° K).

The corresponding heat capacity equations are

($\alpha$): $C_p = 31.00 + 0.78 \times 10^{-3}T - 3.42 \times 10^{5}T^{-2}$;

($\beta$): $C_p = 32.00$.

## Ytterbium Sesquioxide

The measured heat content data for ytterbium oxide are listed in table 7. This substance had a minor thermal anomaly near 1,365° K, with a heat absorption of 150 cal/mole. With the exception of this anomaly, the results were regular.

TABLE 7. - Heat content of $Yb_2O_3$ (measured values)

| T, ° K | $H_T - H_{298.15}$, cal/mole | T, ° K | $H_T - H_{298.15}$, cal/mole |
|---|---|---|---|
| 400.2... | 2,900 | 1,344.4... | 32,340 |
| 499.6... | 5,880 | 1,358.2... | 32,880 |
| 598.5... | 8,900 | 1,370.9... | 33,360 |
| 699.4... | 12,040 | 1,382.6... | 33,710 |
| 789.0... | 14,830 | 1,400.4... | 34,300 |
| 887.7... | 17,960 | 1,499.8... | 37,460 |
| 1,003.9... | 21,630 | 1,594.5... | 40,550 |
| 1,104.0... | 24,810 | 1,698.7... | 43,970 |
| 1,198.5... | 27,750 | 1,797.6... | 46,990 |
| 1,298.4... | 30,910 | | |

Table 8 gives the smooth heat content values and entropy increments for ytterbium oxide.

TABLE 8. - Heat content and entropy increments for $Yb_2O_3$ (smooth values)

| T, ° K | $H_T - H_{298.15}$, cal/mole | $S_T - S_{298.15}$, cal/deg mole | T, ° K | $H_T - H_{298.15}$, cal/mole | $S_T - S_{298.15}$, cal/deg mole |
|---|---|---|---|---|---|
| 400.. | 2,910 | 8.38 | 1,365.. | 33,000 (α) | 46.42 (α) |
| 500.. | 5,890 | 15.03 | 1,365.. | 33,150 (β) | 46.53 (β) |
| 600.. | 8,950 | 20.61 | 1,400.. | 34,280 | 47.35 |
| 700.. | 12,060 | 25.40 | 1,500.. | 37,500 | 49.57 |
| 800.. | 15,200 | 29.59 | 1,600.. | 40,720 | 51.65 |
| 900.. | 18,350 | 33.30 | 1,700.. | 43,940 | 53.60 |
| 1,000.. | 21,500 | 36.62 | 1,800.. | 47,160 | 55.44 |
| 1,100.. | 24,650 | 39.62 | 1,900.. | 50,380 | 57.18 |
| 1,200.. | 27,800 | 42.36 | 2,000.. | 53,600 | 58.83 |
| 1,300.. | 30,950 | 44.88 | | | |

The following equations represent the smooth heat content data:

$$Yb_2O_3 \text{ (cubic)}: (\alpha): H_T - H_{298.15} = 32.58T - 0.31 \times 10^{-3}T^2 + 4.62 \times 10^5T^{-1} - 11,236;$$

(0.1 pct; 298° - 1,365° K);

$$(\beta): H_T - H_{298.15} = 32.20T - 10,800;$$

(0.1 pct; 1,365° - 2,000° K).

The corresponding heat capacity equations are

$$(\alpha): C_p = 32.58 - 0.62 \times 10^{-3}T - 4.62 \times 10^5T^{-2};$$

$$(\beta): C_p = 32.20.$$

## DISCUSSION

The heat contents of the four substances are similar in magnitude despite the minor thermal anomalies exhibited by two of them. For example, the values of $H_{1000} - H_{298.15}$ vary by only 4 percent, from 20,660 to 21,500 cal/mole. Similarly, the values of $H_{1800} - H_{298.15}$ vary by only 2 percent, from 46,440 to 47,160 cal/mole.

The minor thermal anomalies found for thulium and ytterbium sesquioxides were reproducible. It is believed that they are associated with intra-atomic phenomena. Similar anomalies were found previously[10] for the monoclinic variety of europium sesquioxide, the hexagonal variety of neodymium sesquioxide, and the monoclinic variety of samarium sesquioxide. The small

[10] Work cited in footnote 4.

magnitude of the heat absorptions, as well as the observations of Stecura and Campbell[11] and of Roth and Schneider,[12] would appear to eliminate the possibility of ascribing these anomalies to any macrocrystalline transformation.

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[11] Stecura, S., and W. J. Campbell. Thermal Expansion and Phase Inversion of Rare-Earth Oxides. BuMines Rept. of Inv. 5847, 1961, 47 pp.

[12] Roth, S. S., and S. J. Schneider. Phase Equilibrium in Systems Involving the Rare-Earth Oxides. Part 1. Polymorphism of the Oxides of the Trivalent Rare-Earth Ions. NBS J. Research, v. 64A, 1960, pp. 309-332.