The heats of combustion of some rare-earth metals

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The heats of combustion of some rare-earth metals

Abstract
A bomb calorimeter for measuring the heats of combustion of neodymium, samarium, gadolinium and erbium is described. The heats of combustion of these metals and the heats of formation of their oxides are reported.

Disciplines
Chemistry
THE HEATS OF COMBUSTION OF SOME RARE-EARTH METALS

by F. H. Spedding, R. E. Eberts and A. W. Naumann

AMES LABORATORY
RESEARCH AND DEVELOPMENT REPORT
U.S.A.E.C.
THE HEATS OF COMBUSTION OF SOME RARE-EARTH METALS

by F. H. Spedding, R. E. Eberts and A. W. Naumann

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THE HEATS OF COMBUSTION OF SOME RARE-EARTH METALS*

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Abstract

A bomb calorimeter for measuring the heats of combustion of neodymium, samarium, gadolinium and erbium is described. The heats of combustion of these metals and the heats of formation of their oxides are reported.

INTRODUCTION

Up until about 1950 the calorimetric data for rare-earth metals and compounds were sparse, and the data available were of somewhat doubtful validity due to the uncertainty as to the purity of the materials. The ion


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exchange separation techniques \(^1\) developed at the Ames Laboratory have made quantities of all the rare earths available in high purity. An extensive program was initiated to study these metals and their compounds. This is a report on one phase of this program.

Shortly after the experimental work for this paper had been completed, Huber and Holley\(^2\) reported on the combustion of several of these metals. The metals they used were of high purity and were analyzed for metallic and non-metallic impurities. Comparisons will be made between their results and those reported here.

**APPARATUS**

The apparatus was adapted from a Series 1300 Parr Oxygen Bomb Calorimeter.\(^3\) The calorimeter container was placed in a stainless steel

---

   
   (b) F. H. Spedding, J. E. Powell and E. J. Wheelwright, *ibid.*, 76, 612, 2557 (1954).

2. (a) E. J. Huber, Jr., and C. E. Holley, Jr., *ibid.*, 74, 5530 (1952);
   
   (b) *Ibid.*, 75, 3595 (1953);
   
   (c) *Ibid.*, 75, 5645 (1953);
   
   (d) *Ibid.*, 77, 1444 (1955);
   
   (e) E. J. Huber, Jr., C. O. Mathews and C. E. Holley, Jr., *ibid.*, 77, 6493 (1955).

air jacket, with thin brass convection shields located between the two walls. The bomb was suspended from the jacket lid by a cylindrical case which enclosed the calorimeter heater. An alumina bomb liner was used in the first few series of experiments to protect the combustion bomb from the spattering of the molten metallic oxide during combustion. This precaution was found unnecessary, and the liner's absence improved the thermal conductivity from the bomb. The air jacket was placed in a 100-gallon constant temperature water bath, which was held within 0.02° of 25°C.

The temperature of the calorimeter was measured with a platinum resistance thermometer and an L and N type G-2 Mueller Bridge. The thermometer was calibrated by the National Bureau of Standards.

The calorimeter heater, which was used to calibrate the system, had a resistance of 93.360 ohms. Current was supplied by six Willard low discharge, 6-volt storage batteries connected in series. The current through the heater was determined by measuring the potential across a 0.1 ohm calibrated standard resistor in series with the heater. The heating period was measured to 0.01 seconds by an electronic timer. A 10-cm. piece of 34 B and S gauge Ni-Cr resistance wire fuse, connected to a Parr Series 2900 Ignition Unit, was used to initiate the combustion reaction.
The benzoic acid used in this work was obtained from the National Bureau of Standards. A value of 6317.8 ± 0.6 calories/gram was given as its heat of combustion. The benzoic acid was compacted into small tablets, of about 0.5 grams, one of which was used per run.

MATERIALS

The metals used were supplied by the rare-earth metals group of the Ames Laboratory of the Atomic Energy Commission and were of the highest purity available. The spectrographic analysis for metallic impurities is given in Table I; the quantities listed represent the maximum possible percent of the given impurity. No analysis was made for non-metallic impurities.

The metals were machined into fine turnings with a jeweler's lathe in a dry box flushed with helium. The turnings were stored in vacuum or under helium until used.

For the experiments with gadolinium, the combustion pan consisted of a cerium oxide disk placed in an alumina crucible. For the other metals, crucibles were fabricated from the appropriate rare-earth oxide. Because these were subject to fracture, they were placed within a slightly larger alumina crucible.
Table I
Spectrographic Analysis of Metal Samples

<table>
<thead>
<tr>
<th>Element</th>
<th>Gd</th>
<th>Nd(I)</th>
<th>Nd(II)</th>
<th>Sm</th>
<th>Er</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>0.04</td>
<td>0.04</td>
<td>0.07</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>Mg</td>
<td>-</td>
<td>0.02</td>
<td>0.05</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Fe</td>
<td>0.005</td>
<td>0.01</td>
<td>0.005</td>
<td>0.01</td>
<td>-</td>
</tr>
<tr>
<td>Si</td>
<td>0.05</td>
<td>0.02</td>
<td>0.025</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>Ta</td>
<td>0.1</td>
<td>?</td>
<td>0.2</td>
<td>-</td>
<td>0.1</td>
</tr>
<tr>
<td>Al</td>
<td>0.05</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Dy</td>
<td>0.05</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ho</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Tb</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Y</td>
<td>0.03</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.01</td>
</tr>
<tr>
<td>Cu</td>
<td>-</td>
<td>interfered</td>
<td>0.07</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pr</td>
<td>-</td>
<td>-</td>
<td>0.08</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cu</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.30</td>
<td>-</td>
</tr>
<tr>
<td>Nd</td>
<td>-</td>
<td>*</td>
<td>*</td>
<td>0.05</td>
<td>-</td>
</tr>
<tr>
<td>Gd</td>
<td>*</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sm</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>*</td>
<td>-</td>
</tr>
<tr>
<td>Er</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>*</td>
</tr>
</tbody>
</table>

* Main constituent
PROCEDURE

In preparation for a run, the fuse wire was weighed and attached to
the bomb in the prescribed manner. Next, the combustion pan was weighed,
first empty and then containing the sample. The weight of metal or benzoic
acid was obtained by difference and corrected to weight in vacuo. The pan
was quickly positioned in the bomb, which was then sealed. The bomb was
flushed several times with oxygen and then filled to a pressure of 30 atmos-
pheres. Exactly 1882.3 grams of water were weighed into the calorimeter
container from a weight burette. Assembly of the calorimeter was completed
and it was placed in the water bath.

Electrical heating calibrations were often run before and/or after a
combustion experiment. The procedure for either type run was quite similar.
The system was brought to some initial temperature which was chosen so
that the total radiation correction for a given run would be a minimum.
Readings of the calorimeter temperature were taken every 30 seconds during
a 10-minute fore period, after which either an electrical heating was begun
or a sample was ignited. The temperature was followed during the heating
period and until a steady state was again obtained. And finally, a 10-minute
after period was recorded.

For an electrical calibration, the potential across the standard resistor
was measured every 25 seconds with an L and N type K-2 potentiometer by a
second operator. The heat liberated was calculated by the formula:

\[ Q_{el} = \frac{1}{4.184} \frac{R_h}{R_s^2} E_s^2 \Delta t \]

where \( Q_{el} \) = heat in defined calories

\( R_h \) = heater resistance

\( R_s \) = standard resistance

\( E_s \) = potential across standard resistor

\( \Delta t \) = heating period.

Heat leakage corrections were evaluated in the standard way. 4, 5, 6, 7

After the run, the unburned fuse wire was weighed to determine the amount of heat liberated in burning the fuse. The combustion pan was also weighed to check on the material balance of the combustion.

RESULTS OF CALIBRATION EXPERIMENTS

Each time the calorimeter was modified the system had to be re-calibrated. Three series of calibrations were made: the first corresponds


to the original system; the second was required when the convection shields were altered; and the third was made following minor alterations and removal of the bomb liner. The calibration data are summarized in Table II. Series A applies to the data for neodymium(I) and gadolinium, series B to erbium, and series C to neodymium(II) and samarium.

Table II
Summary of Calibrations

<table>
<thead>
<tr>
<th>Series</th>
<th>Method</th>
<th>Trials</th>
<th>Water Equivalent (calories/degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Electrical heating</td>
<td>10</td>
<td>2523.4 ± 3.5</td>
</tr>
<tr>
<td></td>
<td>Benzoic acid combustion</td>
<td>1</td>
<td>2521.5</td>
</tr>
<tr>
<td>B</td>
<td>Electrical heating</td>
<td>11</td>
<td>2516.4 ± 2.1</td>
</tr>
<tr>
<td></td>
<td>Benzoic acid combustion</td>
<td>5</td>
<td>2512.2 ± 0.8</td>
</tr>
<tr>
<td>C</td>
<td>Electrical heating</td>
<td>10</td>
<td>2493.9 ± 1.9</td>
</tr>
<tr>
<td></td>
<td>Benzoic acid combustion</td>
<td>6</td>
<td>2492.6 ± 0.7</td>
</tr>
</tbody>
</table>

* Four electrical heatings and all the benzoic acid combustions were run without the bomb liner. In these cases, the calculated value was added to the experimental value to give the value listed.
For series A and B, the calibration value for the electrical heatings was used to determine the heat of combustion of the metal. For series C, an average water equivalent was computed by giving equal weight to the benzoic acid and electrical heating calibrations.

As can be seen, the calibration values obtained for the benzoic acid combustions were lower than those for the electrical heatings. Incomplete combustion of the benzoic acid occurred occasionally. However, a correction factor based on the weight of the carbon residue in the combustion pan was introduced in these cases.

RESULTS OF COMBUSTION OF THE METALS

The heat of combustion was determined from the temperature rise of the calorimeter, $\Delta T$, and the water equivalent, $W$. That is,

$$\Delta Q_{\text{comb}} = \Delta T \cdot W + Q_c,$$

where $Q_c$ = the heat leakage correction term.

The results for the heats of combustion of the rare-earth metals and the heats of formation of the rare-earth oxides are summarized in Table III. Two separate determinations were made on neodymium and are listed as Nd(I) and Nd(II). As explained in the footnote to the table, some determinations were not used in the average because of incomplete combustion, molten oxide interaction, or contamination of the sample material.
### Table III

Heats of Combustion of Rare-Earth Metals
Heats of Formation of Rare-Earth Oxides

<table>
<thead>
<tr>
<th>Metal</th>
<th>Number of Combustions Reported</th>
<th>Heat of Combustion (cal/gm)</th>
<th>Heat of Combustion (kcal/mole)</th>
<th>Heat of Formation of $\text{R}_2\text{O}_3$</th>
<th>$E$</th>
<th>$H_{25^\circ}$&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd(I)</td>
<td>3&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1486.2±0.4</td>
<td>214.41±0.06</td>
<td>428.82</td>
<td>-429.75</td>
<td></td>
</tr>
<tr>
<td>Nd(II)</td>
<td>5&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1478.8±1.8</td>
<td>213.35±0.26</td>
<td>426.70</td>
<td>-427.63</td>
<td></td>
</tr>
<tr>
<td>Sm</td>
<td>7&lt;sup&gt;d&lt;/sup&gt;</td>
<td>1408.8±3.3</td>
<td>211.93±0.50</td>
<td>423.86</td>
<td>-424.79</td>
<td></td>
</tr>
<tr>
<td>Gd</td>
<td>4&lt;sup&gt;e&lt;/sup&gt;</td>
<td>1357.5±0.5</td>
<td>212.99±0.08</td>
<td>425.98</td>
<td>-426.91</td>
<td></td>
</tr>
<tr>
<td>Er</td>
<td>4&lt;sup&gt;f&lt;/sup&gt;</td>
<td>1257.2±2.2</td>
<td>210.20±0.37</td>
<td>420.40</td>
<td>-421.33</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> $-\Delta H = \Delta E T_1 P + \int_P n \left( \frac{\partial\Delta E}{\partial P} \right) dP + \Delta nRT$

Rossini and Frandsen's value of $\left( \frac{\partial\Delta E}{\partial P} \right)_{301^\circ K} = 6.51$ cal/atom/mole for oxygen was used.

<sup>b</sup> A total of six experiments was carried out; one value was discarded because of improper combustion, and two because of oxide contamination of the sample.

<sup>c</sup> A total of eight determinations was carried out; two were discarded because the molten rare-earth oxide interacted with the alumina crucible, and one because insufficient metal was used for the sample.

<sup>d</sup> A total of nine determinations was carried out; one was discarded because the molten rare-earth oxide interacted with the alumina crucible, and one because of an anomalous result.

<sup>e</sup> A total of nine determinations was carried out; three values were discarded because of improper combustion, and two because of oxide contamination of the sample.

<sup>f</sup> A total of six determinations was carried out; two values were discarded because of very low results.

---

DISCUSSION

1. Comparison with other work. - In Table IV, the values obtained by this Laboratory are compared to the work of others. In the case of the data of Huber and Holley, both their "raw" value and the value corrected for non-metallic impurities are listed. The superscripts refer to the literature cited.

Table IV

Comparison of Heats of Combustion Values

(in calories/gram)

<table>
<thead>
<tr>
<th>Metal</th>
<th>This work</th>
<th>Huber and Holley</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(Raw) (Corrected)</td>
</tr>
<tr>
<td>Nd</td>
<td>1486.2</td>
<td>1474.7 1494.4^2a</td>
</tr>
<tr>
<td></td>
<td>1478.8</td>
<td></td>
</tr>
<tr>
<td>Sm</td>
<td>1408</td>
<td>1448.2 1438.8^2e</td>
</tr>
<tr>
<td>Gd</td>
<td>1357.5</td>
<td>1355.5 1380^2d</td>
</tr>
<tr>
<td>Er</td>
<td>1257.2</td>
<td>-      -</td>
</tr>
</tbody>
</table>

* Calculated from heat of solution data.


2. Completeness of Combustion. - In the calculations, it was assumed that 100 per cent complete combustion was attained. Some of the combustion products were treated with dilute hydrochloric acid. Usually a very slight bubbling, presumably of hydrogen, was observed. Since the amount of metal used was small, it can be safely assumed that the combustion was at least 99.9 per cent complete.

3. Combustion Products. - The temperatures at which the combustion occurred were sufficiently high that the rare-earth oxides were undoubtedly molten during and immediately after the combustion. When removed from the calorimeter they appeared as a glassy mass, which was quite hard and brittle.

4. Material Balance. - It was noted that the weight of the final system was usually slightly less than the calculated amount. The difference in mass was not a function of the weight of metal used nor of the heat released in the combustion. It was subsequently found that the rare-earth oxide crucibles lost about this amount of weight when heated at 800°C overnight. Since the temperature in the combustion pan is much higher than this during the combustion, the lack of material balance is probably due to vaporization of
adsorbed water and/or the wax used in fabricating the crucibles.

5. Discrepancy in the Value for Neodymium Metal. - A 0.5 per cent difference was obtained for the two neodymium metal samples used. This difference could well have been due to the presence of different amounts of nonmetallic impurities in the samples. The two were run in slightly different systems and by different operators, which probably had some bearing on the difference.

6. Materials. - The metals used in these experiments were the best available. It is unfortunate that analytical techniques were not available at the time to determine the nonmetallic impurities present in the samples, since the presence of relatively small amounts of these impurities would introduce a fairly large correction factor.

SUMMARY AND CONCLUSIONS

The heats of combustion of four rare-earth metals and the heats of formation of their oxides have been reported. The accuracy and precision obtained for the calorimetric measurements are, in the authors' opinion, equal to those of other workers in this field.

The metals used in this work were of the highest purity then available. The final results do contain an uncertainty due to the lack of analytical data for nonmetallic impurities and of a quantitative estimate of the completeness of combustion.