

[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY]

The Heat of Combustion of Samarium¹

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Calorimetric combustions of samarium metal were conducted at an initial temperature of 25° under an oxygen pressure of 25 atm. The energy of combustion under these conditions was found to be 6020.0 ± 6.6 joules/g. The corresponding standard heat of formation of the sesquioxide (B-type) from the elements is calculated to be -1815.4 ± 2.0 kjoules/mole.

Introduction

This paper is the fifth in a series reporting measurements of the heats of formation of the more common rare earth oxides. The results from the combustion of analyzed samarium metal are reported.

Method.—The method involved the determination of the heat evolved from the combustion of a weighed sample of the metal in a bomb calorimeter at a known initial pressure of oxygen. The energy equivalent of the calorimeter was determined from the heat of combustion of benzoic acid (NBS sample 39g). The completeness of combustion was determined by treating the combustion products with 8 *N* hydrochloric acid and measuring the amount of hydrogen evolved from any unburned metal present.

The uncertainties given are twice the standard deviations.

The units of energy used are the absolute joule and the defined calorie: 1 defined calorie = 4.1840 absolute joules.

The unit of mass is the gram mass *in vacuo*. The samarium metal was weighed to the nearest 0.0001 g. The water for the calorimeter was weighed to the nearest 0.01 g.

Apparatus.—The details of the construction and calibration of the calorimeter have been described.² The bomb used in this work is the same as there described. Its volume is approximately 360 ml. A new calorimeter can was used. The energy equivalent, based on 22 runs, was found to be $10,006.0 \pm 3.8$ joules/degree.

Samarium Metal.—The samarium metal was supplied by E. I. Onstott of this Laboratory. The method of preparation has been described.³ This metal was analyzed at this Laboratory with the following results: Ca, 0.015%; Na, 0.15%; Mg, 0.005%; H, 0.0746%; C, 0.061%; N, 0.0043%; O, 0.003%. Any other metallic impurities were present in amount too small to be detected by the spectroscopic method used. Using absorption spectra Nd was estimated at $0.07 \pm 0.04\%$ and Pr at less than 0.05%. No other rare earths were detected. The determination of the oxygen present by the capillary trap method⁴ was not satisfactory because of the high volatility of the samarium which interfered with the blank.⁵ It was therefore estimated metallographically. Also, as a result of the metallographic examination, the hydrogen impurity was shown to be present as SmH₂, as described below.

Exclusive of other rare earths, the samarium thus contained about 0.31% impurities. The chemical state of the impurities except for the hydrogen is unknown. However, if it is assumed that the nitrogen, carbon and oxygen are combined with samarium as SmN, SmC₂ and Sm₂O₃, respectively, and not combined with the metallic impurities, then the material is 92.98 mole % samarium metal. A Debye X-ray pattern of the metal showed only lines of the metal in the rhombohedral form.

Metallographic Examination.—Conventional metallographic methods for mounting the specimen in Bakelite and mechanical polishing were followed. Samarium is a soft metal with a microhardness of DPHN 55 (25-g. load). The polished sample had a bright silvery appearance. It had solidified in large crystals. Under the microscope the metal showed a Widmanstätten distribution of a gray, metallic phase that was identified as SmH₂. These hydride inclusions occurred as many plates which were oriented parallel to one another within each samarium crystal.

(1) This work was performed under the auspices of the A. E. C.

(2) C. E. Holley, Jr., and E. J. Huber, Jr., *THIS JOURNAL*, **73**, 5577 (1951).

(3) E. I. Onstott, *ibid.*, **77**, 812 (1955).

(4) W. G. Smiley, *Anal. Chem.*, **27**, 1098 (1955).

(5) W. G. Smiley, private communication.

The separation of the SmH₂ from the body of the metal was made by dissolving the samarium matrix, leaving the hydride phase only moderately attacked. The procedure used involved electro-etching the specimen at 1.6 volts and 180 ma./cm.² in normal chromic acid solution. The lower portion of the mounted specimen was submerged in the acid solution, which was contained in a small porcelain evaporating dish. A hole through the back of the Bakelite mount provided a means for an electrical contact with the specimen, and a circle of stainless steel wire was placed in the solution for the cathode. About 10 mg. of the inclusion had settled to the bottom of the dish after 20 minutes of etching and this was washed and dried. Under the microscope the particles were metallic and dendritic. They were identified as SmH₂ by powder X-ray diffraction.

The amount of SmH₂ was estimated by areal analysis using the classical method of Julien.⁶ The hydride particle images were cut from a photomicrograph of a representative area of the specimen and the ratio of their area to the total area determined by weight ratios. This ratio is assumed to be a measure of the volume fraction of the inclusions present. The SmH₂ content thus determined was 4.8 volume %, which is equal to 0.056% hydrogen, a value somewhat lower than that obtained by chemical analysis. However, considering the sampling errors involved, the agreement is considered satisfactory.

In addition to the hydride there were several hundredths of a volume per cent. of unidentified inclusions. Some of these appeared transparent and crystalline and are believed to be the sesquioxide since a burned specimen of samarium metal showed these characteristics for Sm₂O₃. These amounted to less than 0.02 volume % Sm₂O₃, or less than 0.0026% oxygen. A small portion of unidentified inclusion may be carbide but would not account for 0.06% C as found by chemical analysis. Possibly the carbide was present as inclusions too small to be seen under the microscope.

Combustion of Samarium.—The samarium was burned as chunks on sintered discs of >99% Sm₂O₃ supported on a platinum platform weighing 103.8 g. A piece of the metal showed no increase in weight after 1.5 hours in O₂ at 25 atm. New discs were used for each run. The discs were made by mixing 2% beeswax in carbon tetrachloride with the powder and pressing in a steel die at 10,000 p.s.i. They were fired in air for eight hours at 1430°. The oxygen used analyzed greater than 99.5%. Pure magnesium was used for the fuse wire. The amount varied from 0.0045 to 0.0055 g. On the assumption that magnesium burns to the simple oxide, the value of 24,667 joules/g. was used for its heat of combustion.² Even if a double oxide was formed from the magnesium and samarium oxides the amount of magnesium is believed too small to account for any significant heat change from such a reaction. Correction was made for the electrical energy used in igniting the wire. The total energy equivalent of the calorimeter and contents was used, taking into account the discs, the platinum, and the difference in energy equivalent between the samarium oxide formed and the oxygen used.⁷ Combustion varied from 99.83 to 100.00% of completion. The initial temperature was 25.0° and the average final temperature was 26.3°. The results of the eight runs are listed in Table I.

Correction for Impurities.—If it is assumed that the nitrogen is present as SmN which burns to Sm₂O₃ and NO₂ and the carbon as graphite, the percentage composition of the metal by weight is Sm metal, 94.06; SmN, 0.050; SmH₂, 5.64; Sm₂O₃, 0.02; C, 0.061; Ca, 0.015; Mg, 0.005; Na, 0.15. The carbon is probably present as SmC₂, but the heat of formation of the latter is not known and is probably small. Since the amount of carbon is small, the error thus

(6) A. A. Julien, *Bull. Geol. Soc. Am.*, **14**, 466 (1903).

(7) The specific heat of Sm₂O₃ is estimated at 0.28 joules/g./°.

TABLE I
 THE HEAT OF COMBUSTION OF SAMARIUM

Run	Mass Sm burned, g.	Wt. Sm ₂ O ₃ , g.	Wt. Mg, g.	Joules/deg., total	ΔT, °K.	Energy total	Energy from—				Dev. from mean
							Firing, j.	Mg, j.	Sm, j.	Sm, j./g.	
1	1.9478	57.8	0.0055	10035.9	1.1895	11937.7	9.5	136.9	11791.3	6053.7	5.7
2	1.9308	57.5	.0048	10035.8	1.1771	11813.1	8.7	118.3	11686.1	6052.5	6.9
3	2.0591	58.1	.00465	10035.9	1.2565	12610.1	6.0	114.9	12489.2	6065.4	6.0
4	1.9359	54.6	.0052	10035.0	1.1841	11882.4	9.6	128.5	11744.3	6066.6	7.2
5	2.0885	59.8	.00505	10036.4	1.2736	12782.4	8.3	124.8	12649.3	6056.6	2.8
6	1.8905	55.1	.0047	10035.1	1.1560	11600.6	8.0	116.1	11476.5	6070.6	11.2
7	2.0544	55.6	.0045	10035.3	1.2508	12552.2	8.5	111.2	12432.5	6051.6	7.8
8	2.0073	56.9	.0051	10035.6	1.2251	12294.6	8.3	125.5	12160.8	6058.3	1.1
									Av. ^a	6059.4	6.1
									Standard dev.		2.54

^a This average value of 6059.4 ± 5.1 joules/g. must be corrected for the impurities present.

introduced is small. The calcium, sodium and magnesium are assumed to contribute according to their heats of combustion in the pure state. Heats of solution and of alloy formation are ignored. The heat of combustion, Q , of pure samarium metal, per gram, is obtained from the equation: $0.9406Q + 3,400 \times 0.00050 + 33,000 \times 0.00061 + 16,000 \times 0.00015 + 6,350 \times 0.0564 + 9,000 \times 0.0015 + 24,670 \times 0.00005 = 6,059.4$ joules, where the first term is the heat from the samarium metal, the second term from the SmN, 3,400 being the heat of combustion per gram of SmN to Sm₂O₃ and NO₂,⁸ the third term is from the C, the fourth term from the Ca, the fifth term from the SmH₂, 6,350 being the heat of combustion of SmH₂, per gram, to Sm₂O₃ and H₂O,⁹ the sixth term from the Na and the seventh term from the Mg. Solving the equation for the heat of combustion of samarium metal gives a value of 6,020.0 joules/g. The correction due to impurities amounts to 0.65% of the uncorrected value.

Calculation of the Uncertainty.—The uncertainty to be attached to the corrected value includes the uncertainty in the energy equivalent which is 0.04%, the uncertainty in the calorimetric measurements which is 5.1 joules/g. or 0.08%, and the uncertainty introduced in the correction for the impurities.

The main uncertainty introduced in the correction for the impurities is the accuracy of the analyses. The N, C and H were determined chemically and are estimated to be correct to 2%. The Ca, Mg and Na were determined spectroscopically and are estimated to be correct to 50%. The oxygen was determined metallographically. In the similar case of the hydride, as shown above, the microscopic examination showed 0.056% hydrogen whereas by chemical analysis 0.075% hydrogen was actually present, a difference of 34% based on the microscopic value. As the amount of inclusion gets smaller, the sampling difficulties would be expected to increase; therefore the error in the oxygen analysis is arbitrarily assumed to be 50%. However, the amount of oxide is sufficiently small that a large percentage error in its estimation has only a small effect on the final result. It has not been proved that the oxygen is present as Sm₂O₃ instead of SmO. The amount of oxygen is so small, however, that the uncertainty in the result from this cause is small compared to the other uncertainties. If the amounts of impurities are increased by the above-mentioned percentages and the heat of combustion recalculated, the value 6016.6 joules/g. is obtained. On this basis, the uncertainty

(8) The heat of formation of SmN is estimated at -75 kcal./mole.

(9) The heat of formation of SmH₂ is estimated at -45 kcal./mole from the unpublished work of R. N. Mulford of this Laboratory on PrH₂ and NdH₂.

introduced in the correction is the difference between 6020.0 and 6016.6 or 3.4 joules/g. which is 0.06%.

An additional uncertainty is introduced by the relatively large amount of hydrogen present. In the calculation it has been assumed that the hydrogen burned to gaseous H₂O. Since the Sm₂O₃ discs were ignited at 1430° and the Sm₂O₃ from the combustion was fused by the heat of the reaction it was felt that these oxides would probably not react with the water in the short time available and no correction is applied for such reaction. There are additional small uncertainties not taken into account which already have been discussed.

Combining these uncertainties, the over-all uncertainty = $\sqrt{0.04^2 + 0.08^2 + 0.06^2} = 0.11\% = 6.6$ joules/g. The final corrected value is 6,020.0 ± 6.6 joules/g. for the heat of combustion of samarium metal in oxygen at 25 atm. pressure.

Composition of the Samarium Oxide.—The samarium oxide formed was tan in color. An X-ray pattern showed only lines of B type Sm₂O₃. Analysis by the method of Barthauer and Pearce¹⁰ showed no oxygen above that necessary for the sesquioxide.

Heat of Formation of Sm₂O₃.—The heat of combustion reported above gives for the reaction in the bomb a value of $\Delta E_{25.0}^{\circ} = -1,811.2 \pm 2.0$ kjoules/mole (atomic weight Sm = 150.43). To obtain the heat of formation it is necessary to correct for the deviation of oxygen from the perfect gas law and to convert from ΔE to ΔH . Using Rossini and Frandsen's¹¹ value of $(\partial \Delta E / \partial P)_{301.15} = -6.51$ joules/atm./mole for oxygen and taking $\Delta H = \Delta E + \Delta(PV)$, we have for the heat of formation of Sm₂O₃, $\Delta H_{25}^{\circ} = -1,815.4 \pm 2.0$ kjoules/mole. In defined calories this is -433.89 ± 0.48 kcal./mole. Bichowsky and Rossini give the value -430 kcal./mole.¹²

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(10) G. L. Barthauer and D. W. Pearce, *Ind. Eng. Chem.*, **18**, 479 (1946).

(11) F. D. Rossini and M. Frandsen, *J. Research Natl. Bur. Standards*, **9**, 733 (1932).

(12) F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publ. Corp., N. Y., 1936, p. 109.