

[CONTRIBUTION FROM THE MINERALS THERMODYNAMICS BRANCH, REGION III, BUREAU OF MINES, UNITED STATES  
DEPARTMENT OF THE INTERIOR]

## Heats of Formation of Stannic and Stannous Oxides from Combustion Calorimetry

BY G. L. HUMPHREY AND C. J. O'BRIEN

RECEIVED FEBRUARY 7, 1953

The heats of formation of stannic and stannous oxides at 298.16°K. were determined by combustion calorimetry to be  $-138,820 \pm 80$  and  $-68,850 \pm 160$  cal./mole, respectively.

### Introduction

This paper presents new determinations of the heats of formation of stannic and stannous oxides. The work was instigated by a discrepancy that appeared between experimental results of the College Park Station of the Bureau of Mines and thermodynamically calculated values for the reaction



One of the possible sources of discrepancy was error in the heat of formation of stannic oxide, making it desirable that this quantity be redetermined. At the same time, measurements of stannous oxide were included as they could be conducted with the same apparatus and substantially the same techniques.

### Materials

Highly purified tin, in the form of a small bar, was obtained from the Vulcan Detinning Co. Spectrographic analysis showed 0.0007% silicon, 0.0007% magnesium, < 0.0005% aluminum, < 0.0005% iron, < 0.00005% calcium, < 0.00003% copper, and no detectable lead. It appears safe to consider the tin content as 99.99 +%. Very thin lathe turnings, taken from the interior of the bar by a carbonyl cutting tool, were used in the measurements.

Stannous oxide was prepared from reagent-grade stannous chloride ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ) and pure tin. The chloride was dissolved in freshly boiled, distilled water with addition of enough hydrochloric acid to clear the solution. Several pieces of pure tin were added, and the solution was boiled for at least an hour to reduce any stannic ion. A carbon dioxide atmosphere was maintained above the solution during this and subsequent operations. Boiling was continued while ammonium hydroxide was added from a dropping funnel. At first a dense-white precipitate formed which turned black with continued boiling. Addition of ammonium hydroxide was stopped at the first appearance of the black color; and boiling was continued for an additional hour, during which the precipitate became completely black and the supernatant liquid clear. The precipitate was removed by filtration in a carbon dioxide atmosphere, washed with freshly boiled and cooled distilled water until tests for chloride ion were negative, and then dried in a vacuum desiccator, first over Dehydrite and finally over phosphorus pentoxide.

According to the literature,<sup>1</sup> this method of preparation should yield highly pure stannous oxide but data to substantiate this were not found. In the present instance, four separate preparations all fell considerably short of 100% stannous oxide as based upon the following three methods of analysis: hydrogen reduction to metallic tin, oxidation to stannic oxide and titration with standard triiodide solution. Moreover, during trial combustion experiments evidence of chlorine was found and there was some corrosion of the walls of the combustion bomb. To circumvent this difficulty, the stannous oxide was heated in hydrogen at 220–256° for 4 hours. The product after this treatment analyzed 99.5% stannous oxide, 0.18% water and 0.10% carbon dioxide, leaving 0.15% undetermined. There was evidence of the presence of stannic oxide which probably

accounts for the bulk of this 0.15%. Spectrographic analysis showed 0.014% silicon as the only important detectable elemental impurity.

### Measurements and Results

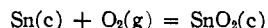
The heat of combustion measurements were conducted with previously described<sup>2</sup> apparatus and methods, employing benzoic acid (N. B. S. Standard Sample 39 g.) as the medium for determining the energy equivalent of the calorimeter.

The combustions were made in silica-glass crucibles, previously lined with pure stannic oxide and ignited. The oxygen pressure was 30 atm., and no water was added to the bomb. The sample was ignited by using a filter-paper fuse and an electrically heated platinum spiral. In the case of the tin combustions it was found necessary to wrap the filter-paper fuse with a few tin turnings to produce ignition of the tin.

The tin combustions gave a light-gray product in the combustion crucible and a superficial, finely divided, white deposit on the bomb walls. The product in the crucible contained some unburned metallic tin but no stannous oxide. The amount of unburned tin was determined for each combustion experiment. This was accomplished by determining the total tin content of the combustion product in the crucible by the hydrogen reduction method. The unburned tin ranged from 1.02 to 4.11% of the total, and the corresponding correction was made in the heat measurement. The combustion product in the crucible was shown by X-ray diffraction to be tetragonal stannic oxide, as was also the superficial wall deposit.

The stannous oxide combustions gave a pure white product, all of which remained in the crucible. A thin film of moisture, originating with the water content of the sample, appeared on the bomb walls. Tests showed the combustions to be 100% complete, and the gain in weight agreed exactly with that calculated from the previously mentioned analysis of the stannous oxide. X-Ray diffraction of the combustion product gave only lines corresponding to the tetragonal form of stannic oxide.

Seven determinations of the heat of combustion of tin at 303.16°K. gave 1162.90, 1163.99, 1164.79, 1164.29, 1164.71, 1164.81 and 1163.32 cal./g. under bomb conditions, after correction for unburned tin. The mean is  $1164.12 \pm 0.58$  cal./g. Corrections for impurities in the tin, made by use of the N. B. S. Tables,<sup>3</sup> reduce this value by 0.006%, to 1164.05 cal./g. or 138,170 cal./mole. Correction to unit fugacity of oxygen (47 cal.), to constant pressure (602 cal.), and to 298.16°K. ( $-4$  cal.) leads to  $\Delta H_{298.16} = -138,820 \pm 80$  cal./mole for the heat of formation of stannic oxide



Uncertainties were calculated according to methods of Rossini.<sup>4</sup>

Five determinations of the heat of combustion of stannous oxide at 303.16°K. gave 517.12, 517.27, 517.37, 517.37, 517.41 and 517.08 cal./g. under bomb conditions. The mean value is 517.25

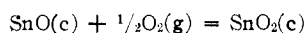
(1) (a) A. Ditte, *Pogg. Ann.*, **27**, 145 (1882); (b) W. Fraenkel and K. Snipschsky, *Z. anorg. Chem.*, **125**, 235 (1922); (c) C. G. Fink and C. L. Mantell, *J. Phys. Chem.*, **32**, 103 (1928).

(2) G. L. Humphrey, *This Journal*, **73**, 1587 (1951).

(3) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, *Natl. Bur. Standards Circular* 500 (1952).

(4) F. D. Rossini, *Chem. Revs.*, **18**, 233 (1936).

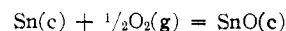
$\pm 0.13$  cal./g. Correction for the water, carbon dioxide and stannic oxide contents of the stannous oxide increases this value by 0.692%, to 520.83 cal./g., corresponding to 70,156 cal./mole. Correction to unit fugacity of oxygen (23 cal.), to constant pressure (301 cal.), and to 298.16°K. (-7 cal.) results in  $\Delta H_{298.16} = -70,470 \pm 140$  cal./mole for the reaction



The uncertainty interval is composed largely of the allowance for error in correcting for impurities (ca. 0.2%).

Combination of the values for the heats of oxida-

tion of tin and stannous oxide leads to  $\Delta H_{298.16} = -68,350 \pm 160$  cal./mole for the heat of formation of stannous oxide



Previous values of the heats of formation of stannic and stannous oxide have been considered by Rossini and co-workers<sup>3</sup> in formulating the N. B. S. Tables, in which  $\Delta H_{298.16} = -138,800$  and  $\Delta H_{298.16} = -68,400$ , respectively, were adopted from data showing considerable variation. The present work confirms this choice of values and reduces the uncertainties to a large extent.

BERKELEY 4, CALIFORNIA

[CONTRIBUTION FROM THE MINERALS THERMODYNAMICS BRANCH, REGION III, BUREAU OF MINES, UNITED STATES  
DEPARTMENT OF THE INTERIOR]

## Heats of Formation of Hafnium Oxide and Hafnium Nitride

BY G. L. HUMPHREY

RECEIVED FEBRUARY 7, 1953

The heats of formation of hafnium oxide and hafnium nitride were determined by combustion calorimetry to be  $\Delta H_{298.16} = -266,060 \pm 280$  and  $\Delta H_{298.16} = -88,240 \pm 340$  cal./mole, respectively.

Thermodynamic studies of hafnium and its compounds have been lacking, largely because of the scarcity of substances of suitable purity. Only recently has substantially pure hafnium been available in sufficient quantity to satisfy scientific needs. This paper reports precision heat of combustion measurements of hafnium metal and hafnium nitride (HfN) and the corresponding heats of formation of the oxide and nitride.

### Materials

The hafnium metal was obtained from the Albany, Oregon, Station of the Bureau of Mines in the form of a circular cylinder of 2 in. diameter and 0.5 in. height. The impurity analysis, furnished with the sample, is as follows: 2.4% zirconium, 0.25% iron, 0.08% carbon, 0.05% titanium, 0.01% chromium, 0.007% nitrogen, 0.005% tungsten, 0.005% nickel, < 0.005% zinc, 0.002% aluminum, 0.002% silicon, 0.001% copper, < 0.001% manganese, < 0.001% molybdenum, 0.0005% lead, 0.0005% magnesium and 0.0001% tin. Very thin lathe turnings, taken from the interior of the cylinder by a carboloy cutting tool, were used in the measurements.

Hafnium nitride was prepared by treating the metal with purified, dry nitrogen for 10 hours at 1400-1500° (with intervening cooling to room temperature and grinding). The nitrogen was purified by passing over hot copper, freshly prepared by hydrogen reduction of copper oxide, and through a drying tower containing magnesium perchlorate.

The hafnium nitride was olive-drab and had virtually the correct composition, as may be seen from the tests to be described. First, the increase in weight during the nitriding process was 7.49%. This is to be compared with the theoretical 7.51%, calculated upon the assumption that the metal would be converted to 96.96% hafnium nitride, 2.56% zirconium nitride, 0.41% iron nitride, 0.06% titanium nitride and 0.01% chromium nitride, in accordance with the metallic impurity contents of 0.01% or above. All these were considered to be nitrides having a 1:1 atomic ratio of metal to nitrogen, as it might be expected that the impurities would merely replace hafnium in the nitride lattice. Second, the increase in weight on conversion of the nitride preparation to oxide was 9.74%, as compared with the theoretical, 9.72%, calculated from the above assumption of nitride composition.

The X-ray diffraction pattern of the nitride appeared iden-

tical, except for magnitude of lattice parameter, with those of zirconium nitride (ZrN) and titanium nitride (TiN).

### Measurements and Results

The heat of combustion measurements were conducted with previously described<sup>1</sup> apparatus and techniques. Benzoic acid, N. B. S. Standard Sample 39 g., was used as the calibration medium for obtaining the energy equivalent of the calorimeter.

The combustions were carried out in silica-glass crucibles that (except in one experiment) were heavily lined with pure hafnium oxide and strongly ignited prior to use. Ignition of the samples was accomplished by a filter-paper fuse and an electrically heated platinum spiral. The oxygen pressure was 30 atm. and no water was added to the bomb. The calorimeter was operated to give results at 303.16°K.

The interior of the bomb after the combustions was clean and dry and there was no spattering of the combustion product. A test for incomplete combustion was conducted after each individual heat of combustion measurement, by prolonged ignition of the combustion product in a muffle furnace. In all instances when lined crucibles were used no increase in weight was observed in these tests, indicating that combustion in the bomb was 100% complete. In the single hafnium nitride combustion conducted in an unlined crucible, the combustion was found by this test to be only 94.41% complete. However, the corresponding correction of the measurement for incomplete combustion brought it into good agreement with those made with lined crucibles. This is considered confirmation of the validity of the method of testing for incomplete combustion.

X-Ray diffraction of the products from both the hafnium and hafnium nitride combustions gave a pattern analogous to that of monoclinic zirconium oxide.

Correction for oxides of nitrogen, formed in the combustions to a superficial extent, was made by passing the bomb gases after combustion into standard sodium hydroxide and back-titrating with standard nitric acid, using brom cresol green as indicator. The correction averaged 0.04 cal. in the hafnium combustions and 0.33 cal. in the hafnium nitride combustion, or 0.0007 and 0.007%, respectively, of the total heat evolved.

The experimental data are shown in Table I. The corrections for impurities, which amount to -2.46% in the hafnium results and -2.02% in the hafnium nitride results, are based upon the author's

(1) G. L. Humphrey, *THIS JOURNAL*, **73**, 1587 (1951).