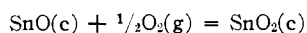


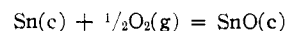
± 0.13 cal./g. Correction for the water, carbon dioxide and stannic oxide contents of the stannous oxide increases this value by 0.692%, to 520.83 cal./g., corresponding to 70,156 cal./mole. Correction to unit fugacity of oxygen (23 cal.), to constant pressure (301 cal.), and to 298.16°K. (-7 cal.) results 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-workers³ 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.

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[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

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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 described¹ 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).

unpublished heat of combustion values for zirconium and zirconium nitride, previously reported values for titanium oxide¹ and nitride,² and the data from the N. B. S. Tables.³ It should be noted that the bulk of these corrections (69.8% for the hafnium and 85.9% for the hafnium nitride) is attributable to the zirconium content alone. In each instance the energy equivalent of the calorimeter was corrected to conform with the specific conditions of the experiment. The precision uncertainties in Table I and subsequently in this paper are calculated according to the methods of Rossini.⁴

TABLE I
HEAT OF COMBUSTION DATA AT 303.16°K.

Mass, g. in vac.	Energy equiv. of calorimeter, cal./ohm	Total heat evolved, cor. to 303.16°K., cal.	Heat from fuse, Blt and HNO ₃ , cal.	$-\Delta U_B/m$, cal./g.	Dev. from mean, cal./g.
Hafnium					
3.99969	32442.5	6109.50	14.05	1523.87	+0.38
4.00076	32437.5	6107.75	12.94	1523.41	-.08
3.99934	32443.8	6109.22	13.61	1524.15	+.66
3.99923	32448.1	6102.15	12.90	1522.61	-.88
4.00003	32467.5	6106.11	13.41	1523.16	-.33
3.99966	32438.8	6108.32	13.92	1523.73	+.24
		Mean		1523.49	$\pm 0.45^a$
		Cor. for impurities		1486.05	± 0.45
Hafnium nitride					
4.99969	32423.0	4716.67	11.90	941.01	+0.46
5.00002	32413.7	4717.23	9.77	941.49	+.94
5.00074	32408.7	4452.52 ^b	11.53	940.64 ^c	+.09
5.00018	32413.6	4711.98	11.06	940.15	-.40
5.00023	32413.5	4713.91	12.90	940.16	-.39
4.99080	32413.0	4702.36	13.56	939.49	-1.06
4.99700	32412.5	4709.74	9.89	940.53	-0.02
4.99871	32426.3	4715.83	12.57	940.89	+0.34
		Mean		940.55	$\pm 0.43^a$
		Cor. for impurities		921.51	± 0.43

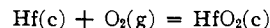
^a Precision uncertainty. ^b No lining, combustion 94.41% complete. ^c Corrected for incomplete combustion.

(2) G. L. Humphrey, *THIS JOURNAL*, **73**, 2261 (1951).

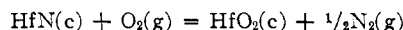
(3) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Joffe, *Natl. Bureau Standards Circular* 500, 1952.

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

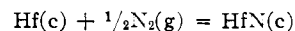
The mean value of the heat of combustion of hafnium under bomb conditions corresponds to 265,410 cal./mole. Correction to unit fugacity of oxygen (47 cal.), to constant pressure (602 cal.), and to 298.16°K. (6 cal.) leads to $\Delta H_{298.16} = -266,060 \pm 280$ cal./mole as the heat of formation of hafnium oxide



The mean value of the heat of combustion of hafnium nitride under bomb conditions corresponds to 177,490 cal./mole. Correction to unit fugacity of reactant oxygen and product nitrogen (25 cal.), to constant pressure (301 cal.), and to 298.16°K. (1 cal.) yields $\Delta H_{298.16} = -177,820 \pm 190$ cal./mole for the reaction



Combination of the combustion heats of the metal and nitride results in $\Delta H_{298.16} = -88,240 \pm 340$ cal./mole as the heat of formation of hafnium nitride



No previous heat of formation value has been reported for hafnium nitride. The N. B. S. Tables³ list $\Delta H_{298.16} = -271,500$ for the oxide. The source of this value is two combustions, made by Roth and Becker,⁵ that differ in heat value by 2,900 cal./mole. No analysis of the metal was given and so much paraffin oil was used as a kindler that only 12 to 18% of the measured heat was attributable to the hafnium. The latter alone would increase the normal error of measurement by a factor of 6 to 8. As a consequence, the value of Roth and Becker appears worthy of little weight.

Employing entropy values for hafnium, nitrogen and oxygen given by Kelley,⁶ the unpublished entropy value of hafnium oxide obtained in this Laboratory, and an estimate of the entropy of hafnium nitride ($S_{298.16}^\circ = 13.1$), there are obtained $\Delta F_{298.16}^\circ = -251,770 \pm 290$ and $\Delta F_{298.16}^\circ = -81,400 \pm 500$ cal./mole, respectively, as the free energies of formation of hafnium oxide and hafnium nitride.

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(5) W. A. Roth and G. Becker, *Z. physik. Chem.*, **A159**, 1 (1932).

(6) K. K. Kelley, *U. S. Bureau Mines Bull.* 477, 1950.