

## Heat capacities of $\text{HfB}_{2.035}$ and $\text{HfC}_{0.968}$ from 5 to 350 K<sup>a</sup>

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Heat capacities were determined by adiabatic calorimetry on well-characterized samples of  $\text{HfB}_{2.035}$  and  $\text{HfC}_{0.968}$ . The results are simply sigmoid except for a peak in the first derivative of the  $\text{HfB}_2$  smoothed results (not characteristic of our  $\text{ZrB}_2$  or  $\text{NbB}_{1.963}$  data) near 110 K possibly occasioned by a Schottky anomaly due to crystal field effects. At 298.15 K the heat capacity  $C_p$ , entropy increment  $\{S^\circ(T) - S^\circ(0)\}$ , and function  $\{G^\circ(T) - H^\circ(0)\}/T$  for  $\text{HfB}_{2.035}$  are 11.90, 10.25, and  $-4.323 \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$ . Those for  $\text{HfC}_{0.968}$  are 8.931, 9.407, and  $-4.311 \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$ .

### 1. Introduction

Increasing demand for thermodynamic data on carbides, borides, and related compositions of the Group IV elements is the consequence of technological developments of nuclear reactors, missiles, and other high-temperature applications of refractory materials. This need has prompted the present endeavor to procure reliable thermodynamic data over the cryogenic range on hyperstoichiometric hafnium diboride ( $\text{HfB}_{2.035}$ ) and on hypostoichiometric hafnium carbide ( $\text{HfC}_{0.968}$ ) by adiabatic calorimetry. Previous studies from these laboratories have already provided values for the thermodynamic properties of zirconium carbide<sup>(1)</sup> and of zirconium diboride.<sup>(2)</sup>

### 2. Experimental

#### CRYOSTAT AND CALORIMETER

Measurements were made in the Mark II adiabatic vacuum cryostat previously described.<sup>(2)</sup> The gold-plated copper calorimeter (Laboratory designation W-31) has a capacity of  $50 \text{ cm}^3$ , and an offset thermometer well which projects through the bottom of the calorimeter. Temperatures were determined with a capsule-type strain-free platinum resistance thermometer (Laboratory designation 85) contained

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within an entrant well in the calorimeter. Temperatures were determined on the IPTS-48 and are considered to accord with thermodynamic temperatures within 0.03 K from 10 to 90 K and within 0.04 K from 90 to 350 K. Temperature increments were determined with higher precision and are probably correct to a few tenths of a mK after correction for quasi-adiabatic drift. All measurements of mass, resistance, potential, temperature, and time are referred to calibrations performed by the National Bureau of Standards. The heat capacity of the samples represented between 25 and 75 per cent of the total heat capacity of the sample plus the calorimeter and was the favorable fraction of the total over most of the range. The mass of the calorimetric sample was 346.3930 g for the diboride and 251.7050 g for the dicarbide. Buoyancy corrections were made on the basis of densities of  $10.80 \text{ g cm}^{-3}$  for the diboride and  $14.65 \text{ g cm}^{-3}$  for the carbide. A pressure of 5.3 kPa of helium measured at 300 K was used to facilitate thermal equilibration within the calorimetric sample space.

#### PROVENANCE OF HAFNIUM DIBORIDE

Hafnium diboride powder obtained from the Wah Chang Corporation contained mass fraction 0.106 of boron plus the following mass fractions of major impurities: 0.0026 of carbon, 0.0014 of oxygen, 0.0005 each of iron and of silicon, 0.00045 of zirconium, and 0.0001 of nitrogen. To reduce the surface area available for helium adsorption and further to purify this material, it was sintered into rods 1 cm diameter by 18 cm long and zone-refined in an (argon + 5 volume per cent hydrogen) atmosphere using high-frequency induction heating by a previously described technique.<sup>(2)</sup> A 10 per cent molar excess of boron (based on the theoretical stoichiometric value of 10.81 mass per cent) was added to the powder before sintering, in order to compensate for boron evaporation during melting. The product was obtained in the form of macrocrystalline rods 6 to 8 mm in diameter coated with a layer of dendritic crystals apparently formed by sublimation from the molten zone. This dendritic layer was removed without introducing contamination by rubbing the bars against one another. It was followed by a light etch in aqueous (HF + HNO<sub>3</sub>). Chemical and spectrographic analysis of the zone-refined product indicated mass fractions of impurities: 0.0016 of carbon, 0.00045 of zirconium, 0.000042 of nitrogen, 0.00003 each of iron and of titanium, 0.000026 of oxygen, and 0.00001 each of silicon, of chromium, of copper, and of magnesium.

Boron and hafnium analyses in mass fractions were:

Sample No.	A	B	C	Theoretical
Hafnium	0.8911	0.8910	0.88745	0.8919
Boron	0.1098	0.1098	0.10945	0.1081
Total	1.0009	1.0008	0.9969	1.0000
$n(\text{B})/n(\text{HF})$	2.034	2.035	2.036	2.000

Samples A and B were analyzed by one laboratory, sample C by another.

The presence of a small amount of a second phase was disclosed by metallographic examination of several bars. X-ray diffraction showed the presence of a trace of material believed to be  $\text{HfB}_{12}$ . Although  $\text{ZrB}_{12}$  is known as a high-temperature phase metastable at low temperatures,<sup>(4)</sup> the analogous  $\text{HfB}_{12}$  was not found in earlier studies of the  $\text{Hf} + \text{B}$  system.<sup>(5)</sup> However, electron-probe microanalysis showed that the second phase contains mass fraction less than 0.01 of hafnium, and is composed of a substance of low atomic number. It might be free boron arising from the decomposition of  $\text{HfB}_{12}$ , although the occurrence of  $\text{B}_4\text{C}$  cannot be entirely excluded.

From the carbon analysis and the mean  $n(\text{B})/n(\text{Hf})$  ratio of 2.035, the proximate analysis of the sample is calculated as 0.9965 of  $\text{HfB}_2$ , 0.0019 of B, and 0.0016 of C.  $\text{HfB}_{12}$  and other impurities are not considered significant; carbon is probably present in solid solution in  $\text{HfB}_2$ , although some may be combined with excess boron.

#### PROVENANCE OF HAFNIUM CARBIDE

The hafnium carbide used for this sample was made by the Carborundum Company from high-purity hafnium oxide furnished by Wah Chang Corporation. The following analysis was obtained in mass fractions on this material: 0.0625 of carbon, 0.0040 of iron, and 0.0009 of oxygen, plus traces of spectrographically detected impurities. Repeated attempts were made to zone refine this material by the method used for  $\text{HfB}_2$ . Although a few small zone-refined pieces were made, the equipment then available was not suitable for reaching the required high temperature on a consistent and regular basis. Therefore, the sample was prepared for calorimetry by arc-melting the sintered bars on a water-cooled copper hearth using a water-cooled tungsten electrode. To reduce loss of carbon during melting, the operation was conducted in an atmosphere of Ar containing mole fractions 0.0314 of  $\text{C}_2\text{H}_4$  and 0.114 of  $\text{H}_2$ .

In spite of this precaution, the arc-melted sample was slightly non-uniform in carbon content, probably because of preferential carbon loss in the areas directly acted upon by the arc. Two analyses on composite samples gave mass fractions 0.0608 and 0.0618 of total carbon with an average of 0.0613. Spot analyses on similar arc-melted specimens indicates that the local mass fraction of carbon content might deviate by a few tenths of a per cent plus or minus from this average value.

Duplicate analyses for free carbon gave mass fractions 0.000129 and 0.000145 or an average value of 0.000137. This low value is in agreement with the results of metallographic examination which disclosed no visible second phase. The free carbon found is probably due largely to a small amount of pyrolytic carbon deposited on some parts of the sample surface during arc-melting.

Subtracting the free carbon from the total carbon gives a mass fraction 0.0612 of combined carbon, corresponding to a formula of  $\text{HfC}_{0.968}$  for the sample.

Chemical and spectrographic analyses gave the following mass fractions for the arc-melted product: 0.00035 of zirconium, 0.00031 of nitrogen, 0.00005 of iron, 0.00003 of oxygen, 0.00002 each of titanium and of silicon, and 0.00001 each of hydrogen, copper, manganese, and magnesium. No tungsten (from the electrode) could be detected.

## 3. Results and discussion

The experimental heat capacities are presented, in chronological sequence at the mean temperatures of the determinations, in table I. These results are based upon molar masses of  $200.49 \text{ g mol}^{-1}$  for the hyperstoichiometric hafnium diboride and

TABLE 1. Heat capacities of hafnium diboride and hafnium carbide  
( $\text{cal}_{\text{th}} = 4.184 \text{ J}$ )

$T$ K	$C_p$ $\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$	$T$ K	$C_p$ $\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$	$T$ K	$C_p$ $\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$
Hafnium diboride ( $\text{HfB}_{2.035}$ )					
Series I		47.74	1.082	156.37	6.434
5.80	0.0020	52.69	1.391	165.45	6.832
6.39	0.0026	57.51	1.696	174.37	7.230
7.42	0.0031	59.28	1.807	183.57	7.631
8.41	0.0038	64.53	2.135	187.92	7.798
9.49	0.0054	71.10	2.514	194.89	8.129
10.78	0.0074	77.69	2.873	203.93	8.502
11.90	0.0086	84.62	3.246	212.95	8.876
13.20	0.0118	92.06	3.601	222.14	9.250
14.66	0.0164	100.35	3.970	231.51	9.620
16.34	0.0217	108.86	4.342	240.90	9.982
18.07	0.0314			250.20	10.321
19.86	0.0426			259.35	10.680
21.83	0.0610			268.38	10.958
23.88	0.0871			277.33	11.254
26.63	0.1277	98.88	3.902	286.45	11.554
28.90	0.1888	105.62	4.201	295.76	11.834
31.69	0.2727	113.15	4.528	305.10	12.113
34.85	0.3945	121.33	4.876	314.43	12.380
38.46	0.5558	129.80	5.257	323.70	12.633
39.51	0.6107	138.61	5.650	334.41	12.899
43.38	0.8212	147.43	6.040	344.93	13.168
		Series II			
Hafnium carbide ( $\text{HfC}_{0.968}$ )					
Series I		42.24	0.9987	194.79	6.903
5.09	0.0017	46.93	1.2965	203.96	7.128
6.39	0.0026	52.22	1.637	212.90	7.339
7.16	0.0035	57.97	1.999	221.97	7.542
8.50	0.0053	63.77	2.356	231.05	7.740
9.50	0.0070	69.85	2.694	240.11	7.927
10.50	0.0093	77.17	3.071	249.28	8.104
12.09	0.0143	85.67	3.478	258.53	8.281
13.25	0.0194	94.77	3.845	267.88	8.458
14.59	0.0265	95.28	3.864	277.07	8.597
16.15	0.0343	102.52	4.132	286.20	8.761
17.89	0.0507	111.39	4.447	295.35	8.889
19.75	0.0720	120.68	4.761	304.47	9.032
21.75	0.1080	129.96	5.061	313.47	9.149
23.81	0.1503	139.20	5.355	322.37	9.259
26.36	0.2188	148.56	5.636	331.16	9.370
29.03	0.3108	157.91	5.913	339.68	9.367
31.88	0.4305	167.14	6.173	346.90	9.557
34.91	0.5777	176.27	6.425	350.00	9.588
38.29	0.7617	185.46	6.668		

TABLE 2. Thermodynamic functions for HfB<sub>2.035</sub>  
(cal<sub>th</sub> = 4.184 J)

$T$ K	$C_p$ cal <sub>th</sub> K <sup>-1</sup> mol <sup>-1</sup>	$S^\circ(T) - S^\circ(0)$ cal <sub>th</sub> K <sup>-1</sup> mol <sup>-1</sup>	$H^\circ(T) - H^\circ(0)$ cal <sub>th</sub> mol <sup>-1</sup>	$-\{G^\circ(T) - H^\circ(0)\}/T$ cal <sub>th</sub> K <sup>-1</sup> mol <sup>-1</sup>
5	0.0016	0.0006	0.002	0.0001
10	0.0055	0.0027	0.018	0.0008
15	0.0172	0.0068	0.071	0.0020
20	0.0440	0.0148	0.214	0.0041
25	0.1046	0.0303	0.567	0.0076
30	0.2199	0.0586	1.352	0.0136
35	0.3989	0.1052	2.873	0.0231
40	0.6356	0.1733	5.439	0.0373
45	0.9159	0.2640	9.302	0.0573
50	1.2224	0.3763	14.640	0.0834
60	1.854	0.6549	30.02	0.1546
70	2.459	0.9868	51.62	0.2492
80	3.007	1.3516	79.02	0.3639
90	3.501	1.7348	111.59	0.4949
100	3.958	2.1276	148.90	0.6385
110	4.395	2.525	190.67	0.7918
120	4.829	2.927	236.80	0.9530
130	5.264	3.330	287.26	1.120
140	5.706	3.737	342.11	1.292
150	6.150	4.145	401.38	1.469
160	6.596	4.557	465.11	1.649
170	7.039	4.970	533.29	1.832
180	7.478	5.384	605.88	2.018
190	7.910	5.800	682.84	2.207
200	8.336	6.217	764.08	2.397
210	8.753	6.634	849.54	2.588
220	9.161	7.050	939.11	2.781
230	9.558	7.466	1032.73	2.977
240	9.944	7.881	1130.25	3.172
250	10.316	8.295	1231.58	3.369
260	10.674	8.706	1336.5	3.566
270	11.016	9.116	1444.9	3.764
280	11.345	9.522	1556.8	3.963
290	11.659	9.926	1671.8	4.161
300	11.962	10.326	1789.9	4.360
310	12.252	10.723	1911.0	4.558
320	12.531	11.117	2034.9	4.758
330	12.794	11.506	2161.6	4.956
340	13.045	11.892	2290.8	5.154
350	13.291	12.274	2422.5	5.352
273.15	11.12	9.24	1480	3.826
298.15	11.90	10.25	1768	4.323

TABLE 3. Thermodynamic functions for hafnium carbide ( $\text{HfC}_{0.998}$ )  
 ( $\text{cal}_{\text{th}} = 4.184 \text{ J}$ )

$T$ K	$C_p$ $\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$	$S^\circ(T) - S^\circ(0)$ $\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$	$H^\circ(T) - H^\circ(0)$ $\text{cal}_{\text{th}} \text{mol}^{-1}$	$- \{G^\circ(T) - H^\circ(0)\}/T$ $\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$
5	0.0016	0.0006	0.002	0.0001
10	0.0088	0.0031	0.022	0.0009
15	0.0281	0.0094	0.103	0.0025
20	0.0774	0.0232	0.348	0.0058
25	0.1803	0.0503	0.964	0.0117
30	0.3491	0.0970	2.258	0.0216
35	0.5820	0.1675	4.561	0.0372
40	0.8630	0.2631	8.158	0.0591
45	1.1723	0.3824	13.238	0.0883
50	1.4943	0.5226	19.901	0.1245
60	2.128	0.8517	38.05	0.2175
70	2.705	1.2239	62.27	0.3343
80	3.209	1.6188	91.90	0.4701
90	3.650	2.0229	126.25	0.6201
100	4.033	2.4281	164.75	0.7807
110	4.402	2.830	206.99	0.9488
120	4.739	3.228	252.70	1.122
130	5.062	3.620	301.72	1.299
140	5.375	4.007	353.91	1.479
150	5.679	4.388	409.19	1.660
160	5.972	4.764	467.45	1.843
170	6.255	5.135	528.60	2.025
180	6.526	5.500	592.51	2.208
190	6.786	5.860	659.09	2.391
200	7.034	6.214	728.19	2.573
210	7.271	6.563	799.73	2.755
220	7.497	6.907	873.58	2.936
230	7.714	7.245	949.64	3.116
240	7.921	7.577	1027.82	3.295
250	8.118	7.905	1108.03	3.473
260	8.306	8.227	1190.16	3.649
270	8.483	8.544	1274.11	3.825
280	8.650	8.855	1359.78	3.999
290	8.808	9.162	1447.08	4.172
300	8.957	9.463	1535.91	4.343
310	9.097	9.759	1626.19	4.513
320	9.230	10.050	1717.83	4.681
330	9.356	10.336	1810.77	4.849
340	9.475	10.617	1904.93	5.014
350	9.589	10.893	2000.25	5.178
273.15	8.537	8.641	1300.9	3.880
298.15	8.931	9.407	1519.4	4.311

190.12  $\text{g mol}^{-1}$  for hypostoichiometric hafnium carbide. Since the heat capacity values are listed chronologically, the  $\Delta T$ 's used in the heat-capacity determinations can usually be inferred from the increments between adjacent mean temperatures shown in table 1. Precision reflected by standard deviations decreasing from about 5 per cent at 5 K to 1 per cent at 10 K to less than 0.08 per cent above 50 K are considered to characterize the results for both compounds.

Below 5 K the results were extrapolated by the relation:  $C_p = \gamma T + cT^3$ . The values of  $\gamma$  were found to be  $1.8 \times 10^{-4}$  and  $1.5 \times 10^{-4}$   $\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$  for the diboride and the dicarbide.†

The heat capacities and thermodynamic functions at selected temperatures are presented in tables 2 and 3 and were obtained from the heat capacities by a least-squares-fitted curve through the experimental points (and carefully compared with the large scale plot of the results) or by the integration thereof. Both the fitting and the quadrature were performed by digital computers.

The thermodynamic functions are considered to have a precision corresponding to a probable error of less than 0.1 per cent above 100 K. Additional digits beyond those significant are given in table 2 for internal consistency and to permit interpolation and differentiation.

The entropies and Gibbs energies have not been adjusted for contributions from nuclear spins and isotopic mixing and hence are practical values for use in chemical thermodynamic calculations.

The first derivative of the heat capacity with respect to temperature for  $\text{HfB}_{2.035}$  indicates above the major Debye extremum a minimum near 110 K followed by a small maximum. A similar feature led Flotow and Osborne to postulate the presence of an extraneous—possibly Schottky—contribution to the heat capacity of  $\text{UB}_2$ .<sup>(6)</sup> Certainly the presence of a higher electronic state would not be inconsistent with the observed effect; however, we are unaware of spectroscopic or other evidence for the presence of such a level. It is further noted that similar effects are found in the first temperature derivative of the heat capacity of lanthanide trichlorides having Schottky contributions<sup>(7)</sup> clearly established by spectroscopic studies. No similar effect is observed for  $\text{ZrB}_2$ ,<sup>(2)</sup> or for  $\text{ZrC}$ ,<sup>(1)</sup> or for  $\text{HfC}_{0.968}$ .

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† Throughout this paper  $\text{cal}_{\text{th}} = 4.184 \text{ J}$ .