High-Temperature Heat Content of Hafnium

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High-temperature heat contents of hafnium were measured over the temperature range 298° to 1346° K., using a diphenyl ether calorimeter. The results are well represented by the analytical expression:

$$H^\circ_T - H^\circ_{298.15} = 5.607T + 0.911 \times 10^{-3}T^2 - 1753$$

Smoothed values of the thermal properties of hafnium, $H^\circ_T - H^\circ_{298}$, Cp, $S^\circ_T - S^\circ_{298}$, and $(F^\circ_T - H^\circ_{298})/T$, have been derived and are tabulated at even 100° intervals.

THE DIFFICULTY of obtaining hafnium of sufficient purity has contributed to a relative lack of reported thermodynamic data for this element. Existing low-temperature heat capacity data do not extend above 200° K., making necessary a considerable extrapolation in order to obtain values of the standard thermodynamic properties at 298.15° K. (*5*). The only reported high-temperature thermal value is the single heat content measurement of Adenstedt (*1*) at 373° K.

Interest in hafnium as a high-temperature refractory metal having a large neutron absorption cross section, plus the availability of a sample of satisfactorily pure material, made it desirable to determine the high-temperature thermal properties of hafnium by means of heat content measurements. This paper reports the results of such measurements in the range between 298° and 1346° K.

EXPERIMENTAL

The hafnium used was obtained from the Lawrence Radiation Laboratory, Livermore, which also supplied the results of chemical and spectrographic analyses. The sample contained 2.8 wt. % (5.3 at. %) Zr and less than a total of 0.055 wt. % of remaining impurities, principally 0.020% Fe, 0.010% Ni, and 0.008% O.

Heat content measurements were made using a diphenyl ether Bunsen-type drop calorimeter. The apparatus and experimental procedures have been described in detail previously (*4*, *8*) and will be mentioned only briefly here. The specimen, consisting of 1.3703 grams of hafnium enclosed in 0.6245 grams of platinum foil, was heated in an argon atmosphere in a vertical tube furnace to a measured temperature, then dropped into the calorimeter. Heat from the specimen entered a surrounding chamber containing liquid and solid diphenyl ether at its melting point, 300.0° K., melting some of the solid isothermally. The resulting increase in volume was measured by displacement of mercury from the bottom of the calorimeter chamber into a horizontal calibrated capillary tube. The heat effect was obtained from the measured volume change using the calibration factor determined by Jessup (*6*) and routinely checked throughout the measurements by dropping a solid platinum specimen in the calorimeter (*8*). Corrections were made for the heat content of the platinum capsule and the heat lost during the drop using data previously reported (*8*), and for the small difference between the calorimeter temperature, 300° K., and the standard reference temperature, 298.15° K.

The results were corrected for the Zr content of the sample by assuming the Kopp-Neumann rule of additive heat capacities to apply throughout the measured range. Heat contents of Zr tabulated by Kelley (*7*) were used to 1135° K., the $\alpha(hcp) - \beta(bcc)$ transformation temperature, above which values for α-Zr were extrapolated. Hafnium itself does not undergo the $\alpha - \beta$ transition until it reaches 2023 ± 20° K. (*3*). Starting with the runs at 984° K. and continuing at higher temperatures, the specimen gained small amounts of weight, presumably because of oxygen absorption. The total increase in weight, reached at the highest temperature runs (1346° K.) was 0.0036 grams, amounting to 0.26% by weight. The relative amounts of the absorbed oxygen in the surface oxide layer and in solution were not known; neither were the partial molar properties of oxygen dissolved in hafnium. Correction for the absorbed oxygen was thus based on known heat content values (*7*) for HfO_2, the only stoichiometric oxide known to be formed by hafnium. After completion of the high-temperature runs, two final runs (indicated in Table I) were repeated at a lower temperature, 837° K., in order to check the method of correction. The results,

Table I. Experimental Results

T, ° K.	$H^\circ_T - H^\circ_{298.15}$ Cal./G. Atom	T, ° K.	$H^\circ_T - H^\circ_{298.15}$ Cal./G. Atom
338.9	241	837.2[a]	3604
341.7	274	837.2[a]	3589
341.9	286	841.4	3572
342.2	279	841.8	3605
390.0	562	842.2	3595
392.5	597	842.4	3587
392.9	582	920.0	4188
398.3	612	920.2	4140
398.4	617	921.0	4125
486.6	1193	983.5	4637
486.6	1205	983.8	4645
486.8	1166	983.9	4639
492.7	1236	1109.7	5593
492.7	1234	1109.8	5585
576.6	1801	1109.9	5505
576.6	1781	1182.8	6164
576.8	1795	1187.1	6141
589.0	1873	1187.1	6170
687.8	2557	1187.6	6173
687.9	2524	1271.2	6827
697.3	2623	1272.1	6846
697.7	2610	1306.5	7138
697.7	2596	1307.0	7136
791.0	3257	1346.2	7448
791.6	3262	1346.5	7493

[a] Runs made to confirm method of correcting for oxygen absorption (see text).

after correction, were in excellent agreement with the values found before oxidation had occurred.

RESULTS

The experimental results, after correction for Zr content and oxygen absorption, are listed in Table I and are shown plotted in terms of the function $(H_T^\circ - H_{298.15}^\circ)/(T - 298.15)$ in Figure 1 along with the single result of Adenstedt (*1*). The measurements are fitted within an average deviation of 0.4% by the analytical expression:

$$H_T^\circ - H_{298.15}^\circ = 5.607T + 0.911 \times 10^{-3}T^2 - 1753$$

which results from the straight line shown in Figure 1. The selected curve joins smoothly in both Cp and (dCp/dT) with the low-temperature Cp data of Burk, Estermann, and Friedberg (*2*) when extrapolated to 298.15° K.

Smoothed values of the thermal properties of hafnium corresponding to the selected curve are tabulated in Table II. Values of the free energy function are based on $S_{298.15}^\circ = 10.50 \pm 0.5$ as given by Hultgren *et al.* (*5*).

Table II. Thermal Properties of Hafnium

		Cal./Deg. G. Atom		
T, ° K.	$H_T^\circ - H_{298.15}^\circ$ Cal./G. Atom	Cp	$S_T^\circ - S_{298.15}^\circ$	$-\frac{F_T^\circ - H_{298.15}^\circ}{T}$
298.15	0	6.15	0.00	10.50
300	11	6.15	0.04	10.50
400	636	6.34	1.83	10.74
500	1278	6.52	3.26	11.20
600	1939	6.70	4.47	11.74
700	2618	6.88	5.52	12.28
800	3316	7.06	6.45	12.80
900	4031	7.25	7.29	13.31
1000	4765	7.43	8.06	13.80
1100	5517	7.61	8.78	14.26
1200	6287	7.79	9.45	14.71
1300	7076	7.98	10.08	15.14
1350	7477	8.07	10.38	15.34

NOMENCLATURE

- T = Temperature, ° K.
- Cp = Heat capacity at constant pressure, cal./deg. g. atom.
- $S_{298.15}^\circ$ = Standard entropy at 298.15° K., cal./deg. g. atom.
- $H_T^\circ - H_{298.15}^\circ$ = Heat content (enthalpy) increment between 298.15° K. and temperature, T.
- $S_T^\circ - S_{298.15}^\circ$ = Entropy increment between 298.15° K. and temperature, T.
- $(F_T^\circ - H_{298.15}^\circ)/T$ = Free energy function with respect to 298.15° K.

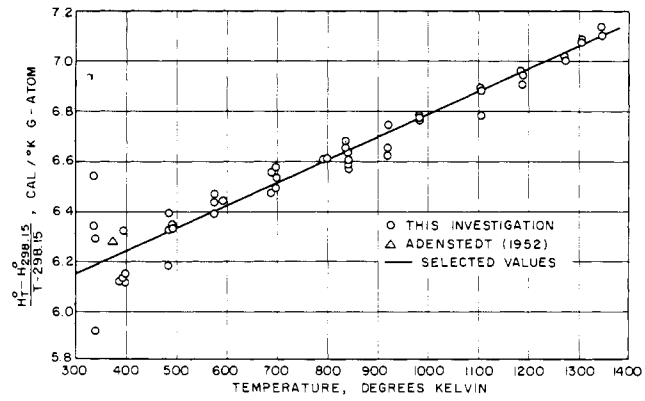

Figure 1. Heat content of hafnium expressed in terms of the function: $(H_T^\circ - H_{298.15}^\circ)/(T - 298.15)$.

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