Zirconium Diboride: Heat Capacity and Thermodynamic Properties from 5° to 350° K.

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The heat capacity of a characterized, zone-melted sample of zirconium diboride has been measured over the low temperature range by adiabatic calorimetry and found to be of a normal sigmoid shape without transitions or thermal anomalies. The values of the heat capacity at constant pressure (C_p), the entropy ($S°$), and the Gibbs function ($-[G° - H_0°]/T$) are 11.53, 8.59, and 3.25 cal. (g.f.m. ° K.)$^{-1}$, respectively, at 298.15° K.

ALTHOUGH in increasing demand as a consequence of technological developments in nuclear reactors, missiles, and other high temperature applications of refractory materials, accurate thermodynamic data on carbides, borides, and related compositions on the group IV elements are relatively rare. The major difficulty is preparing these substances in high-purity, well-characterized states suitable for thermodynamic reference use. This study endeavors to procure reliable thermodynamic data on zirconium diboride (ZrB_2) by adiabatic calorimetry.

EXPERIMENTAL

Cryostat and Technique. Measurements were made in the Mark II adiabatic, vacuum cryostat schematically similar to one previously described (*20*), but modified and improved in several respects to give an instrument of greater compactness, mechanical rigidity, and operating convenience. The cryostat is provided with an economizer, with perforated silver foil discs. This economizer serves as a heat exchanger between the bundle of electrical leads Constantan thermocouples monitor the difference in temperature between calorimeter and shield and between shield and ring. Three separate channels of recording electronic circuitry with proportional, rate, and reset control actions are used for shield control above 50° K. This instrumentation controls temperature to within about a millidegree over the temperature range and makes the uncertainty in the (enameled around it) and the heat capacity of the cold effluent helium gas and thereby minimizes vaporization of liquid helium from the reservoir. The calorimeter is surrounded by a cylindrical adiabatic shield. The top, bottom, and cylindrical sections of this shield are individually controlled by separate channels of automatic regulation which provide a.c. power to the respective shield heaters. Copper-energy exchange between the calorimeter and surroundings comparatively negligible. Below 50° K. manual control of the adiabatic shield is employed. The manner of adiabatic operation employed has been described (*20*).

Calorimeter. The copper calorimeter (laboratory designation W-31) with a capacity of 50 cc. was specially constructed for measurement on the rod-like, zone-refined cylinders of the sample. It is gold plated on all exterior and interior surfaces. It is similar to one previously described (*17*) except that no vanes are employed and that the thermometer well is located off-center and projects through the bottom of the calorimeter for about 1 cm. The sample space has a diameter of 3.2 cm. and an internal length of 6.3 cm. The heat capacity of the empty calorimeter was determined in a separate series of measurements in which identical amounts of indium-tin (Cerroseal) solder for sealing the calorimeter and Apiezon-T grease for thermal contact with the heater-thermometer assembly were used. At the lowest temperatures the heat capacity of the calorimeter-heater-thermometer assembly represented about 50% of the total. This increased to 74% at 20° K., decreased again to 50% at 60° K., then more gradually decreased to 30% at 140° K., 20% at 200° K. and 15% at 350° K. Therefore, a favorable fraction of the total measured heat capacity was that of the sample over most of the range. The mass of the calorimetric sample was 165.246 grams (in vacuo). Buoyancy corrections were made on the basis of the density of ZrB_2 as 6.09 grams/cc. determined from the lattice structure by Norton and others (*16*). This figure accords well with the measured density of Cotter (*4*) (5.97 grams cc.$^{-1}$) and with that obtained by Baroch and Evans (*2*) (5.96 grams cc.$^{-1}$) for zirconium diboride prepared from the oxide and is somewhat higher than that reported by McKenna (*13*) (5.64 grams cc.$^{-1}$) for the diboride prepared from zirconium oxide, carbon, and boric oxide. A pressure of 19.6 cm. of helium at 300° K. was used to facilitate thermal equilibrium in the sample space.

Temperatures determined with a capsule-type, strain-free, platinum-resistance thermometer (laboratory designation A-5) contained within an entrant well in the calorimeter are considered to be in accord with the thermodynamic temperature scale within 0.03° K. from 10 to 90° K. and within 0.04° K. from 90 to 350° K. Temperature increments may, of course, be determined with more precision than absolute temperatures and are probably correct to a few tenths of a millidegree after correction for quasi-adiabatic drift. A 150-ohm Constantan heater was bifilarly wound on a grooved cylindrical copper sleeve closely fitted to the resistance thermometer. Apiezon-T grease permitted the ready removal of this heater-thermometer from the calorimeter. All measurements of resistance, potential, temperature, time, and mass are referred to calibrations made by the National Bureau of Standards.

Preparation and Characterization of the Sample. The zirconium diboride was obtained (Carborundum Co.) in lumps of high purity with respect to hafnium and other trace metals. The analysis as received, however, showed a B to Zr ratio of 2.104, as well as the presence of 0.57% carbon and 0.2% oxygen. To improve the stoichiometry and to reduce the level of impurities, powdered ZrB_2 was prepared for zone-refining by sintering into rods about 1 cm. in diameter by 18 cm. in length, using a split mold of boron nitride and heating by direct passage of current through the sample, followed by zone-melting in argon using the vertical, floating-zone technique with induction heating. The zone-refining apparatus was similar in principle to that described by Wernick and others (*19*) except that the high frequency heating coil rather than the sample was moved. Power was furnished by a 10 kw., 450 kc. radio-frequency supply equipped with a manually-operated thyratron output control. It was desirable to melt ZrB_2 in argon at about 1 atm. pressure to prevent arcing of the high frequency current and to minimize evaporation of boron from the molten zone. The molten zone was moved at the rate of about 50 cm. per hour.

The zone-refined product was obtained in the form of macrocrystalline rods about 6 to 8 mm. in diameter. Prior to use in the measurements the product was lightly etched in aqueous HF-HNO_3 in order to remove a slight surface formed during zone refining. Spectrochemical analyses of samples taken from various portions of the rods indicated that the content of most of the metallic impurities was reduced by about an order of magnitude during zone refining. Since no significant trend of impurity level with position in the bar was found, it is assumed that most of the purification is due to vaporization of impurities at the high temperatures involved (about 3000° C.), rather than to zone refining as such. Representative results (in p.p.m.) were: Ag, Ca, Cu, Ti, V, Cr, and Mn, 10; Al and Mg, 10–100; Hf and Fe, 10–1000; and Si, 100–1000. Two samples gave an average oxygen content of 52 p.p.m. and three samples gave an average carbon content of 215 p.p.m., a 40-fold and a 25-fold reduction, respectively, compared to the starting material. Nitrogen was present to the extent of 134 p.p.m. and hydrogen to the extent of 1.52 p.p.m.

Duplicate analyses for zirconium and boron on samples from the "final" end of the zone-melted rods gave the following results (in per cent by weight):

	Sample A			Sample B		
	1	2	Average	1	2	Average
Zr	80.05	79.60	79.82	80.74	80.40	80.57
B	18.70	18.90	18.80	18.98	19.09	19.04
		Total	98.62			99.61
	B to Zr Ratio		1.96			1.99

Metallographic examination of specimens cut normal and parallel to the growth axis showed a lamellar structure within the crystal grains running parallel to the growth axis. This structure consisted of thin, regularly-spaced layers of a second phase alternating with much thicker layers of the main phase. Because of this simple geometry it was possible to make a rough estimate that the second phase was present to the extent of about 1.53% by volume. X-ray diffraction studies at high gain disclosed the presence of several weak lines attributable to ZrB but none assignable to metallic Zr. Assuming that the second phase is pure ZrB (x-ray density 6.7) the weight fraction is 1.67%, giving a calculated boron content for the whole sample of 19.1% in good agreement with the analytical results for Sample B above. It should be noted that the published phase diagram (*6*) indicates that ZrB is stable only in the range between 800° and 1250° C. If the diagram is correct, it is necessary to assume that ZrB was formed by a solid-state reaction below 1250° and that it failed to decompose below its lower stability limit.

The major reported impurities in the calorimetric sample lead to the following proximate composition by weight in spite of Aronsson's expressed doubt concerning the existence of ZrB (*1*): ZrB_2 100-97%, ZrB 0-3%, ZrC 0.2%, ZrN 0.1%, and ZrO_2 0.02%. Because the zirconium and boron analyses are taken from the final end of the zone-refined bars, they represent the regions most likely impure; also, because the precision in the analyses does not exclude the possibility of substantially pure zirconium diboride or provide a firm proportion of lower boride, no attempt has been made to correct the heat capacity and thermodynamic functions for ZrB present. Even if the maximum impurity indicated above is correct, the differences in the heat capacities of ZrB and ZrB_2 are such that the apparent heat capacity of pure zirconium diboride would be increased less than a tenth of the percentage of impurity above 100° K. Hence, if 1.7% ZrB is present, the heat capacity would be about 0.2% higher than shown in Table II below. The thermodynamic functions near 300° K. would be even less affected. Under the circumstances correction for impurity present is inappropriate.

RESULTS AND DISCUSSION

Heat Capacities and Thermal Properties. The experimental heat capacities are presented in chronological order at the mean temperatures of the determinations in Table I. These data are presented in terms of the defined thermochemical calorie equal to 4.1840 abs. joules, an ice point of 273.15° K., and a gram formula mass (g.f.m.) of 112.864 for ZrB_2. These data have been corrected for curvature—i.e., for the difference between the measured $\Delta H/\Delta T$ and the limit as ΔT approaches 0. The approximate values of ΔT used in the heat capacity determinations can usually be estimated from the increments between adjacent mean temperatures shown in Table I. These heat capacity values are considered to have a probable error decreasing from less than 5% at 5° K., to 1% at 10° K., and to less than 0.1% above 50° K., but are further subject to the purity of the sample as noted earlier.

Heat capacities and thermodynamic functions at selected temperatures, as presented in Table II, are obtained from the heat capacity data by a least squares-fitted curve through the experimental points (carefully compared with a large scale plot of the data) and the integration thereof. Both the fitting and the quadrature are performed by high-speed digital computer programs (*8*). The thermodynamic functions are considered to have a precision indicated by a probable error of less than 0.1% above 100° K. An additional digit beyond those significant is giving in Table II for internal consistency and to permit interpolation and differentiation. The entropies and Gibbs

Table I. Heat Capacity of Zirconium Diboride

ZrB_2: g.f.m. = 112.86 Units: cal. (g.f.m. °K.)$^{-1}$

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
Series I		Series III		152.81	5.554
				161.47	5.992
67.62	1.2495	18.05	0.0154	169.96	6.411
73.24	1.518	19.76	0.0200	172.64	6.551
79.29	1.822	21.62	0.0259	181.64	6.975
86.15	2.176	22.80	0.0304	190.21	7.385
93.23	2.529	25.11	0.0417	198.74	7.781
100.79	2.905	27.90	0.0588	207.14	8.161
108.87	3.312	31.13	0.0868	217.19	8.601
		34.70	0.1309	224.60	8.920
Series II		38.37	0.1926	233.49	9.271
		42.29	0.2765	242.55	9.628
5.50	0.0015	46.80	0.3972	251.46	9.979
6.86	0.0019	51.88	0.5701	260.17	10.287
8.12	0.0023	57.41	0.7871	268.66	10.589
9.16	0.0035	62.44	1.0083	277.25	10.877
10.21	0.0044	68.91	1.3086	286.43	11.174
11.42	0.0051			295.78	11.460
12.55	0.0062	Series IV		304.56	11.729
13.67	0.0075			312.70	11.955
14.93	0.0093	119.42	3.850	320.44	12.165
16.41	0.0118	127.64	4.270	328.67	12.383
		135.78	4.686	336.97	12.576
		144.07	5.113	345.25	12.768

Table II. Thermodynamic Properties of Zirconium Diboride

ZrB_2: g.f.m. = 112.86 Units: cal., g.f.m., °K.

T	C_p	S°	$H^\circ - H^\circ_0$	$\frac{-G^\circ - H^\circ_0)}{T}$
5	0.001	0.0003	0.001	0.0001
10	0.0037	0.0018	0.012	0.0005
15	0.0094	0.0042	0.043	0.0013
20	0.0206	0.0083	0.116	0.0025
25	0.0408	0.0148	0.264	0.0043
30	0.0762	0.0251	0.549	0.0068
35	0.1354	0.0409	1.066	0.0105
40	0.2250	0.0645	1.953	0.0157
45	0.3456	0.0977	3.368	0.0228
50	0.5026	0.1419	5.474	0.0324
60	0.8986	0.2672	12.404	0.0604
70	1.3628	0.4400	23.67	0.1018
80	1.858	0.6541	39.76	0.1570
90	2.363	0.9021	60.87	0.2258
100	2.870	1.1773	87.03	0.3070
110	3.375	1.4745	118.26	0.3994
120	3.881	1.7898	154.5	0.5021
130	4.390	2.1206	195.9	0.6137
140	4.900	2.4645	242.3	0.7336
150	5.410	2.8200	293.9	0.8608
160	5.917	3.1854	350.5	0.9946
170	6.416	3.5591	412.2	1.1134
180	6.904	3.9396	478.8	1.2787
190	7.379	4.3257	550.2	1.4298
200	7.840	4.716	626.3	1.584
210	8.286	5.109	707.0	1.743
220	8.717	5.505	792.9	1.905
230	9.134	5.902	881.3	2.070
240	9.534	6.299	974.6	2.238
250	9.919	6.696	1071.9	2.408
260	10.285	7.092	1172.9	2.581
270	10.635	7.487	1277.6	2.755
280	10.967	7.880	1385.6	2.931
290	11.285	8.270	1496.8	3.109
300	11.589	8.658	1611.2	3.287
310	11.879	9.043	1728.6	3.467
320	12.155	9.424	1848.8	3.647
330	12.412	9.802	1971.6	3.828
340	12.648	10.176	2096.9	4.009
350	12.878	10.546	2224.6	4.190
273.15	10.74	7.61	1311	2.811
298.15	11.53	8.59	1590	3.254

energies have not been adjusted for nuclear spin and isotopic mixing contributions and are hence practical values for use in chemical thermodynamic calculations.

High temperature enthalpy determinations on zirconium diboride have been reported by Mezaki and others (*14*). High accuracy is not to be anticipated in a derived function such as the heat capacity from enthalpy increment determinations near the temperature of the block into which the drop-calorimeter is equilibrated. However, heat capacities derived from these enthalpy data (*14*) are higher by 14% than the direct determination in the present research at 300° K. and higher by 8% than the extrapolated value at 400° K. Reconciliation of the high temperature heat capacity data except for determinations between 300 and 500° K. is possible by the use of a Shomate plot (*18*). The low temperature data can be faired into the high temperature data near 600° K. This would require an adjustment of about −240 cal. (g.f.m.)$^{-1}$ in the reported enthalpy increment at 634° K. and higher temperatures and a corresponding adjustment in the other functions. More recent high temperature data by R.H. Valentine and others in the same laboratory (*11*) appear to be in much better accord with these measurements. It is to be noted further that the measurements reported by Mezaki and others were made on finely divided granular, less carefully characterized samples than those of the present research and that, in all probability, the ratio of heat capacity of sample to total was not as favorable. Even higher values are reported by Neel and others (*15*). Krestovnikov and Vendrikh (*10*) determined enthalpies to 800° C. calorimetrically and compiled values differing by less than 10% from Maydel's equations (*12*) for the estimation of heat capacity from the position of the elements in the periodic table and the enthalpy of formation of the compound involved. Significant differences apparently exist in the thermal properties of borides of different stoichiometries and impurity content. In view of the relatively high quality of the present samples and the nature of the measurements involved, data from the present research are recommended as the most reliable over the range of overlap.

Thermodynamics of Formation. Epel'baum and Starostina (*5*) found the enthalpy of formation of $ZrB_{2.05}$ to be −75.02 ± 3.35 kcal. (g.f.m.)$^{-1}$ subsequent to determinations of the enthalpy of combustion of boron as −287.8 ± 2.17 or −289.47 ± 3.1 kcal. (g.a.m.)$^{-1}$. Since the value for boron appears to be low, the enthalpy of formation of $ZrB_{2.05}$ may be in error from incomplete combustion or the possible use of a low value for the enthalpy of formation of B_2O_3. Holley and others (*7*) have also determined the enthalpy of combustion of ZrB_2. Because the samples were relatively impure the results were not considered to be complete, and (g.f.m.)$^{-1}$ and −73.1 ± 3.1 kcal. (g.f.m.)$^{-1}$. Of these measurements that by Holley and others (*7*) on their purest sample is taken as the best value, −76.4 kcal. (g.f.m.)$^{-1}$. Because of the inherent uncertainty in this work, the value by Epel'baum and Starostina, the estimate of −78 kcal. (g.f.m.)$^{-1}$ by Brewer and Haraldsen (*3*) on the basis of its stability in the presence of graphite, and the fact that zirconium will reduce molybdenum boride and tungsten boride, an uncertainty of ± 3 kcal. (g.f.m.)$^{-1}$ is assigned. Combining this value with the entropies of zirconium and boron (*9*) and the data from the present research yields an entropy of formation (ΔSf°) and a Gibbs energy (ΔGf°) of formation of −3.5 ± 0.1 cal. (g.f.m. °K.)$^{-1}$ and −75.4 ± 3 kca. (g.f.m.)$^{-1}$, respectively, at 298.15° K.

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The Solubility of Tetraethyllead in Water

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Tetraethyllead (I) vapor, water and air were equilibrated in all-glass apparatus. The phases were separated, the I extracted into pentane, and the pentane analyzed for lead. In the separated phases, no decomposition products of I were detected. Between 0.2 and 0.3 mg. of I saturate a liter of water at 0–38° C.

THE SOLUBILITY of tetraëthyllead (TEL) in water has been measured to aid in the understanding of the aqueous solubility of nonelectrolytes. The immiscibility of TEL and water is known, but no quantitative information has been published. Results are here reported that indicate the magnitude of the solubility of TEL in water saturated with air.

Two useful techniques of separation have been developed in this work, one for the separation of TEL from small volumes of air and the other for its separation from small volumes of water. These new techniques have been used in conjunction with an older method of equilibrating and separating gases and liquids (*6*) to obtain data on the distribution of TEL between air and water. From these data and data on the vapor pressure of TEL (*1*), the solubility of TEL in water has been calculated. A liquid phase of TEL has been avoided because of the uncertainty of complete separation of emulsions of TEL and water and because of the need to reach equilibrium before appreciable decomposition of TEL occurred. Both problems were encountered in preliminary experimentation.

RESULTS AND DISCUSSION

The concentrations of TEL in the aqueous and gaseous phases were calculated from the analytical data (Table I). From these concentrations and the following equation for the vapor pressure of TEL, the aqueous solubilities at saturation were calculated, assuming Henry's law:

$$\log_{10} P_{\text{TEL}} = 9.34286 - \frac{2908.43}{{}^\circ\text{K.}}$$

where P_{TEL} is the vapor pressure of TEL in mm. of mercury and 0° C. is taken as 273.16° K. This equation was obtained from a least squares fit of the data of Buckler and Norrish (*1*); it differs slightly from their equation. The aqueous solubility in the temperature range from 0° to 38° C. is between 0.2 and 0.3 mg. of TEL per liter of water.

Detailed thermodynamic calculations (*2*) on the results are unwarranted in view of the variability of the findings relating solubility to temperature. As usual with non-