Hypostoichiometric titanium diboride (TiB₁.₉₄) and hyperstoichiometric tantalum diboride (TaB₂.₁₁): the heat capacity and thermodynamic properties from 5 to 350 K [a]

EDGAR F. WESTRUM, JR.

Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109, U.S.A.

and

GERALD A. CLAY

Arthur D. Little Inc., Acorn Park, Cambridge, Massachusetts 02139, U.S.A.

Heat capacities of TiB_2 and $TaB_{2.11}$ have been measured by adiabatic cryogenic calorimetry and found to have an essentially normal sigmate temperature dependence without thermal anomalies. Values at 298.15 K of the heat capacity at constant pressure C_p, the standard entropy $S°$, the function $\{H°(T) - H°(0)\}/T$, and the function $-\{G°(T) - H°(0)\}/T$ are 10.58, 6.805, 4.469, and 2.336 cal_{th} K^{-1} mol^{-1} for TiB_2, and 11.88, 10.57, 6.034, and 4.539 cal_{th} K^{-1} mol^{-1} for $TaB_{2.11}$, respectively.

1. Introduction

An increasing need for thermodynamic data on borides as a consequence of technological developments in nuclear reactors, missiles, and other high-temperature applications of refractory materials has resulted in studies on ZrB_2,[1] $NbB_{1.963}$,[2] and HfB_2.[3] Thermal data on two additional nearly stoichiometric members of this important class of materials, provided by the present study, are of scientific interest as well since they broaden the base of our meager information on refractory compounds.

2. Experimental

CRYOSTAT AND CALORIMETER

Measurements on TiB_2 were made in the Mark II adiabatic vacuum cryostat[4] using calorimeter W-28 as a sample container because this sample was finely divided. This calorimeter is essentially the same size as W-35,[2] but has four vanes soldered to the (thermometer + heater) well and is provided with a small cupola of monel which

permits the soldering of the cap in place with Cerroseal (indium + tin) solder without appreciably heating either the calorimeter or the sample. Measurements on $TaB_{2.11}$ were made in the Mark III adiabatic cryostat and the W-35 calorimeter. This cryostat differs from Mark II only in not having a heat exchanger to utilize the enthalpy of the effluent helium gas to furnish a thermal dam against the conduction of heat by the lead wires and thus minimize the vaporization of the liquid helium from the lowest-temperature reservoir. Since cryostats and calorimeters have been described previously, it is sufficient to note that temperatures were determined with capsule-type strain-free platinum-resistance thermometers (laboratory designations A-5 and A-3, respectively) contained within the entrant well in each calorimeter. These have been calibrated against IPTS-48 and probably agree with the thermodynamic scale to within 0.03 K from 10 to 90 K and within 0.04 K from 90 to 350 K. Temperature increments are probably usually correct to ± 0.04 mK after adjustments have been made for quasi-adiabatic drift. All measurements of resistance, potential, temperature, time, and mass are referred to standards and calibrations of the National Bureau of Standards.

The heat capacity of the (calorimeter + heater + thermometer) assembly 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. A pressure of about 13 kPa of helium gas at 300 K was used to facilitate thermal equilibrium within the sample space. In the measurements on TiB_2 the heat capacity of the sample represented about 40 per cent of the total at 10 K, a minimum of 17 per cent at 35 K, 55 per cent at 100 K, and increased gradually to 85 per cent at 350 K. The variation was somewhat less pronounced for $TaB_{2.11}$, for which the heat capacity represented about 35 per cent of the total at 10 K, a minimum of 27 per cent at 16 K, increased rapidly to 48 per cent at 60 K, and then gradually to 62 per cent at 350 K.

PROVENANCE AND CHARACTERIZATION OF TITANIUM DIBORIDE

A sample of titanium diboride powder was obtained from the Millmaster Chemical Corporation. The sample contained (in mass per cent): Ti, $(68.8_5 \pm 0.2)$; B, $(30.4_8 \pm 0.6)$; C, 0.12; N, 0.10; and O, 0.11. Spectrographic analyses on the same basis indicates Fe, 0.06; Co, 0.1; Cr, 0.1; Ni, 0.01; Si, 0.01; and Al, Mg, and Mo, 0.001. All other elements detectable by spectrographic analysis gave 0.001 or less. The average composition of the powder is $TiB_{1.960}$, and the particle size varies between 2 and 5 μm.

The appreciable volatility of this substance at the melting temperature resulted in vaporized material condensing on the high-frequency coil and caused severe arcing during an attempted zone-refining operation. Heat-capacity measurements were, therefore, made on the powder as received.

PROVENANCE AND CHARACTERIZATION OF TANTALUM DIBORIDE

Powdered TaB_2 was obtained from the Kawecki Chemical Company, containing mass percentages: Ta, 88.80; B, 10.34; C, 0.36; O, 0.68; and traces of metallic impurities. This represented an average composition of $TaB_{1.945}$. In order to improve

stoichiometry and to reduce the level of impurities, the powdered TaB$_2$ was prepared for zone refining by sintering into rods about 1 cm diameter by 18 cm long, using a split mold of boron nitride, and heating by direct passage of current through the sample. To compensate for boron losses during melting, 9 per cent excess boron (based on the theoretical content of boron in TaB$_{2.00}$) was added to the powder before sintering. This treatment was followed by zone melting at atmospheric pressure using the vertical floating-zone technique with induction heating. The zone-refining apparatus was similar in principle to that described by Wernick et al.[5] except that the high-frequency heating coil rather than the sample was moved. Power was furnished by a 10 kW 450 kHz radio-frequency supply equipped with a manually-operated thyratron output control. It was found desirable to do the melting at about 95 kPa pressure to minimize evaporation of boron from the molten zone, and to add 5 per cent by volume of hydrogen to the atmosphere, to eliminate minor arcing difficulties. A tendency toward severe cracking was reduced by increasing the rate of zone travel to 76 cm h^{-1}.

The zone-melted product was obtained in the form of polycrystalline rods about 7 mm diameter, which were established to be single phase by metallographic and X-ray diffraction examination of several representative samples. Chemical analyses for Ta and B gave the results shown in table 1. Chemical analyses for non-metallic

TABLE 1. Mass fractions w of impurities in the TaB$_{2.11}$ sample

| Sample | $10^2 w$ | | | $n(\text{B})/n(\text{Ta})$ |
	Ta	B	Ta + B	
576–5	89.1$_1$	10.9$_2$	100.03	2.04
659–3	88.5$_6$	11.5$_6$	100.12	2.18
679–2	88.5$_5$	11.4$_8$	100.03	2.16
675–3	89.0	10.9	99.9	2.05
	($\pm$ 0.3)^a	($\pm$ 0.2)^a	Mean:100.02	2.11

^{a} Overall accuracy claimed by professional analysts

impurities show 10^6 (mass fractions): C, 51 and 35; N, 22; O, 32, and qualitative spectrographic analysis indicated Ag, Al, As, Ca, Fe, Mg, Ni, and Si mass fractions to be about 10^{-5} with Ti and Cr 10^{-5} to 10^{-4}. All other detectable elements were present at mass fractions less than 10^{-6}.

The mass of the TiB$_2$ calorimetric sample was 202.8139 g, that of TaB$_{2.11}$ was 210.7972 g. Buoyancy corrections were made on the basis of densities of 4.50 g cm^{-3} for TiB$_2$ and 11.5 g cm^{-3} for TaB$_{2.11}$.

3. Results and discussion

HEAT CAPACITIES AND THERMAL PROPERTIES

The experimental heat capacities are presented in table 2 in chronological order at the mean temperatures of the individual determinations. These results are presented in terms of IPTS-48, and molar masses of 69.54 g mol^{-1} for TiB$_2$, and 203.78 g mol^{-1}

TABLE 2. Heat capacities of titanium and tantalum diborides
(cal_{th} = 4.184 J)

$\frac{T}{K}$	$\frac{C_p}{cal_{th} \, K^{-1} \, mol^{-1}}$	$\frac{T}{K}$	$\frac{C_p}{cal_{th} \, K^{-1} \, mol^{-1}}$	$\frac{T}{K}$	$\frac{C_p}{cal_{th} \, K^{-1} \, mol^{-1}}$	$\frac{T}{K}$	$\frac{C_p}{cal_{th} \, K^{-1} \, mol^{-1}}$

Titanium (hypostoichiometric) diboride, $TiB_{1.98}$, calculated on the basis $TiB_{2.00}$
(M = 69.54 g mol^{-1}) [a]

$\frac{T}{K}$	C_p	$\frac{T}{K}$	C_p	$\frac{T}{K}$	C_p	$\frac{T}{K}$	C_p
Series I		9.75	0.0070	Series IV		196.74	6.569
138.02	3.652	10.83	0.0080	59.74	0.3711	206.02	6.995
143.63	3.946	12.12	0.0089	63.37	0.4580	215.15	7.412
150.87	4.314	13.68	0.0097	69.02	0.6106	224.41	7.817
158.58	4.702	15.40	0.0106	74.23	0.7701	233.90	8.216
166.94	5.124	17.17	0.0116	80.02	0.9751	243.40	8.608
		18.96	0.0134	86.75	1.2397	252.62	8.976
Series II		20.76	0.0158	93.87	1.532	261.69	9.313
111.37	2.323	22.60	0.0189	101.92	1.883	259.06	9.213
118.25	2.660	24.68	0.0230	110.68	2.293	268.23	9.553
122.47	2.868	26.88	0.0285	121.48	2.817	277.24	9.879
130.28	3.261	29.26	0.0351	128.42	3.163	286.27	10.190
137.86	3.648	32.02	0.0449	135.88	3.545	295.40	10.491
		35.27	0.0598	143.78	3.950	304.48	10.783
Series III		38.83	0.0805	152.39	4.386	313.54	11.059
5.79	0.0009	42.32	0.1069	161.33	4.840	322.91	11.333
6.44	0.0016	45.95	0.1430	169.96	5.273	332.18	11.585
7.10	0.0021	50.37	0.1988	178.39	5.689	340.53	11.821
7.93	0.0032	55.50	0.2830	187.32	6.121	347.25	12.000
8.78	0.0051	60.74	0.3933				

Tantalum (hyperstoichiometric) diboride, $TaB_{2.11}$, calculated on the basis $TaB_{2.11}$
(M = 203.78 g mol^{-1})

$\frac{T}{K}$	C_p	$\frac{T}{K}$	C_p	$\frac{T}{K}$	C_p	$\frac{T}{K}$	C_p
Series I		254.17	10.497	8.06	0.0063	36.68	0.5525
126.62	5.306	263.08	10.792	9.15	0.0081	40.35	0.7535
134.73	5.660	271.94	11.084	10.31	0.0109	44.54	1.0095
143.67	6.050	281.07	11.371	11.67	0.0122	49.26	1.3171
152.53	6.435	290.40	11.656	13.10	0.0164	54.43	1.658
161.50	6.826	299.73	11.924	14.54	0.0212	60.47	2.057
170.52	7.207	309.07	12.185	16.08	0.0276	67.25	2.480
179.67	7.590	318.35	12.431	17.80	0.0374	74.37	2.881
188.71	7.972	327.49	12.673	19.65	0.0519	81.55	3.276
197.77	8.348	336.58	12.898	21.60	0.0730	88.20	3.619
207.30	8.736	345.64	13.104	23.67	0.1040	96.16	3.983
216.98	9.125			25.91	0.1478	104.24	4.332
226.38	9.491	Series II		27.97	0.2006	112.58	4.696
235.74	9.842	6.10	0.0038	30.24	0.2713	120.96	5.063
245.06	10.191	7.01	0.0051	33.24	0.3894		

[a] Because the imprecision in the analyses for boron in this compound does not exclude the stoichiometric composition, the observed specific heat capacity was multiplied by M.

for $TaB_{2.11}$. The results have been adjusted for curvature, *i.e.* for the difference between the measured $\Delta H/\Delta T$ and the corresponding derivatives $(\partial H/\partial T)_p$. The approximate values of the temperature increments used in the determinations may usually be estimated from the differences between adjacent (mean) temperatures shown in table 1. These heat-capacity values are considered to have probable errors decreasing from less than 5 per cent at 5 K, to 1 per cent at 10 K, and less than 0.2 per cent above 50 K, but are further subject to the purity of the sample as noted
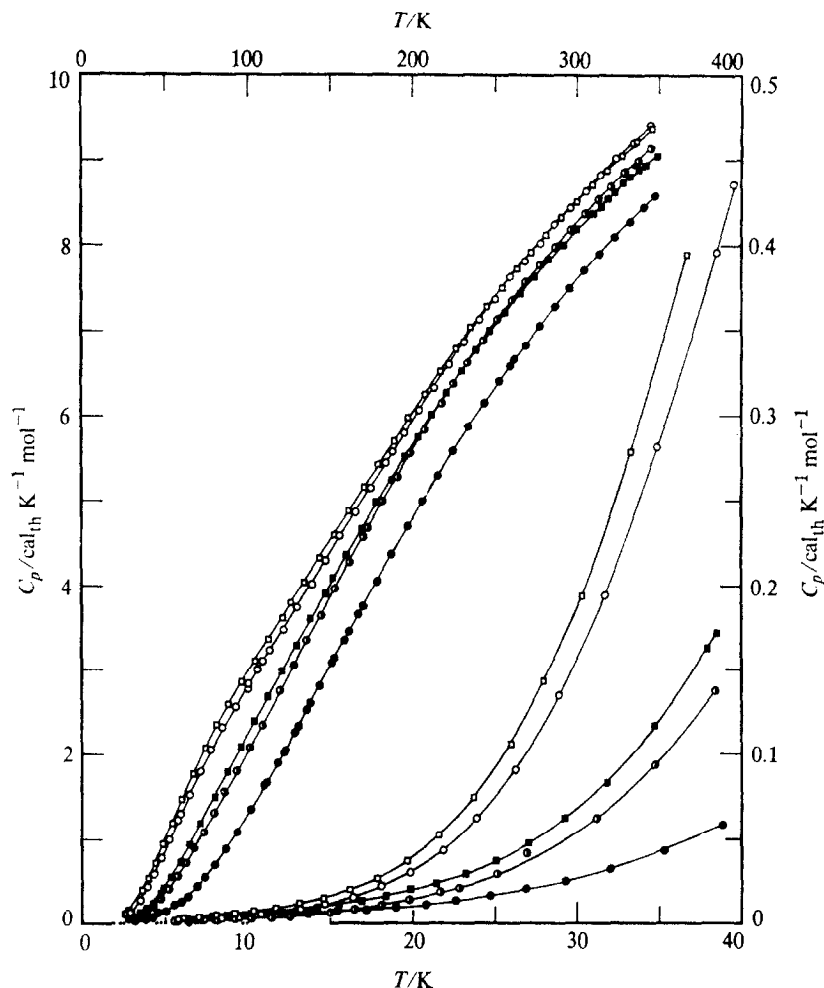
FIGURE 1. Heat capacities of transition element diborides: ●, TiB$_2$; □, TaB$_{2.11}$; ◑, ZrB$_2$;[1] ■, NbB$_{1.963}$;[2] and ○, HfB$_2$[3].

earlier. These heat capacities are compared with those of other diborides in figure 1. Below 5 K the results were extrapolated by relation $C_p = \gamma T + cT^3$. The value of γ was found to be about 2.5×10^{-4} cal$_{th}$ K^{-2} mol^{-1} for the tantalum diboride.†

We cannot obtain a reliable value of γ for TiB$_2$, as the heat capacity is somewhat high in the 5 to 12 K region for unknown reasons. However, the magnitude of the heat capacity even at 12 K is so small that the deviation from normal sigmate behavior is estimated to contribute an excess entropy of only about 0.003 cal$_{th}$ K^{-1} mol^{-1}.

The heat capacities and thermodynamic functions at selected temperatures are presented in tables 3 and 4. These values are obtained from the heat capacities by a least-squares-fitted curve through the experimental points (carefully compared with a large scale plot) and the integration thereof. Both the fitting and the quadrature are

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

TABLE 3. Thermodynamic functions of titanium (hypostoichiometric) diboride,
$TiB_{1.96}$, calculated on the basis $Tib_{2.00}$
($M = 69.54$ g mol^{-1}; $cal_{th} = 4.184$ J)

T	C_p	$S°(T) - S°(0)$	$H°(T) - H°(0)$	$-\{G°(T) - H°(0)\}/T$
$\overline{K}$	cal_{th} K^{-1} mol^{-1}	cal_{th} K^{-1} mol^{-1}	cal_{th} mol^{-1}	cal_{th} K^{-1} mol^{-1}
5	0.0015	0.0005	0.002	0.0001
10	0.0038	0.0021	0.014	0.0007
15	0.0082	0.0044	0.043	0.0015
20	0.0147	0.0076	0.100	0.0026
25	0.0238	0.0118	0.195	0.0040
30	0.0374	0.0173	0.345	0.0057
35	0.0579	0.0244	0.580	0.0079
40	0.0887	0.0341	0.941	0.0105
45	0.1331	0.0469	1.490	0.0138
50	0.1944	0.0640	2.301	0.0179
60	0.3759	0.1142	5.083	0.0295
70	0.6397	0.1909	10.094	0.0467
80	0.9755	0.2975	18.12	0.0711
90	1.3655	0.4345	29.78	0.1036
100	1.797	0.6004	45.56	0.1447
110	2.258	0.7930	65.82	0.1947
120	2.745	1.0103	90.82	0.2535
130	3.247	1.2498	120.77	0.3208
140	3.756	1.509	155.8	0.3963
150	4.266	1.786	195.9	0.4796
160	4.774	2.077	241.1	0.5702
170	5.276	2.382	291.4	0.6678
180	5.768	2.697	346.6	0.7717
190	6.251	3.022	406.7	0.8816
200	6.721	3.355	471.6	0.9969
210	7.178	3.694	541.1	1.1172
220	7.622	4.038	615.1	1.2421
230	8.052	4.386	693.5	1.3712
240	8.467	4.738	776.1	1.504
250	8.868	5.092	862.8	1.641
260	9.253	5.447	953.4	1.780
270	9.623	5.803	1047.8	1.922
280	9.977	6.160	1145.8	2.068
290	10.316	6.516	1247.3	2.215
300	10.639	6.871	1352.0	2.364
310	10.948	7.225	1460.0	2.515
320	11.244	7.577	1571.0	2.668
330	11.529	7.928	1684.8	2.822
340	11.805	8.276	1801.5	2.977
350	12.078	8.622	1920.9	3.134
273.15	9.736	5.915	1078.3	1.968
298.15	10.581	6.805	1332.4	2.336

TABLE 4. Thermodynamic properties of tantalum (hyperstoichiometric) diboride, TaB$_{2.11}$, calculated on the basis TaB$_{2.11}$

(M = 203.78 g mol^{-1}; cal$_{th}$ = 4.184 J)

T K	C_p cal$_{th}$ K^{-1} mol^{-1}	$S°(T) - S°(0)$ cal$_{th}$ K^{-1} mol^{-1}	$H°(T) - H°(0)$ cal$_{th}$ mol^{-1}	$-\{G°(T) - H°(0)\}/T$ cal$_{th}$ K^{-1} mol^{-1}
5	0.0027	0.0009	0.003	0.0002
10	0.0096	0.0047	0.033	0.0014
15	0.0232	0.0108	0.110	0.0035
20	0.0550	0.0212	0.294	0.0065
25	0.1283	0.0403	0.730	0.0111
30	0.2641	0.0747	1.682	0.0186
35	0.4688	0.1299	3.487	0.0303
40	0.7332	0.2092	6.470	0.0474
45	1.0390	0.3129	10.887	0.0709
50	1.3660	0.4392	16.90	0.1013
60	2.026	0.7468	33.87	0.1823
70	2.642	1.1062	57.26	0.2882
80	3.195	1.4958	86.50	0.4145
90	3.692	1.9013	120.97	0.5571
100	4.152	2.3143	160.2	0.7121
110	4.591	2.7308	203.9	0.8767
120	5.023	3.1488	252.0	1.0486
130	5.454	3.5679	304.4	1.2263
140	5.887	3.9879	361.1	1.4085
150	6.322	4.409	422.2	1.594
160	6.756	4.831	487.5	1.784
170	7.187	5.253	557.3	1.975
180	7.613	5.676	631.3	2.169
190	8.032	6.099	709.5	2.365
200	8.443	6.522	791.9	2.562
210	8.846	6.943	878.3	2.761
220	9.240	7.364	968.8	2.960
230	9.623	7.783	1063.1	3.161
240	9.994	8.200	1161.2	3.362
250	10.352	8.616	1262.9	3.564
260	10.696	9.029	1368.2	3.766
270	11.024	9.438	1476.8	3.969
280	11.339	9.845	1588.6	4.172
290	11.640	10.248	1703.5	4.374
300	11.929	10.648	1821.4	4.576
310	12.209	11.044	1942.1	4.779
320	12.478	11.435	2065.5	4.981
330	12.736	11.823	2191.6	5.182
340	12.977	12.207	2320.2	5.383
350	13.196	12.587	2451.1	5.584
273.15	11.12	9.57	1512	4.033
298.15	11.88	10.57	1799	4.539

performed by high-speed digital computation using routine programs. The thermo-dynamic functions are considered to have a precision indicated by a probable error of less than 0.2 per cent above 100 K. An additional digit beyond those significant is frequently given in tables 3 and 4 for purposes of internal consistency and to permit interpolation and differentiation. The entropies $S°$ and the functions $-\{G°(T) - H°(0)\}/T$ have not been adjusted for nuclear-spin and isotope-mixing contributions and, hence, are practical values for use in chemical-thermodynamic calculations.

The heat capacities of these compounds may be estimated by Kaufman's adaptation of an empirical method.[6] The 298.15 K values of C_p and $S°$ for TiB_2 are 8.4 and 4.9 cal_{th} K^{-1} mol^{-1} which are to be compared with the corresponding experimental values of 10.58 and 6.808 cal_{th} K^{-1} mol^{-1}, as are the corresponding estimated value for C_p of $TaB_{2.11}$, which is 13.2 and the observed value of 11.58 cal_{th} K^{-1} mol^{-1}. Krestovnikov and Vendrikh[7] have determined the enthalpy increments by method-of-mixtures calorimetry above 300 K and calculate $C_p(298.15 K) \approx 10.62$ cal_{th} K^{-1} mol^{-1}, which appears to be in accord with our value as well as may be expected.

REFERENCES

1. Westrum, E. F., Jr.; Feick, G. *J. Chem. Eng. Data* **1963**, 8, 193.
2. Westrum, E. F., Jr.; Clay, G. A. *J. Phys. Chem.* **1963**, 67, 2385.
3. Westrum, E. F., Jr.; Feick, G. *J. Chem. Thermodynamics* **1977**, 9, 293.
4. Westrum, E. F., Jr.; *J. Chem. Educ.* **1962**, 39, 443.
5. Wernick, J. H.; Dorsi, D.; Byrnes, J. J. *J. Electrochem. Soc.* **1959**, 106, 245.
6. Kaufman, L. *Trans. Amer. Inst. Mech. Eng.* **1962**, 224, 1006; and Data Sheet No. 42, AF 33 (657)-8635 Contract (1962).
7. Krestovnikov, A. N.; Vendrikh, M. S. *Izv. Vyz Tsvet. Metall.* **1959**, 2, 54.