HEAT CAPACITY AND THERMODYNAMIC PROPERTIES OF DITUNGSTEN CARBIDE, W_2C_{1-x}, FROM 10 TO 1000 K

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ABSTRACT

Thermodynamic properties of tungsten carbide, $W_2C_{0.833}$, have been derived from heat capacities measured by adiabatic calorimetry in the range 10–1000 K on a sample rich in this phase. The standard entropy of $W_2C_{0.833}$ was found to be 75.80 J K^{-1} mol^{-1} at 298.15 K and 159.8 J K^{-1} mol^{-1} at 1000 K. Thermodynamic formation values for $W_2C_{0.833}$ were deduced from the reported coexistence of this phase with tungsten and tungsten monocarbide at about 1550 K.

INTRODUCTION

The thermodynamic properties of ditungsten carbide are mainly based on estimates, with the exception of the value of the enthalpy of formation at 298 K derived by Mah [1] from combustion calorimetry. W_2C is unstable at ambient temperature, but is retained in different structural forms depending on quenching and other conditions. The tungsten atoms are hexagonally (or pseudohexagonally) close packed and the carbon atoms are in octahedral interstices. The arrangement was originally reported to be of the anti-Cd(OH)$_2$ type [2], while in more recent studies both the ε-Fe$_2$N- and the ζ-Fe$_2$N-type arrangements have been found. Thus, in an X-ray and neutron diffraction study Yvon et al. [3] reported the former type of arrangement in samples quenched from 2670 K, but with randomization of some of the carbon atoms. The site occupation was studied in detail by Hårsta et al. [4] for samples heat treated for 30–50 h at 1920 K before quenching, and was

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Dedicated to Professor Oswald Kubaschewski in honour of his contribution to thermochemistry.

studied more recently for arc-melted material by Lönnberg et al. [5]. In an earlier study by Rudy and Windisch [6] the orthorhombic (pseudohexagonal) ζ-Fe_2N-type structure was observed in W_2C samples quenched from above 2300 K.

The value of the enthalpy of formation obtained by Mah [1], $\Delta_f H^{\ominus}(W_2C, 298 \text{ K}) = -(26.4 \pm 2.5)$ kJ mol^{-1}, was determined by combustion calorimetry on a W_2C sample containing about 2 wt% WC and 3 wt% W. The value superseded the earlier estimate by Krikorian [7] of $-(46 \pm 17)$ kJ mol^{-1}. Krikorian also estimated $S^{\ominus}(W_2C, 298 \text{ K}) = 81.6$ J K^{-1} mol^{-1} and a heat-capacity equation for use from ambient to melting temperature. The thermodynamic tables by Schick [8], Barin et al. [9] and Pankratz et al. [10] were based on these estimates. This study was carried out to provide a better basis for the thermophysical properties of the ditungsten carbide phase.

EXPERIMENTAL

Sample

The tungsten carbide sample was placed at our disposal by AB Sandvik Coromant, Sweden. It was obtained by very rapid quenching of a tungsten carbide melt in order to prevent disproportionation of W_2C_{1-x} into WC + W below about 1520 K [11]. According to the analysis provided, the sample contained (in mass %): C(total), 4.02; C(uncombined), 0.21; Fe, 0.29; O, 0.050; Cr, 0.035; Ni, 0.017; N, 0.01. Other elements were less then (in p.p.m. by mass): Mo, 40; Si, 25; Ti, 20; Mn, 20; Zn, 20; As, 20; Co, 15; Al, 15; Ca, 10; Pb, 10; Cu, 10; V, 10; Sn, 5; Bi, 2; Mg, 2. The crystalline grey–black sample had grain sizes between 110 and 160 μm.

X-ray powder diffraction photographs were taken in an 80 mm diameter Guinier camera with Cu $K\alpha_1$ radiation with silicon as a calibration substance ($a(293 \text{ K}) = 543.1065$ pm [12]). The sample consisted of a mixture of hexagonal W_2C and hexagonal WC. Unit cell dimensions derived by a least-squares method were W_2C_{1-x}: $a = 517.90(10)$ pm and $c = 471.87(8)$ pm; WC: $a = 290.18(5)$ pm and $c = 283.40(7)$ pm (the numbers in parentheses indicate one standard deviation in terms of the last digits).

The value of the a axis for the W_2C_{1-x} phase refers to the ε-Fe_2N-type cell orientation with $a = a'3^{1/2}$. The lattice constants are slightly smaller than those reported by Hårsta et al. [4]: $a = 518.52(4)$ pm and $c = 472.32(5)$ pm for a sample with composition $W_2C_{0.89(1)}$, and $a = 518.33(5)$ pm and $c = 472.32(5)$ pm for $W_2C_{0.86(1)}$. The results of Lönnberg et al. [5] were $a = 518.09(2)$ pm and $c = 472.16(4)$ pm for a sample with composition $W_2C_{0.844(18)}$. The composition dependence of the lattice constants was studied earlier by Rudy [13]. He obtained values of $a = a'3^{1/2} = 517.0$ pm and

$c = 471.6$ pm for $W_2C_{0.837}$, and $a = 519.6$ pm and $c = 472.1$ pm for $W_2C_{0.976}$. Thus, the composition of the W_2C_{1-x} phase in the present sample appears to be about $W_2C_{0.84}$, which is remarkably close to the stoichiometry $W_{12}C_5$ or $W_2C_{0.833}$, which will be used here.

Iron is the major foreign element in the sample. It is not known whether it is dissolved in the tungsten carbides or exists as an iron carbide. The elemental carbon presumably stems from the graphite crucible and not from the decomposition of the metastable W_2C phase. Neglecting other impurities, assuming stoichiometry for WC, and that iron is present as Fe_3C, the mass fractions of the phases are: $W_2C_{0.833}$, 0.6638; WC, 0.3310; Fe_3C, 0.0031; C(gr), 0.0021.

Calorimetry from 5 to 350 K (University of Michigan)

The Mark X cryostat and adiabatic method employed have been described [14]. A gold-plated copper calorimeter (W-139, which incorporates a gold-gasketed screw closure and copper vanes) with a volume of 22.72 cm^3 was used. Helium gas was added to the sample space (4.6 kPa at 300 K) to enhance thermal equilibration. The calorimeter was surrounded by a shield system provided with automatic temperature control. Temperatures were measured with a capsule-type, strain-free, platinum resistance thermometer (laboratory designation A-5), located in a central re-entrant well in the calorimeter. The programming, data logging and calorimetry were computerized, as described elsewhere [15].

Calorimetry from 300 to 1000 K (University of Oslo)

The calorimetric apparatus and measuring techniques have been described elsewhere [16]. The calorimeter was intermittently heated and surrounded by electrically heated and electronically controlled adiabatic shields. The substance was enclosed in an evacuated and sealed vitreous silica tube, with a volume of about 50 cm^3, which was tightly fitted into the silver calorimeter. A central well in the tube served for the heater and platinum resistance thermometer.

Calibrations and adjustments

The platinum resistance thermometer for the low-temperature calorimeter was calibrated by the U.S. National Bureau of Standards and that for the high-temperature calorimeter was calibrated locally, at the ice, steam, zinc and antimony points. Temperatures were judged to correspond to IPTS-68 to within 0.02 K from 4 to 350 K, to within 0.05 K from 350 to 900 K, and to within 0.1 K at 1000 K. All determinations of mass, electrical potential, resistance, etc. were measured with reference to instruments calibrated by the U.S. National Bureau of Standards.

TABLE 1

Measured specific heat capacity of tungsten carbide sample

T (K)	$10^3 C_{\mathrm p}$ (J K^{-1} g^{-1})	T (K)	$10^3 C_{\mathrm p}$ (J K^{-1} g^{-1})	T (K)	$10^3 C_{\mathrm p}$ (J K^{-1} g^{-1})	T (K)	$10^3 C_{\mathrm p}$ (J K^{-1} g^{-1})	T (K)	$10^3 C_{\mathrm p}$ (J K^{-1} g^{-1})
Subambient temperature determinations (University of Michigan)									
Series I		221.84	143.14	297.73	166.44	21.39	2.827	73.21	61.76
140.81 [a]	110.23	226.98	145.27	304.43	168.17	22.78	3.559	77.11	65.82
145.60	111.95	232.12	147.35	311.14	170.12	24.29	4.458	Series VI	
150.72	114.33	237.28	148.59	317.85	171.13	25.82	5.521	79.07	67.98
155.82	116.90	242.43	150.40	324.56	172.30	26.60	6.060	83.13	71.96
160.93	118.95	247.58	152.16	329.98	173.93	28.28	7.484	88.05	76.44
166.04	121.42	252.73	154.38	334.11	174.62	30.01	8.999	92.97	80.28
171.16	123.62	257.90	155.09	338.24	175.54	31.76	10.713	97.93	83.87
176.28	125.73	Series III		342.77	177.00	33.54 [a]	12.620	102.92	87.33
181.40	127.89	253.55	154.39	347.30	178.78	35.55	14.629	112.44	93.68
Series II		259.31	156.18	Series V		40.23	20.442	117.26	96.57
170.40	123.27	266.03	157.61	9.02	0.222	42.05	22.878	122.29 [a]	100.23
175.61	125.70	272.72	159.75	10.97 [a]	0.289	44.36	25.918	127.35	102.56
180.74	127.53	279.40	161.33	11.41 [a]	0.525	46.68	28.954	132.42	105.24
185.87	129.36	286.09	163.46	12.18	0.488	49.02	32.078	137.49	108.03
190.99	131.89	292.79	164.57	14.50 [a]	0.822	51.60	35.455	142.59 [a]	109.72
196.12	134.00	299.48	167.29	15.51 [a]	0.870	54.43	39.166	147.55 [a]	121.42
201.26	135.67	Series IV		16.50	1.133	57.27	42.960	152.71	115.68
206.41	137.40			17.63	1.409	60.13	46.516	157.85 [a]	119.35
211.54 [a]	140.17	284.27	163.17	18.88	1.795	63.02	50.22		
216.69	141.10	291.04	164.98	20.13	2.267	65.92	53.81		
						69.33	57.57		

Superambient temperature determinations (University of Oslo)

Series I				Series III					
346.43	177.1	292.03	164.6	311.58	168.8	491.66	198.7	711.22	214.9
358.55	179.6	301.74	167.1	318.59	171.6	500.18	199.5	720.11	214.7
368.60	181.5	311.38	169.6	325.55	173.3	508.69	200.2	729.05	214.8
378.61	183.3	320.94	171.9	332.49	174.8	517.22	201.8	738.03	215.4
388.59	185.1	330.44	174.1	339.41	176.4	525.77	202.2	747.05	215.4
398.54	186.8	339.87	175.1	346.32	177.9	534.33	202.9	756.13	215.8
408.48	188.3	349.26	178.2	353.20	179.4	542.90	203.7	765.25	216.6
418.41	189.8	358.51	180.1	360.06	180.8	551.50	204.5	774.26	216.5
428.33	191.2	367.92	181.8	366.91	182.1	560.13	204.6	783.21	216.4
438.24	192.6	377.20	183.6	373.75	183.4	568.81	205.4	792.19	216.8
448.15	193.7	386.46	184.1	380.58	184.7	577.51	205.8	801.12	218.6
458.05	194.9	395.69	186.7	387.40	185.4	586.25	205.8	809.84	217.2
467.96	196.0	404.96	188.0	394.21	186.9	595.02	206.6	818.69	215.8[a]
477.88	196.6	414.16	189.4	401.01	188.1	603.83	206.8	827.54	216.6[a]
487.94	198.0	423.34	190.6	407.81	189.0	612.66	207.8	836.47	213.6[a]
497.88	199.3	432.52	191.9	414.61	190.0	624.13	210.4	845.40	216.0[a]
507.80	200.1	441.69	192.9	421.41	191.0	632.80	210.8	854.52	213.6[a]
517.72	201.0	450.85	194.0	428.17	191.1	641.52	209.2	864.59	221.1
527.66	202.2	459.99	195.2	434.87	192.3	650.08	211.8	875.63	221.2
537.52	203.0	469.13	196.2	449.28	194.0	658.70	211.2	886.76	222.6
Series II		478.26	197.0	457.76	195.6	667.33	212.0	897.95	226.6[a]
272.31	158.2	487.40	198.0	466.22	196.7	676.01	211.4	910.28	222.1
282.24	161.7			474.70	196.8	684.72	213.4	923.39	223.2
				483.17	198.5	693.52	213.9	936.57	224.1
						702.37	213.5	949.89	225.8
								962.93	225.0
								976.24	224.6
								989.74	225.0

[a] Not used in final fitting.

The heat capacities of the empty calorimeters were determined in a separate series of experiments. They represented less than 35% of the total in the case of the low-temperature calorimeter, and about 60% in the case of the high-temperature calorimeter.

Small adjustments were applied for temperature excursions of the shields from the calorimeter temperature and for "zero drift" of the calorimeter temperature. Further small corrections were applied for differences in masses of the gold gasket, helium gas and Apiezon-T grease for the low-temperature calorimeter and for differences in mass of the vitreous silica containers for the high-temperature calorimeter. The mass of sample used was 195.92 g in the low-temperature calorimeter and 319.20 g in the high-temperature calorimeter. The buoyancy correction was made on the basis of an estimated density of 17.0 g cm^{-3}.

RESULTS

The experimental values of the specific heat capacity of the tungsten carbide are given in Table 1 in chronological order. Smoothed heat capacities were obtained by fitting one set of orthogonal polynomials below 50 K, one from 50 to 300 K and one from 300 to 1000 K. Up to 300 K, polynomials of order 9 were selected, and above 300 K of order 6. The resulting standard deviations in the three regions were 0.2%, 0.2% and 0.3%, respectively.

The smoothed specific heat capacity of the sample was corrected for the presence of 0.3310 g WC, 0.031 g Fe_3C and 0.0021 g elemental carbon. For WC, the results of Andon et al. [17] were used in the subambient temperature region. In the higher temperature region the heat capacity equation derived by Uhrenius [18] from the DSC results of Andon et al. [17] and the drop calorimetric results of Chang [19] and Levinson [20] was used:

$$C_p(\text{J K}^{-1}\ \text{mol}^{-1}) = 40.777 + 12.418 \times 10^{-3}(T/\text{K}) - 2.1146 \times 10^{-6}(T/\text{K})^2$$

$$- 761.9 \times 10^3(\text{K}/T)^2$$

The heat-capacity results of Seltz et al. [21] and Mazur and Zacharko [22] in the low-temperature region were bridged from 20 to 68 K by the Debye limiting equation, $C_p = aT^3$, with a evaluated from the average value at 15 and 20 K, and data between 35 and 65 K obtained from the equation [21]

$$C_p \approx C_v = 3D(360/T) + D(1000/T)$$

In the high-temperature region the heat capacity of Fe_3C was taken from the compilation by Hultgren et al. [23]. The uncombined carbon was corrected for with the use of published values for graphite [24,25].

TABLE 2

Thermodynamic properties of ditungsten carbide $W_2C_{0.833}$

T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	$S_m^{\ominus} - S_{m,0}^{\ominus}$ (J K^{-1} mol^{-1})	$H_m^{\ominus} - H_{m,0}^{\ominus}$ (J mol^{-1})	$-(G_m^{\ominus} - H_{m,0}^{\ominus})/T$ (J mol^{-1})
0	0	0	0	0
5	(0.025)	(0.015)	(0.033)	(0.008)
10	0.141	0.060	0.400	0.020
15	0.430	0.168	1.784	0.0495
20	1.082	0.367	5.309	0.1014
25	2.456	0.741	13.824	0.1882
30	4.552	1.365	31.079	0.3286
35	7.136	2.256	60.156	0.5371
40	9.946	3.391	102.81	0.8206
45	12.82	4.728	159.72	1.179
50	15.71	6.229	231.06	1.608
60	21.26	9.602	416.93	2.654
70	25.93	13.24	653.60	3.904
80	29.78	16.96	932.81	5.304
90	32.93	20.66	1246.9	6.806
100	35.51	24.27	1589.5	8.372
110	37.68	27.76	1955.8	9.978
120	39.56	31.12	2342.2	11.60
130	41.23	34.35	2746.3	13.23
140	42.76	37.46	3166.3	14.85
150	44.19	40.46	3601.1	16.46
160	45.54	43.36	4049.8	18.05
170	46.83	46.16	4511.7	19.62
180	48.05	48.87	4986.2	21.17
190	49.20	51.50	5472.4	22.70
200	50.28	54.05	5969.8	24.20
210	51.30	56.53	6477.8	25.68
220	52.26	58.94	6995.6	27.14
230	53.18	61.28	7522.9	28.57
240	54.08	63.56	8059.2	29.98
250	54.95	65.79	8604.3	31.37
260	55.80	67.96	9158.0	32.74
270	56.62	70.08	9720.2	34.08
280	57.42	72.15	10290	35.40
290	58.16	74.18	10868	36.70
298.15	58.66	75.80	11345	37.75
300	58.78	76.16	11453	37.99
310	59.45	78.10	12044	39.25
320	60.14	80.00	12642	40.49
330	60.82	81.86	13247	41.72
340	61.48	83.69	13858	42.93
350	62.13	85.48	14476	44.12
400	65.07	93.97	17658	49.83
450	67.46	101.78	20974	55.17
500	69.28	108.99	24395	60.20
550	70.65	115.66	27895	64.94

(continued)

TABLE 2 (continued)

T (K)	$C_{p,m}$ ($J\,K^{-1}\,mol^{-1}$)	$S_m^\ominus - S_{m,0}^\ominus$ ($J\,K^{-1}\,mol^{-1}$)	$H_m^\ominus - H_{m,0}^\ominus$ ($J\,mol^{-1}$)	$-(G_m^\ominus - H_{m,0}^\ominus)/T$ ($J\,mol^{-1}$)
600	71.71	121.85	31455	69.43
650	72.57	127.63	35063	73.68
700	73.32	133.03	38710	77.73
750	74.00	138.12	42394	81.59
800	74.63	142.91	46109	85.27
850	75.23	147.45	49856	88.80
900	75.84	151.77	53633	92.18
950	76.43	155.89	57440	95.42
1000	76.75	159.82	61270	98.55

$M(W_2C_{0.833}) = 377.71$ g mol^{-1}

Smoothed values of the heat capacity of $W_2C_{0.833}$ from the least-squares fitted polynomial expression, and derived values of the thermodynamic properties, are listed in Table 2 for the selected temperatures.

DISCUSSION

The present results may be useful for the analysis of the range of existence and the importance of carbon atom disorder for the thermodynamic stability of the W_2C phase. However, they are limited by the uncertainty concerning the stoichiometry of the W_2C_{1-x} phase, which determines the amount of that phase actually present in our sample. In view of this uncertainty we have not attempted to correct for impurities other than iron and elemental carbon.

The ε-Fe_2N-type structure of the W_2C_{1-x} phase contains as many octahedral interstices as there are metal atoms. They would all be equivalent if the tungsten atom coordinates for positions 6k in the space group $P\bar{3}1m$ were $\frac{1}{3}$, 0, $\frac{1}{4}$ etc. and $c/a = 1.633/3^{1/2} = 0.9428$. The actual c/a ratio is 0.9111 at ambient temperature and increases only slightly with temperature up to 1300 K according to the expansion study by Lönnberg [26]. The neutron diffraction work of Hårsta et al. [4] on a $W + C$ mixture heat treated at 1920 K for 30–50 h showed definite x and z displacements of the W atoms from the ideal positions. Related results were obtained by Lönnberg et al. [5] for material arc melted on a water-cooled copper hearth. In accordance with the observed W atom displacements, the smallest octahedral interstice (1b: 0, 0, $\frac{1}{2}$) in the cell containing six W atoms was found to be empty. 100% occupation of one of the remaining five interstices (1a: 0, 0, 0) was found by Hårsta et al. [4] for heat-treated material, while two twofold positions were only partially occupied, 65% in 2d: $\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{2}$; $\frac{2}{3}$, $\frac{1}{3}$, $\frac{1}{2}$ and 12% in 2c: $\frac{1}{3}$, $\frac{2}{3}$, 0; $\frac{2}{3}$, $\frac{1}{3}$, 0. For the arc-melted material, Lönnberg et al. [5] found only 82% occupancy of position 1a, 63% occupancy of 2d (practi-

cally unchanged) and 22% occupancy of 2c (increased). Thus, by more rapid quenching a higher configurational entropy is retained at ambient temperature.

For the material heat treated at 1920 K, the configurational entropy amounts to $0.68R$, and for the arc-melted material it amounts to $0.95R$. Complete randomization of the carbon atoms on the octahedral interstices gives $1.36R$ for $W_2C_{0.833}$. The transitions observed for the W_2C_{1-x} phase around 2300 and 2700 K are presumably related to the changes in carbon atom distribution.

Earlier values of the formation properties of tungsten carbides have been reviewed by Storms [27]. The recommended value of the enthalpy of formation, based on the results of McGraw et al. [28] and Mah [1], was $\Delta_f H^{\ominus}(WC, 298 \text{ K}) = -(40\,460 \pm 1700)$ J mol^{-1}. Later Gupta and Seigle [29] reported $\Delta_f H^{\ominus}(WC, 298 \text{ K}) = -(44\,400 \pm 800)$ J mol^{-1} from carbon activity measurements in the range 1150–1575 K. If we take $\Delta_f G^{\ominus}(WC, 1250 \text{ K}) = -(35\,900 \pm 400)$ J mol^{-1} from ref. 29 and the literature values for tungsten [30,31] and carbon [24,25] we derive $\Delta_f H^{\ominus}(WC, 298 \text{ K}) = -(41\,200 \pm 500)$ J mol^{-1}. From galvanic cell measurements with BaF_2–CaC_2 as electrolyte Coltters and Belton [32] presented two equations which give $\Delta_f G^{\ominus}(WC, 1000 \text{ K}) = -(44\,500 \pm 600)$ J mol^{-1}, and we thus derive $\Delta_f H^{\ominus}(WC, 298 \text{ K}) = -48\,800$ J mol^{-1}. The temperature dependence of the Gibbs energy of formation is of the opposite sign and of the order of 3 times larger than expected.

Gas equilibrium studies of the reaction

$$W(s) + 2CO(g) = WC(s) + CO_2(g)$$
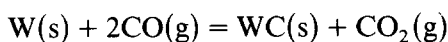
by Gleiser and Chipman [33] gave $\Delta_f G^{\ominus}(WC, 1250 \text{ K}) = -(34\,900 \pm 1300)$ J mol^{-1} and thus $\Delta_f H^{\ominus}(WC, 298 \text{ K}) = -(39\,700 \pm 1400)$ J mol^{-1}. Studies of the reaction

$$W(s) + CH_4(g) = WC(s) + 2H_2(g)$$
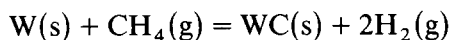
have been performed with variable success by Alekseev and Shvartsman [34], Orton [35] and Iwai et al. [36]. The latter researchers took care not to oxidize the tungsten, by keeping the moisture level sufficiently low, and were able to obtain reasonable results in the range 1173–1573 K. By using more recent values of the Gibbs energy of formation for $CH_4(g)$ than Iwai et al. [36], we find $\Delta_f G^{\ominus}(WC, 1250 \text{ K}) = -(35\,400 \pm 500)$ J mol^{-1} and thus $\Delta_f H^{\ominus}(WC, 298 \text{ K}) = -(40\,200 \pm 600)$ J mol^{-1}. The mean result of the above evaluations, excluding the results of Coltters and Belton [32], is $\Delta_f H^0(WC, 298 \text{ K}) = -(40\,400 \pm 800)$ J mol^{-1}.

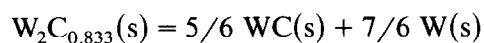For the W_2C_{1-x} phase the Gibbs energy of formation is fixed by the equilibrium reaction at about 1550 K

$$W_2C_{0.833}(s) = 5/6 \, WC(s) + 7/6 \, W(s)$$

TABLE 3

Molar enthalpy, entropy and Gibbs energy of formation of $W_2C_{0.833}$ and WC

T (K)	$M(W_2C_{0.833}) = 377.71$ g mol^{-1}			$M(WC) = 195.86$ g mol^{-1}		
	$\Delta_f H^{\ominus}$ (kJ mol^{-1})	$\Delta_f S^{\ominus}$ (J K^{-1} mol^{-1})	$\Delta_f G^{\ominus}$ (kJ mol^{-1})	$\Delta_f H^{\ominus}$ (kJ mol^{-1})	$\Delta_f S^{\ominus}$ (J K^{-1} mol^{-1})	$\Delta_f G^{\ominus}$ (kJ mol^{-1})
298.15	−13.41	5.75	−15.12	−40.40	−6.28	−38.53
300	−13.40	5.77	−15.13	−40.39	−6.26	−38.52
400	−12.96	7.02	−15.77	−40.00	−5.13	−37.95
500	−12.38	8.31	−16.53	−39.62	−4.28	−37.48
600	−11.80	9.37	−17.42	−39.34	−3.76	−37.08
700	−11.27	10.19	−18.40	−39.13	−3.44	−36.72
800	−10.78	10.85	−19.45	−38.95	−3.21	−36.39
900	−10.31	11.40	−20.57	−38.79	−3.02	−36.08
1000	−9.86	11.87	−21.73	−38.64	−2.85	−35.79
1100	(−9.46)	(12.24)	(−22.94)	−38.49	−2.71	−35.51
1200	(−9.13)	(12.54)	(−24.28)	−38.34	−2.58	−35.24
1300	(−8.86)	(12.75)	(−25.44)	−38.20	−2.46	−34.99
1400	(−8.64)	(12.92)	(−26.72)	−38.05	−2.36	−34.75
1500	(−8.46)	(13.04)	(−28.02)	−37.90	−2.25	−34.52
1550	(−8.38)	(13.10)	(−28.68)	−37.81	−2.20	−34.41
1600	(−8.30)	(13.14)	(−29.33)	−37.73	−2.14	−34.30
1700	(−8.18)	(13.22)	(−30.65)	−37.55	−2.03	−34.09
1800	(−8.08)	(13.28)	(−31.98)	−37.36	−1.93	−33.89
1900	(−8.01)	(13.31)	(−33.30)	−37.18	−1.83	−33.71
2000	(−7.98)	(13.32)	(−34.37)	−37.01	−1.74	−33.53

for the presently assumed composition of the W_2C_{1-x} phase. In addition we have the result of Mah [1], $\Delta_f H^{\ominus}(W_2C, 298$ K$) = -(26.4 \pm 2.5)$ kJ mol^{-1}, which can be combined with the present data when extrapolated to 1550 K. We have done so by assuming a linear heat capacity increase for $W_2C_{0.833}$ from 76.75 J K^{-1} mol^{-1} at 1000 K to 82 J K^{-1} mol^{-1} at 2000 K. The results are, however, not mutually consistent. Thus, when the equilibrium reaction is combined with our results for $W_2C_{0.833}$ and the formation results for WC as given in Table 3, we find $\Delta_f H^{\ominus}(W_2C_{0.833}, 298$ K$) = -13.4$ kJ mol^{-1}. The assumption of configurational zero point entropy in $W_2C_{0.833}$, corresponding to the results of Hårsta et al. [4], would increase the disagreement with Mah's determination by 8.8 kJ mol^{-1}. We therefore retain the Gibbs energy values for $W_2C_{0.833}$ in Table 2 and give the resulting formation values in Table 3. This assumption means, however, that some disordering of the carbon atoms must take place in the range 1550–1900 K.

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