

Thermodynamic Properties of Hafnium

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New enthalpy measurements above 2000 K have resulted in a complete reassessment and revision of the high temperature thermodynamic properties of hafnium. Values have been assessed to 4900 K and include a selected enthalpy of sublimation at 298.15 K of 621 ± 5 kJ/mol and a derived boiling point of 4850 K at one atmosphere pressure. A comparison is given between selected properties of the Group 4 elements to consider periodic trends.

Keywords gas, hafnium, liquid, solid, thermodynamic properties

1. Introduction

Previous reviews on hafnium were by Hultgren et al.,^[1] Spencer,^[2] Gurvich et al.^[3] and JANAF^[4] whilst Onufriev et al.^[5] reviewed values for the alpha phase. A further review is justified by including new drop calorimetry measurements above 2000 K determined by Rösner-Kuhn et al.^[6] so that definite values can be calculated for the thermodynamic properties of the beta and liquid phases where previously only estimated values were available. As with zirconium, one of the major problems in carrying out experiments on hafnium is the avoidance of oxidation which could explain the rejection of a marked number of transition and melting points determinations as given in Tables 9 and 11 and the significant departure of specific heat and enthalpy values from selected values as given in Tables 12 and 13. A further complication for hafnium is that nearly all measurements were carried out on samples containing zirconium. Specific heat and enthalpy values were corrected using the Kopp-Neumann Rule as described in “[Correction of Specific Heat and Enthalpy Values for Zirconium Content](#)” section but this does introduce an increased uncertainty since this very often required an extrapolation of the zirconium values beyond their limits of phase stability.

From the evaluations in Tables 8 and 10, 2016 ± 20 K is selected for the transformation from the hexagonal close-packed alpha phase to the body-centred cubic beta phase and 2502 ± 20 K for the melting point. Wherever possible values have been corrected to the ITS-90 temperature scale^[7,8] and to the currently accepted atomic weight of 178.49 ± 0.02 .^[9]

2. Alpha Phase

Roberts^[10] selects 0.128 K as the superconducting temperature but there does not appear to be any specific

heat measurements in the superconducting region. Therefore only the normal state is considered with the following values obtained for the electronic coefficient (γ) and the limiting Debye temperature (Θ_D) as given in Table 1.

The selected values were combined with the specific heat measurements of Westrum^[16] (5.8–349 K) to give values covering the range up to 298.15 K as given in Table 17. Additional specific heat determinations in the low temperature region by Cristescu and Simon^[17] (13–210 K), Wolcott^[11,12] (1.2–20 K) and by Burk et al.^[18] (10–200 K) are compared with the selected values in Table 12.

In the high temperature region of the alpha phase, enthalpy measurements of Hawkins et al.^[19] (339–1348 K) and Kats et al.^[20] (1220–2001 K in the alpha phase) agree closely and also show a natural continuity from the low temperature data. The measurements of Hawkins et al. had already been corrected for zirconium content and were therefore only corrected for temperature scale (from IPTS-48 to ITS-90) but although the measurements of Kats et al. were on samples containing 0.78 wt.% zirconium no corrections were applied because of the very large extrapolation which would have been required for the alpha zirconium values. The combined values were fitted to the following equation with an overall accuracy of ± 173 J/mol (1.33%):

$$H_T^\circ - H_{298.15}^\circ (\text{J/mol}) = 23.9215 T + 3.50817 \times 10^{-3} T^2 + 28746.4/T - 7540.46 \quad (\text{Eq 1})$$

The high temperature thermodynamic properties of all of the condensed phases are given in Table 19. The deviations of other specific heat and enthalpy alpha phase measurements from the selected values are given in Tables 12 and 13 respectively except for the specific heat measurements of Rumyantsev et al.^[21] (1000–1900 K) which were given only in the form of a small graph.

3. Beta Phase

New drop calorimetry enthalpy measurements of Rösner-Kuhn et al.^[6] (2096–2455 K in the beta phase) were

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Table 1 Low Temperature Specific Heat Coefficients

Author	Ref	Temperature range, K	γ , mJ/mol K ²	Θ_D , K
Wolcott	[11,12]	1.2-20	2.64	261
Kneip et al.	[13]	1.1-4.5	2.17	251.5
Betterton and Scarbrough	[14]	1.1-4.2	2.15	252.2
Collings and Ho	[15]	1.5-6	2.15	248
Selected			2.15	250

Table 2 Measured enthalpies of transition for hafnium

Authors	Ref	$\Delta H_{\alpha\beta}^\circ$, J/mol
Matynyuk and Tsapkov	[23]	5200
Peletskii and Druzhinin	[24]	5176
Cezairlyan and McClure	[25]	5908
Kats et al	[20]	3376

corrected for 3 wt.% zirconium content using the values for beta zirconium selected by Arblaster^[22] and fitted to the following equation with an overall accuracy of ± 945 J/mol (1.37%):

$$H_T^\circ - H_{298.15}^\circ (\text{J/mol}) = 37.1520 T - 14900.68 \quad (\text{Eq 2})$$

The derived enthalpy of transition is 5040 ± 960 J/mol which can be compared with original experimental values given in Table 2. The derived specific heat is 37.15 ± 1.45 J/mol K.

The highly discrepant value obtained by Kats et al. is the main reason why their beta phase measurements were not included in the evaluation. The deviations of other specific heat and enthalpy beta phase measurements from the selected values are given in Tables 12 and 13 respectively.

4. Liquid

New drop calorimetry enthalpy measurements of Rösner-Kuhn et al.^[6] (2339-2988 K in the liquid phase) were corrected for 3 wt.% zirconium content using the values for liquid zirconium selected by Arblaster^[22] and fitted to the following equation with an overall accuracy of ± 1691 J/mol (1.59%):

$$H_T^\circ - H_{298.15}^\circ (\text{J/mol}) = 36.2590 T + 7218.85 \quad (\text{Eq 3})$$

The derived enthalpy of fusion is 19885 ± 1937 J/mol which can be compared with original experimental values given in Table 3. The derived entropy of fusion is 7.95 ± 0.77 J/mol K and the derived specific heat is 36.26 ± 1.76 J/mol K

Table 3 Measured enthalpies of fusion for hafnium

Authors	Ref	ΔH_m° , J/mol	Notes
Ackermann and Rauh	[26]	25,941	(a)
Rösner-Kuhn et al.	[6]	20,247	(b)
Paradis et al.	[27]	14,623	
Korobenko et al.	[28]	16,064	
Cagran et al.	[29]	14,690	

(a) From vapour pressure measurements
(b) This is the original value uncorrected for zirconium content and based on a melting point of 2471 K

In addition, from entropy trends, Chekhovskoi and Kats^[30] gives an equation which is equivalent to an entropy of fusion of 10.23 J/mol K for hafnium, equivalent to an enthalpy of fusion of 25,600 J/mol whilst Rösner-Kuhn et al.^[31] estimates an entropy of fusion of 8.30 J/mol K equivalent to an enthalpy of fusion of 20,770 J/mol. The deviations of other specific heat and enthalpy liquid phase measurements from the selected values are given in Tables 12 and 13 respectively.

5. Gas Phase

Values are based on one bar standard state pressure and are calculated from the 466 levels given in Table 4 using the method of Kolsky et al.^[32] and the 2010 Fundamental Constants^[33,34] Thermodynamic properties of the monoatomic gas phase are given in Table 20 and vapour pressure data in Table 21.

6. Enthalpy of Sublimation

For values given in Table 5 in the form of the Clausius-Clapeyron equation a “pseudo” Third Law value was calculated by evaluating the enthalpy of sublimation at the temperature extremes and averaging. The values obtained give a reasonable estimate compared to the values which would have been obtained if all of the data had been available. Because of a lack of detail as to what temperature scales were used in the measurements then no attempt was made to correct the values to ITS-90 from would be contemporary temperature scales.

Because of the close agreement between derived Third Law enthalpies of sublimation the measurements of Kibler et al.^[39], Ackermann and Rauh^[26] and Koch et al.^[42] were accepted and averaged, with the assigned accuracy taking into account differences between $\Delta H(\text{II})$ and $\Delta H(\text{III})$ values. Because the other measurements showed poor agreement between $\Delta H(\text{II})$ and $\Delta H(\text{III})$ values they were rejected.

7. Vapour Pressure

The vapour pressure curve for the alpha phase as given in Table 6 was evaluated from free energy functions for the solid and the gas at 25 K intervals from 1400 to 2000 K and the transition temperature. For the beta phase the vapour pressure curve was evaluated at 25 K intervals from 2025 to 2500 K and the transition temperature and melting point and for the liquid at 50 K intervals from 2550 to 4900 K and the melting point.

$$\ln(p, \text{ bar}) = A + B/T + C \ln(T) + D T + E T^2$$

8. Selected Condensed Phase Values at 298.15 K

All reviews as summarised in Table 7 are essentially based on the low temperature specific heat measurements of

Table 4 The number of energy levels for hafnium

Authors	Ref	Number of levels
Meggers and Moore	[35]	320
Wyart	[36]	12
Matsuoka and Hasegawa	[37]	134

Table 5 Enthalpy of Sublimation at 298.15 K

Authors	Ref	Method	Range	$\Delta H(\text{II}),$ kJ/mol	$\Delta H(\text{III}),$ kJ/mol
Panish and Reif	[38]	L	2066-2274	683 ± 66	609.6 ± 2.3
Kibler et al	[39]	L	2035-2325	613 ± 9	619.9 ± 0.4
Blackburn	[40]	L	2200-2363	537 ± 24	624.8 ± 1.3
Trulson et al.	[41]	KE	2000-2273	661 ± 30	631.5 ± 0.7
Ackermann and Rauh	[26]	EMS	1945-2200 (s)	624	621.2 ± 0.1
Koch et al.	[42]	L	2230-2500 (l) 2500-2810	619 586 ± 14	620.8 ± 0.1 621.8 ± 0.7
Selected					621 ± 5
Methods					
L Langmuir, KE Knudsen effusion, EMS Effusion mass spectrometry					

Table 6 Vapour pressure equations

Phase	Range, K	A	B	C	D	E
Alpha	1400-2016	24.22018	-74958.60	-1.078723	-4.69052 × 10 ⁻⁴	-6.89373 × 10 ⁻⁸
Beta	2016-2502	23.91155	-74700.97	-0.9828036	5.77596 × 10 ⁻⁵	0
Liquid	2502-4900	17.01326	-71458.19	-0.1966858	-2.03025 × 10 ⁻⁴	1.65215 × 10 ⁻⁸

Westrum^[16] either as a direct acceptance or as an evaluation and therefore the selected value agree closely.

9. Selection of the Transition Temperature and the Melting Point

Transition temperatures and melting points were corrected for atomic percent zirconium content based on the hafnium-zirconium binary system.^[43] Separate correction values obtained for the solidus and liquidus equations were averaged as were values obtained for the alpha-beta and beta-alpha transition equations. Because of the provisional nature of the phase diagram, samples with high zirconium contents requiring large temperature corrections were not included in evaluating the selected values. Also because of a general lack of knowledge as to what temperature scales were used then only the selected values were corrected to ITS-90. Transition temperatures included in the evaluation are given in Table 8 and those not included in Table 9. Melting points included in the evaluation are included in Table 10 and those not included in Table 11.

10. Correction of Specific Heat and Enthalpy Values for Zirconium Content

Values for specific heat are reduced to J/kg K and for enthalpy to J/kg. Using the Kopp-Neumann Rule;

$$C_p^\circ \text{Hf} = (C_p^\circ \text{alloy} - X C_p^\circ \text{Zr}) / (1 - X)$$

$$(H_T^\circ - H_{298.15}^\circ) \text{Hf} = [(H_T^\circ - H_{298.15}^\circ) \text{alloy} - X(H_T^\circ - H_{298.15}^\circ) \text{Zr}] / (1 - X)$$

where X is the mass fraction of zirconium and C_p° and $(H_T^\circ - H_{298.15}^\circ)$ for zirconium are evaluated at the same experimental temperature as that of the alloy

11. A Comparison Between Experimental Values and the Selected Values

Deviations of specific heat measurements from the selected values are given in Table 12 and deviations of enthalpy values from the selected values are given in Table 13.

Table 7 A comparison of selected condensed phase values at 298.15 K

Authors	Ref	C_p° , J/mol K	$H_{298.15}^\circ - H_0^\circ$, J/mol	S° , J/mol K
Westrum	[16]	25.69	5845	43.56
Hultgren et al	[1]	25.73	5845	43.56
Spencer	[2]	25.72	...	43.51
Gurvich et al	[3]	25.69	5845	43.56
JANAF	[4]	25.69	5842	43.56
This Work	...	25.69	5845	43.56

Table 8 Determinations of the transition temperatures included in the evaluation

Author	Ref	At.% Zr	Original value	Corrected value	Notes
Deardorff and Kato	[44, 45]	0	2019 ± 20	2021	(a), (b)
Krikorian and Wallace	[46]	0	2008 ± 14	2010	(b)
Selected				2016 ± 20	

(a) Originally given as brightness temperature 1868 K. Corrected to 2023 K on IPTS-48 using an emissivity correction of $\varepsilon = 0.40$. Further corrected downwards by 4 K by Krikorian and Wallace^[45] to account for 200 ppm oxygen in the sample

(b) Assumed to be initially on temperature scale IPTS-1948

Table 9 Determinations of the transition temperatures not included in the evaluation

Author	Ref	At.% Zr	Original value	Corrected value	Notes
Zwikker	[47]	?	1600-1900	1750	(a)
Duwez	[48]	?	1583 ± 10	1583	(b)
McGreary	[49]	?	1933	1933	
Fast	[50]	5.7	1980-2100	2082	(c)
Gibson et al.	[51]	0.02	2008	2008	
Peterson and Beernsten	[52]	0.06	1963-2093	2028	
Taylor et al.	[53]	4.4	2223	2255	
Ross and Hume-Rothery	[54]	3.1	2233-2263	2271	
Giessen et al.	[55]	4.4	2148 ± 20	2180	
Giessen et al.	[56]	4.4	1988 ± 15	2020	
Siemens et al.	[57]	3.5	2013 ± 20	2038	
Bedford	[58]	4.7	2027	2061	(d)
Domagala and Ruh	[59]	3.3	2048 ± 25	2072	
Romans et al.	[60]	2.9	2025	2046	
Heetderks et al.	[61]	4.0	2113 ± 25	2113	(e)
Rudy	[62]	4.0	2068 ± 35	2098	
Bates and Barnes	[63]	6.8	2030	2080	
Rudy and Windisch	[64]	0.03	2043 ± 25	2043	
		2.6	2043 ± 25	2062	
Peletskii and Druzhinin	[24]	1.3	1970 ± 5	1979	
Carlson et al	[65]	6.3	1990-2003	2042	
Cezairliyan and McClure	[25]	5.9	2012 ± 10	2056	
Rösner-Kune et al.	[6]	5.7	2012	2054	

(a) Originally given as brightness temperature 1500-1760 K. Corrected to 1600-1900 K on IPTS-48 using emissivity correction $\varepsilon = 0.40$ at wavelength 660 nm

(b) Russell^[66] estimated 6% Zr from the reported lattice parameters

(c) Originally given as brightness temperature 1830-1930 K. Corrected to 1960-2075 K on IPTS-48 using emissivity correction $\varepsilon = 0.45$ at wavelength 650 nm. Further corrected to 1980-2100 K using emissivity correction $\varepsilon = 0.40$

(d) Originally given as brightness temperature 1870 K. Corrected to 2027 K on IPTS-48 using emissivity correction $\varepsilon = 0.40$ at wavelength 650 nm

(e) Published value was already corrected for zirconium content

Table 10 Determinations of the melting points included in the evaluation

Author	Ref	At.% Zr	Original value	Corrected value	Notes
Deardorff and Hayes	[67]	0.02	2495 ± 30	2498	(a)
Krikorian and Wallace	[46]	0	2503 ± 20	2506	(a)
Rudy and Windisch	[64]	0.03	2491 ± 6	2494	(a), (b)
Garg and Ackermann	[68]	< 0.01	2501 ± 3	2500	(c)
Hiernaut et al.	[69]	< 0.2	2512	2511	(c)
Selected				2502 ± 20	

(a) Original temperature scale assumed to be IPTS-1948

(b) A second sample containing 2.6 at.% Zr gave the same initial result

(c) Original temperature scale IPTS-68

Table 11 Determinations of the melting points not included in the evaluation

Author	Ref	At.% Zr	Original value	Corrected value	Notes
De Boer and Fast	[70]	4.8	2480	2509	
Skinner et al.	[71]	?	2498	2498	
Litton	[72]	1.5	2403 ± 15	2413	
Adenstadt	[73]	?	2248	2248	
Spedding	[74]	?	2508 ± 5	2508	
Carlson et al.	[75]	<0.02	2508	2508	(a)
		<0.02	2423	2423	(a)
Peterson and Beernsten	[52]	0.06	2463	2463	
Grigorovich	[76]	?	2116	2116	
Taylor et al.	[53]	4.4	2463	2490	
Giessen et al.	[55]	4.4	2505 ± 35	2532	
Rudy and Stecher	[77]	4.2	2443 ± 20	2469	
Siemans et al.	[57]	3.5	2463 ± 20	2485	
Sara	[78]	4.8	2475-2485	2510	
Rudy	[62]	4.0	2491 ± 6	2516	
Deardorff et al.	[79]	3.1	2463 ± 15	2482	
Ackermann and Rauh	[80]	1.4	2467 ± 4	2476	
Cezairliyan and McClure	[81]	5.9	2471	2507	
Rösner-Kuhn et al.	[6]	5.7	2471	2506	

(a) The first sample was sponge and the second sample was an arc melted crystal

12. A Comparison Between the Present Evaluation and Previous Reviews

The boiling point calculated from the selected values of Gurvich et al.^[3] at 4973 K at one atmosphere pressure is 123 K higher than the presently selected value of 4850 K whilst the boiling point given by JANAF^[4] as 4964 K at one bar pressure is 119 K higher than the selected value of 4845 K. Since enthalpies of sublimation and the calculated free energy functions of the gas phase are similar in all three

reviews then the differences are due to differences between the estimated values for the condensed phases in the previous reviews compared to the experimental values used in the present review. In the case of Gurvich et al. they estimated an enthalpy of fusion 6 kJ/mol higher than the present value and a specific heat for the liquid 8 J/mol K higher whilst JANAF estimated an enthalpy of fusion 9 kJ/mol higher although the selected specific heat of the liquid is only 1.5 J/mol K higher. However the result is that at 4900 K the free energy function of the liquid phase from the evaluation of Gurvich et al. is

Table 12 Deviations of Specific Heat Measurements

Authors	Ref	Range, K	Deviations
Cristescu and Simon	[17]	13-210	Trends from initially 65% low to 180% high at 75 K then falls to 2.5% high at 210 K
Wolcott	[11,12]	1.3-20.2	Initially 5.6% high at 5 K increasing to 11.3% high at 8 K then decreasing to 3.9% high at 13 K before averaging 6.3% high above 17 K
Burk	[18]	10-200	Above 20 K trends to 5.4% high at 100 K then decreases to 1.2% high at 200 K
Milošević and Maglič	[82]	294-2336	Trends to 2.5% high at 1300 K falling to 1.6% high at 1921 K. Interval 1971-2071 K is not considered because of a rapid increase in specific heat due to the alpha-beta transition. At 2121 K and above in the beta region deviations average to 7.7% low
Peletskii and Druzhinin	[24]	1400-2150	In alpha region trends from 2.1% high at 1450 K to 3.9% low at 2050 K. In beta region (2100-2150 K) averages 12.3% low
Filippov and Yurchak	[83,84]	1100-2100	In alpha region averages 9.1% high and in beta region (at 2100 K) 1.9% high
Arutyunov et al	[85]	1100-2050	In alpha region averages 9.1% high and in beta region (at 2050 K) 1.4% high
Cezairliyan and McClure	[86]	1500-2400	In alpha region averages 1.5% high and in beta region (2200-2400 K) trends from 8.2% low to 2.3% low
Paradis et al	[27]	2250-2650	In liquid region trends 8.1% low to 7.1% low
Korobenko et al	[28]	2504-5000	In liquid region trends 18% high to 51% high

Table 13 Deviations of Enthalpy Measurements

Authors	Ref	Range, K	Deviations
Adenstadt	[76]	298-373	0.7% high at 373 K
Fieldhouse and Lang	[87]	534-1884	Scattering 9.1% low to 2.3% high below 1200 K. Trending 3.2% high to 6.9% high above 1200 K
Goluvin and Maslennikova	[88]	551-1334	First sample trends 4.1% low to 0.5% high (652-1299 K). Second sample scatters 9.8% low to 5.7% high (595-1334 K)
Kats et al.	[20]	1220-2349	In beta region (2127-2349 K) averages 3.7% low
Cagran et al.	[29]	1858-3500	Measurements 1858-2146 K rejected by the authors. Others measurements after correction for 3% Zr content trend 3.1% low to 1.4% low in the beta region (2200-2471 K) and 7.1% low to 1.8% high in the liquid region (2471-3500 K)

Table 14 A comparison of the properties of the group 4 elements

Property	Ti ^[88]	Zr ^[22]	Hf This work
Enthalpy $H_{298.15}^{\circ}-H_0^{\circ}$ J/mol	4822	5557	5845
Entropy $S_{298.15}^{\circ}$ J/mol K	30.686	39.149	43.561
Enthalpy of sublimation $\Delta H_{298.15}$ kJ/mol	472.6	600	621
Normal boiling point K	3637	4640	4850
Specific heat of the liquid C_p° J/mol K	46.29	39.92	36.26
Transition temperature $T_{\alpha\beta}$ K	1166	1139	2016
Melting point T_M K	1945	2127	2502
Ratio $T_{\alpha\beta}/T_M$	0.5995	0.5355	0.8058
Enthalpy of transition $\Delta H_{\alpha\beta}$ J/mol	4170	4089	5040
Enthalpy of fusion ΔH_M J/mol	14,550	15,600	19,885
Entropy of transition $S_{\alpha\beta}^{\circ}$ J/mol K	3.58	3.59	2.50
Entropy of fusion S_M° J/mol K	7.48	7.33	7.95
Entropy summation $S_{\alpha\beta}^{\circ} + S_M^{\circ}$ J/mol K	11.06	10.92	10.45

Table 15 Specific heat, enthalpy and entropy equations above 298.15 K

Alpha: 298.15-2016 K
 C_p° (J/mol K) = 23.9215 + 7.01634 × 10⁻³ T - 28746.4/T²
 $H_T^{\circ} - H_{298.15}^{\circ}$ (J/mol) = 23.9215 T + 3.50817 × 10⁻³ T² + 28746.4/T - 7540.46
 S_T° (J/mol K) = 23.9215 ln(T) + 7.01634 × 10⁻³ T + 14373.2/T² - 94.9877

Beta: 2016-2502 K
 C_p° (J/mol K) = 37.1520
 $H_T^{\circ} - H_{298.15}^{\circ}$ (J/mol) = 37.1520 T - 14900.68
 S_T° (J/mol K) = 37.1520 ln(T) - 179.0084

Liquid: 2502-4900 K
 C_p° (J/mol K) = 36.2590
 $H_T^{\circ} - H_{298.15}^{\circ}$ (J/mol) = 36.2590 T + 7218.85
 S_T° (J/mol K) = 36.2590 ln(T) - 164.0730

Table 16 Free energy equations above 298.15 K

Solid alpha: 298.15-2016 K
 $G_T^{\circ} - H_{298.15}^{\circ}$ (J/mol) = 118.9092 T - 3.50817 × 10⁻³ T² + 14373.2/T - 23.9215 T ln(T) - 7540.46

Solid beta: 2016-2502 K
 $G_T^{\circ} - H_{298.15}^{\circ}$ (J/mol) = 216.1604 T - 37.1520 ln(T) - 14900.68

Liquid: 2502-4900 K
 $G_T^{\circ} - H_{298.15}^{\circ}$ (J/mol) = 200.3320 T - 36.2590 T ln(T) + 7218.85

Table 17 Transition values involved with the free energy equations

Transition	T, K	ΔH , J/mol	ΔS , J/mol K
Alpha-Beta	2016.00	5040.106	2.5001
Fusion	2502.00	19885.244	7.9477

Table 18 Low temperature thermodynamic data—condensed phases

T, K	C_p° , J/mol K	$H_T^{\circ} - H_0^{\circ}$, J/mol	S_T° , J/mol K	$-(G_T^{\circ} - H_0^{\circ})/T$, J/mol K
5	0.0263	0.0463	0.0159	0.00667
10	0.165	0.440	0.0654	0.0214
15	0.658	2.297	0.209	0.0562
20	1.699	7.944	0.527	0.130
25	3.234	20.11	1.064	0.259
30	5.053	40.75	1.811	0.453
35	6.965	70.79	2.734	0.911
40	8.833	110.3	3.787	1.029
45	10.573	158.9	4.929	1.398
50	12.157	215.8	6.126	1.811
60	14.827	351.2	8.587	2.734
70	16.829	510.0	11.031	3.746
80	18.399	686.2	13.383	4.805
90	19.658	876.9	15.627	5.884
100	20.577	1078	17.748	6.965
110	21.329	1288	19.745	8.037
120	21.955	1504	21.629	9.092
130	22.474	1727	23.407	10.125
140	22.906	1954	25.089	11.135
150	23.265	2184	26.682	12.119
160	23.566	2419	28.194	13.076
170	23.821	2656	29.630	14.008
180	24.041	2895	30.998	14.914
190	24.236	3136	32.303	15.796
200	24.412	3380	33.551	16.652
210	24.576	3625	34.746	17.486
220	24.732	3871	35.893	18.296
230	24.882	4119	36.995	19.086
240	25.026	4369	38.058	19.854
250	25.163	4620	39.082	20.603
260	25.291	4872	40.071	21.333
270	25.405	5125	41.028	22.045
280	25.499	5380	41.954	22.739
290	25.604	5636	42.850	23.417
298.15	25.690	5845	43.561	23.958

Table 19 High temperature thermodynamic data—condensed phases

T, K	C_p° , J/mol K	$H_T^\circ - H_{298.15}^\circ$, J/mol	S_T° , J/mol K	$-(G_T^\circ - H_{298.15}^\circ)/T$, J/mol K
Alpha				
298.15	25.690	0	43.561	43.561
300	25.707	47.5	43.720	43.561
400	26.548	2661	51.233	44.580
500	27.315	5,355	57.241	46.531
600	28.051	8123	62.286	48.747
700	28.774	10,965	66.665	51.001
800	29.490	13,878	70.554	53.206
900	30.201	16,862	74.068	55.332
1000	30.909	19,918	77.287	57.369
1100	31.616	23,044	80.266	59.317
1200	32.321	26,241	83.047	61.180
1300	33.026	29,508	85.662	62.963
1400	33.730	32,846	88.135	64.674
1500	34.433	36,254	90.486	66.317
1600	35.136	39,733	92.731	67.898
1700	35.839	43,282	94.882	69.423
1800	36.542	46,901	96.951	70.895
1900	37.245	50,590	98.945	72.319
2000	37.947	54,350	100.874	73.699
2016	38.059	54,958	101.176	73.916
Beta				
2016	37.152	59,998	103.676	73.916
2100	37.152	63,119	105.193	75.137
2200	37.152	66,834	106.921	76.542
2300	37.152	70,549	108.573	77.899
2400	37.152	74,264	110.154	79.211
2500	37.152	77,979	111.671	80.479
2502	37.152	78,054	111.700	80.504
Liquid				
2502	36.259	97,939	119.648	80.504
2600	36.259	101,492	121.041	82.006
2700	36.259	105,118	122.410	83.477
2800	36.259	108,744	123.728	84.891
2900	36.259	112,370	125.001	86.252
3000	36.259	115,996	126.230	87.565
3100	36.259	119,622	127.419	88.831
3200	36.259	123,248	128.570	90.055
3300	36.259	126,874	129.686	91.239
3400	36.259	130,499	130.768	92.386
3500	36.259	134,125	131.819	93.498
3600	36.259	137,751	132.841	94.576
3700	36.259	141,377	133.834	95.624
3800	36.259	145,003	134.801	96.642
3900	36.259	148,629	135.743	97.633
4000	36.259	152,255	136.661	98.597
4100	36.259	155,881	137.556	99.537
4200	36.259	159,507	138.430	100.452
4300	36.259	163,133	139.283	101.345
4400	36.259	166,758	140.117	102.217
4500	36.259	170,384	140.932	103.068
4600	36.259	174,010	141.729	103.900

Table 19 continued

T, K	C_p° , J/mol K	$H_T^\circ - H_{298.15}^\circ$, J/mol	S_T° , J/mol K	$-(G_T^\circ - H_{298.15}^\circ)/T$, J/mol K
4700	36.259	177,636	142.508	104.713
4800	36.259	181,262	143.272	105.509
4900	36.259	184,888	144.019	106.287

2.55 J/mol K higher than the present value and from the evaluation of JANAF 3.33 J/mol K higher. The effect on the net free energy function is to lower the vapour pressure curve in both cases and lead to higher boiling points. It is therefore suggested that the much lower boiling point obtained in the present review is due to the use of actual experimental values.

13. A Comparison Between Group 4 Element Properties

The present evaluation for hafnium is combined with reviews on titanium by Desai^[89] and on zirconium by Arblaster^[22] and are summarised in Table 14. Since the three elements have similar electronic structures with the same sequencing of electrons in the outermost shells: Ti 3 s² (10) 4 s² (2); Zr 4 s² (10) 5 s² (2); Hf 5 s² (10) 6 s² (2) then this would suggest that the properties of hafnium could have been predicted. However this does not appear to be the case. The crystallographic and melting transition properties of titanium and zirconium can generally be considered to be similar but the values for hafnium show distinct differences mainly due to the marked increase in the stability of the hexagonal close-packed alpha phase. However in the case of the coherency of the condensed phases the enthalpy of sublimation and boiling points of zirconium and hafnium are very close whilst the values for titanium are different.

14. A Summary of Representative Equations

Specific heat, enthalpy and entropy equations above 298.15 K are given in Table 15. Free energy equations above 298.15 K in Table 16 and transition values involved in the free energy equations in Table 17.

15. Thermodynamic Tables

Low temperature thermodynamic data for the condensed phases is given in Table 18 and high temperature thermodynamic data for the condensed phases in Table 19. Thermodynamic properties for the gas phase are given in Table 20 and vapour pressure data in Table 21.

Table 20 Thermodynamic properties of the gas phase

T, K	C_p° , J/mol K	$H^\circ_T - H^\circ_{298.15}$, J/mol	S°_T , J/mol K	$-(G^\circ_T - H^\circ_{298.15})/T$, J/mol K
298.15	20.804	0	186.898	186.898
300	20.805	30.5	187.027	186.899
400	20.961	2125	193.028	187.716
500	21.397	4240	197.747	189.266
600	22.113	6414	201.707	191.018
700	23.012	8669	205.182	192.798
800	23.991	11,019	208.318	194.545
900	24.978	13,467	211.201	196.238
1000	25.926	16,013	213.882	197.869
1100	26.806	18,650	216.395	199.441
1200	27.603	21,371	218.763	200.953
1300	28.306	24,168	221.000	202.410
1400	28.912	27,029	223.121	203.814
1500	29.424	29,947	225.134	205.169
1600	29.847	32,911	227.047	206.477
1700	30.191	35,914	228.867	207.741
1800	30.466	38,947	230.600	208.963
1900	30.683	42,005	232.254	210.146
2000	30.853	45,082	233.832	211.291
2016	30.877	45,576	234.078	211.471
2100	30.989	48,174	235.341	212.401
2200	31.099	51,279	236.785	213.476
2300	31.193	54,394	238.169	214.520
2400	31.278	57,517	239.499	215.533
2500	31.362	60,649	240.777	216.518
2502	31.364	60,712	240.802	216.537
2600	31.449	63,790	242.009	217.475
2700	31.545	66,939	243.198	218.405
2800	31.652	70,099	244.347	219.311
2900	31.775	73,270	245.460	220.194
3000	31.914	76,455	246.539	221.054
3100	32.071	79,654	247.588	221.893
3200	32.247	82,869	248.609	222.712
3300	32.443	86,104	249.604	223.512
3400	32.658	89,359	250.576	224.294
3500	32.893	92,636	251.526	225.059
3600	33.146	95,938	252.456	225.807
3700	33.418	99,266	253.368	226.539
3800	33.706	10,2622	254.263	227.257
3900	34.010	10,6008	255.142	227.961
4000	34.328	109425	256.007	228.651
4100	34.660	11,2874	256.859	229.329
4200	35.004	11,6357	257.699	229.994
4300	35.357	11,9875	258.526	230.648
4400	35.720	12,3429	259.343	231.291
4500	36.090	12,7019	260.150	231.924
4600	36.467	13,0647	260.947	232.546
4700	36.847	13,4313	261.736	233.159
4800	37.231	13,8017	262.516	233.762
4900	37.617	14,1759	263.287	234.357

$H^\circ_{298.15} - H_0^\circ = 6197.8 \text{ J/mol}$

Table 21 Vapour pressure

T, K	p bar	ΔG_T , J/mol	ΔH_T , J/mol	p bar	T, K
298.15	4.92×10^{-102}	578,264	621,000	10^{-15}	1457
300	2.31×10^{-101}	577,999	620,983	10^{-14}	1527
400	2.42×10^{-74}	563,746	620,464	10^{-13}	1603
500	3.81×10^{-58}	549,622	619,885	10^{-12}	1687
600	2.34×10^{-47}	535,638	619,290	10^{-11}	1781
700	1.17×10^{-39}	521,742	618,704	10^{-10}	1886
800	6.86×10^{-34}	507,929	618,141	10^{-9}	2004
900	2.08×10^{-29}	494,185	617,605	10^{-8}	2139
1000	7.98×10^{-26}	480,499	617,095	10^{-7}	2294
1100	6.78×10^{-23}	466,864	616,606	10^{-6}	2474
1200	1.86×10^{-20}	453,272	616,133	10^{-5}	2692
1300	2.15×10^{-18}	439,719	615,659	10^{-4}	2953
1400	1.25×10^{-16}	426,203	615,183	10^{-3}	3272
1500	4.25×10^{-15}	412,722	614,693	10^{-2}	3668
1600	9.23×10^{-14}	399,274	614,178	10^{-1}	4175
1700	1.39×10^{-12}	385,859	613,632	1	4845
1800	1.55×10^{-11}	372,477	613,046	NBP	4850
1900	1.34×10^{-10}	359,129	612,415		
2000	9.30×10^{-10}	345,816	611,733		
2016	1.25×10^{-9}	343,689	611,618		
2016	1.25×10^{-9}	343,689	606,579		
2100	5.29×10^{-9}	332,746	606,056		
2200	2.56×10^{-8}	319,745	605,446		
2300	1.08×10^{-7}	306,772	604,845		
2400	4.03×10^{-7}	293,826	604,253		
2500	1.35×10^{-6}	280,903	603,670		
2502	1.38×10^{-6}	280,645	603,658		
2502	1.38×10^{-6}	280,645	583,773		
2600	3.98×10^{-6}	268,781	583,298		
2700	1.08×10^{-5}	256,693	582,821		
2800	2.73×10^{-5}	244,623	582,355		
2900	6.47×10^{-5}	232,569	581,900		
3000	1.45×10^{-4}	220,531	581,459		
3100	3.07×10^{-4}	208,507	581,032		
3200	6.20×10^{-4}	196,497	580,622		
3300	1.20×10^{-3}	184,499	580,230		
3400	2.24×10^{-3}	172,512	579,859		
3500	4.02×10^{-3}	160,537	579,511		
3600	6.99×10^{-3}	148,571	579,187		
3700	1.18×10^{-2}	136,613	578,889		
3800	1.93×10^{-2}	124,664	578,619		
3900	3.09×10^{-2}	112,721	578,379		
4000	4.83×10^{-2}	100,784	578,170		
4100	7.38×10^{-2}	88,851	577,993		
4200	0.11	76,923	577,850		
4300	0.162	64,997	577,742		
4400	0.234	53,074	577,670		
4500	0.333	41,152	577,635		
4600	0.466	29,230	577,637		
4700	0.642	17,308	577,677		
4800	0.874	5384	577,755		
4845.15	1	0	577,803		
4900	1.174	-6542	577,871		

NBP Normal boiling point At 1 atmosphere pressure (1.01325 bar) Enthalpy of sublimation at 0 K: ΔH_0° 620647 J/mol

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