Thermodynamic properties of zirconium

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ABSTRACT

The thermodynamic properties of zirconium have been assessed to 4700 K and include a selected enthalpy of sublimation at 298.15 K of 600 ± 9 kJ/mol and a derived boiling point of 4640 K at one atmosphere pressure.

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1. Introduction

Previous reviews on zirconium were by Hultgren et al. [1], Alcock et al. [2], Gurvich et al. [3], Fernández Guillermet [4], Cordfunke and Konings [5], JANAF [6] and Brown et al. [7]. A further review is justified by a number of new measurements in the high temperature region, in particular the enthalpy measurements of Rösner-Kuhn et al. [8] (1821–2105 K) for the beta phase and those of Qin et al. [9] (2027–2901 K) for the liquid phase, both of which lead to marked improvements in the quality of selected values above the alpha–beta transformation temperature. In contrast, the large number of rejected sets of measurements in Tables 11 and 12 are perhaps a clear indication of the extreme difficulties encountered in trying to avoid oxidation during the experiments for a metal which is highly sensitive to contamination.

Fernández Guillermet [4] selected 1139 ± 5 K for the transformation from the hexagonal close-packed alpha phase to the body-centred cubic beta phase. A more recent determination by Milošević and Maglić [10] at 1141.4 K confirms this value. The melting point is a secondary fixed point on ITS-90 at 2127 ± 8 K [11]. Wherever possible values have been corrected to the ITS-90 temperature scale [12,13] and to the currently accepted atomic weight of 91.224 ± 0.002 [14].

2. Alpha phase

Roberts [15] selects 0.61 ± 0.15 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 are identical to those selected by Phillips [22] whilst Fisher and Renken [23] obtain 296 K for the Debye temperature from elastic constant measurements.

Up to 130 K the specific heat measurements of Wolcott [18] (1.2–20.3 K), Todd [24] (53.2–297 K), Skinner and Johnston [25] (14.4–298 K) and Burk et al. [26] (20–200 K) show considerable scatter making a meaningful evaluation very difficult. Fernández-Guillermet [4] overcame this problem by combining electronic and dilation terms with Debye functions and the selected values below 100 K were accepted and reproduced in Table 13 by permission of the author. In the region from 100 K to 130 K the tabulated values of Fernández Guillermet were given only to two decimal places but were extended to three decimal places in Table 13.

From 130 K to 273.15 K the specific heat values of Todd [24] were accepted and fitted to the equation:

$$C_p^\circ \text{ (J/mol K)} = 0.159961T - 6.09037 \times 10^{-4}T^2 + 8.50180$$
$$\times 10^{-7}T^3 - 26168.3/T + 10.3474 \quad (1)$$

Above 273.15 K and up to the transition temperature the enthalpy measurements of Douglas and Victor [27] (373–1124 K) were accepted and after correction to ITS-90 these values can be

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represented by the following equation with an overall accuracy as a standard deviation of ± 47 J/mol (0.30%):

$$H_T^\circ - H_{298.15}^\circ \text{ (J/mol)} = 24.9540T + 3.94024$$
$$\times 10^{-3}T^2 + 114193/T - 8173.30 \quad (2)$$

For the alpha phase the deviations of other experimental specific heat and enthalpy values from the selected values are considered in Tables 11 and 12

3. Beta phase

Specific heat measurements of Cezairliyan and Righini [28] (1500–2100 K) and Petrova et al. [29] (1200–2100 K) were combined with the drop calorimetry enthalpy measurements of Rösner-Kuhn et al. [8] (1821–2105 K) and fitted to the following equation which is considered to have an overall accuracy of 0.8% based on a combination of an individual fit to the specific heat values of Cezairliyan and Righini at 0.7% and a fit to the enthalpy curve of Rösner-Kuhn et al. at 0.3%:

$$H_T^\circ - H_{298.15}^\circ \text{ (J/mol)} = 19.2826T + 7.07475$$
$$\times 10^{-3}T^2 - 2.965743 \times 10^{-6}T^3 + 7.012525$$
$$\times 10^{-10}T^4 + 1611.715 \quad (3)$$

Petrova et al. actually indicate that their individual values are probably accurate to 2.5% whilst Cezairlyan and Righini suggest an accuracy of 3% and Rösner-Kuhn et al. also estimate an accuracy of 3%.

The derived enthalpy of transition is calculated as 4089 ± 250 J/mol and this value can be compared to experimental values as given in Table 2 where the first eight values are directly obtained from the various methods given in the table, where in particular the value found using the zirconium–hydrogen system is from the initial phase

boundary slopes. The remainder is indirect consisting of either extrapolation to the transition temperature of enthalpy values obtained by drop calorimetry or by measuring the enthalpy either side of the transition temperature by rapid pulse heating. The results vary considerably from 2950 to 5656 J/mol but enthalpies of transition selected in reviews as given in Table 4 show a much narrower spread and definitely place the value as being between 3850 J/mol and 4150 J/mol.

For the beta phase the deviations of other experimental specific heat and enthalpy values from the selected values are considered in Tables 11 and 12

4. Liquid phase

After correction of experimental temperature values to correspond to a common melting point of 2127 K, the drop calorimetry enthalpy measurements of Bonnell [43] (2232–3046 K), Kats et al.

Table 3
Experimental values of the enthalpy of fusion.

Authors	Ref.	$\Delta H\,s,l$ (J/mol)	Method
Elyutin et al.	[45]	21087 ± 674	Drop calorimetry
Korobenko et al.	[42]	21500 ± 1290	Rapid pulse heating
Kats et al.	[44]	$14{,}674 \pm 893$	Drop calorimetry
Korobenko and Savvatimski	[41]	$12{,}771 \pm 1277$	Rapid pulse heating
Korobenko et al.	[42]	$13{,}957 \pm 558$	Rapid pulse heating
Rösner-Kuhn et al.	[8]	$17{,}282 \pm 695^a$	Drop calorimetry
Brunner et al.	[46]	13,319	Rapid pulse heating
Selected		**$15{,}600 \pm 1540$**	Present evaluation

^{a} In combination with the complimentary liquid enthalpy measurements of Qin et al. [9]

Table 1
Low temperature specific heat coefficients.

Author	Ref.	Temperature range (K)	γ (mJ/mol K^2)	θ_D (K)
Smith and Daunt	[16]	–	1.64	–
Estermann et al.	[17]	1.8–4.2	2.90	265
Wolcott	[18]	1.2–20.3	3.03	310
Kneip et al.	[19]	1.1–4.5	2.809^a	291.5^a
Dummer	[20]	0.9–1.2	2.77	289.5
Collings and Ho	[21]	1.6–5.3	2.80	291
Selected			**2.80**	**291**

^{a} Average of four determinations.

Table 4
Selected values for the temperatures and enthalpies of transition and fusion.

Authors	Ref.	$T\,\alpha{-}\beta$ (K)	$\Delta H\,\alpha{-}\beta$ (J/mol)	$T\,s,l$ (K)	$\Delta H\,s,l$ (J/mol)
Hultgren et al.	[1]	1136	3937	2125	(16,895)
Alcock et al.	[2]	1136	3891	2125	18,828
Gurvich et al.	[3]	1140	3870	2133	13,700
Fernández Guillermet	[4]	1139	4106	2128	21,000
JANAF	[6]	1135	4017	2125	20,920
Brown et al.	[7]	1141	4009	2128	19,800
This work	–	1139	4089	2127	15,600

Table 2
Experimental values of the enthalpy of the alpha–beta transformation.

Authors	Ref.	$\Delta H\,\alpha{-}\beta$ (J/mol)	Method
Vogel and Tonn	[30]	2950	Cooling curves
Gertsrickin and Slyusar	[31]	2979 ± 250	Differential calorimetry
Scott	[32]	4155 ± 155	Adiabatic calorimetry
Vollmer et al.	[33]	3975 ± 40	Adiabatic calorimetry
Cezairlyan and Righini	[34]	3980 ± 13	Rapid pulse heating
Peletsky and Zaretsky	[35]	4380 ± 200	Transient calorimetry
Peletskii et al.	[36]	5054 ± 292	Rapid pulse heating
La Grange et al.	[37]	4393	Zr–H binary system phase boundary slope
Douglas and Victor	[27]	3740	Drop calorimetry
Skinner	[38]	4360 ± 167	Drop calorimetry
Coughlin and King	[39]	3849	Drop calorimetry
Martynyuk and Tsapkov	[40]	4500	Rapid pulse heating
Korobenko and Savvatimski	[41]	4835 ± 483	Rapid pulse heating
Petrova et al.	[29]	4561	Rapid pulse heating
Korobenko et al.	[42]	5656 ± 226	Rapid pulse heating
Selected		**4089 ± 250**	Present evaluation