Enthalpy of Fusion of Zirconium

Recommendation

The recommendation for the enthalpy of fusion of zirconium is

$$153 \pm 4 \quad J/g = 13.96 \pm 0.36 \quad kJ/mol$$

This value for the enthalpy of fusion is an average enthalpy of fusion obtained by Korobenko, Savvatimskii and Sevostjanov [1,2] from ten precise pulse heating experiments that simultaneously measured the temperature, enthalpy, heat capacity, and electrical resistivity of zirconium foils in the solid and liquid states up to 2350 K.

Uncertainty

The uncertainty in the recommended value for the enthalpy of fusion of zirconium is $\pm$ 3%, the uncertainty given by Korobenko, Savvatimskii and Sevostjanov [1,2]. It is based on the deviations from the average values calculated using standard statistics for a reliability of 0.95. It does not include an uncertainty for identification of the instant of the start of melting and instant of the end of melting in their data analysis.

Discussion

Review of Measurements and Recommendations

Table 1 lists the experimental values and recommended values for the enthalpy of fusion of zirconium available in both the Russian and western literature in chronological order. In 1963, Hultgren et al.[3] recommended 225 J/g (20.5 kJ/mol) for the enthalpy of fusion based on an estimate using Richard’s rule. In 1967, Elyutin et al.[4] recommended 229 J/g (20.9 kJ/mol) from their three measurements of 230 J/g, 224 J/g and 239 J/g that were obtained using the method of mixing in a liquid magnesium calorimeter. In their review of these data, Korobenko and Savvatimskii [14] commented that the heat of mixing of the liquid zirconium and magnesium were neglected by Elyutin et al. in their analysis of the experimental data. The 7% error reported by Elyutin et al. is the uncertainty in the data analysis and does not include the total experimental error.

In his thesis, Bonnell reported 156 J/g (14.2 kJ/mol) for the enthalpy of fusion of zirconium from extrapolation of zirconium enthalpies and heat capacities measured at 2233 -2839 K using magnetic levitation in an adiabatic calorimeter. In 1973, Hultgren et al.[6] gave 185 J/g as an estimate of the enthalpy of fusion of zirconium. This value, which is considerably lower than their previous estimate, appears to take into account the data of Bonnell.

Martynyuk et al. measured the enthalpy of fusion using electrical resistive heating with 20 μsec [16] and 400 μsec pulses [7]. Their first measurements with 20 μsec pulses gave 285 J/g with a 15% uncertainty. This value, reported only in a university publication [16], was not included in their subsequent journal publication. In 1974, Martynyuk and Tsapkov [7] reported a heat of fusion of 236 J/g (21.6 kJ/mol) with a 6% uncertainty from 400 μsec pulse heating experiments. This value, obtained by dynamic methods, was in good agreement with the earlier drop calorimetry value [4] and the calculated enthalpy of fusion [3] and widely accepted. In their review of the measurements of Martynyuk and Tsapkov [7, 16], Korobenko and Savvatimskii [14] question the accuracy of these measurements because the experimenters did not record an inflection in the resistivity that designates the onset of melting, the luminescence, nor the temperature. In addition, Korobenko and Savvatimskii [14] found that heating with long 400 μsec pulses led to sample deformation at the onset of melting due to nonuniform heating. They also noted that the enthalpy of copper near the melting point determined by Martynyuk and Tsapkov [7] was high by about 70% and later refuted by subsequent pulse heating experiments.

In the 1976 IAEA special volume on zirconium, Alcock et al.[8] recommended 206 J/g (18.8 kJ/mol) by combining the new estimate of Hultgren [6] with the value recommended by Elyutin et al.[4] from their calorimetry measurements. Korobenko et al. [1] report that Regel and Glazov [9] recommended 158 J/g (14.4 kJ/mol) with a 2.3% uncertainty from review of the literature data and analysis of all the related properties of zirconium, taking into account information from the periodical table of Mendeleev. The reference compilation by Glushko, ed. [10] gave the enthalpy of fusion as 150 J/g (13.7 kJ/mol) with an uncertainty of 29%. Although this recommendation is consistent with the enthalpy of fusion obtained from measurements by Bonnell, the large uncertainty reflected the inconsistencies in the data.

In 1985, Kats et al. [11] obtained an enthalpy of fusion of 161 J/g (14.7 kJ/mol) with an uncertainty of 6% using magnetic-levitation. These measurements confirmed measurements of the enthalpy of the solid at the melting point and implied that the earlier measurements of the liquid enthalpy by Elyutin et al.[4] and by Martynyuk and Tsapkov [7] are inaccurate. However, the results of Kats et al., which agreed with the extrapolated value of Bonnell, were published only in the Russian edition of Teplofizika Vysokikh Temperatur and not included in the English translation of this journal. Therefore, these results were not readily known outside Russia.

In his thorough review of zirconium properties, Guillermet [12], who was apparently unaware of the data of Katz et al.[11], rejected Bonnell's data because these data disagreed with the data of Elyutin et al.[4] and the data of Martynyuk and Tsapkov [7]. Guillermet stated that the enthalpy measurements of Bonnell appear to have a systematic error but their slope seems reasonable and may be used to obtain a constant liquid heat capacity. He recommended 230 J/g (21 kJ/mol) based on the drop-calorimetric data of Elyutin et al.[4] because this value has been supported by measurements by Martynyuk and Tsapkov [7] by a dynamic method. The assessment and recommendations of Guillermet [12] were also recommended by the Scientific Group Thermodata Europe [13] for use in phase diagram calculations.

Because of the inconsistency in the published zirconium enthalpy of fusion data and recommendations, Korobenko and Savvatimskii [14] performed two series of electric current pulsed heating experiments of zirconium at 20 and 100 µsec. They performed no experiments with a longer pulse (400 µsec) because they have found that for longer pulses the surface tension and electromagnetic forces cause the conductor to deform from the onset of melting, indicating nonuniform heating and making property measurements meaningless. From these two measurements, they obtained 141 J/g and 138 J/g for the enthalpy of fusion, which gave an average value of 140 J/g (12.8 kJ/mol) with an uncertainty of 10%. Their enthalpy of fusion at the melting point is consistent with the values obtained by magnetic levitation of Bonnell [5] and of Kats et al.[11] and is significantly lower than the values obtained by Elyyutin et al. [4] and Martynyuk and Tsapkov [7].

Despite the availability of these new data, the enthalpy of fusion given in the 1995 version of MATPRO [15] remains 225 J/g, the value recommended in 1981[17]. It was based on a 1968 recommendation by Brassfield [18].

Recently, Korobenko, Savvatimski, and Sevostjanov [1,2] obtained an average enthalpy of fusion of 153 $\pm$ 4 J/g from ten precise measurements on zirconium foils.

Measurements by Korobenko, Savvatimski, and Sevostjanov

Because of the disagreements in the available data for the enthalpy of fusion, Korobenko, Savvatimski, and Sevostjanov [1,2] used state-of-the art techniques to precisely determine the enthalpy, heat capacity, and electrical resistivity of zirconium in the melting region. In these measurements, an electrical pulse current of 3-5 kA for 3-5 microseconds heated zirconium strips of foils of 1-2 mm in width and 30-40 mm in length that had been obtained from three different manufacturers. The enthalpy, resistivity, temperature, and heat capacity in the solid and liquid states up to 2350 K were measured simultaneously. Temperature was measured from 1800 to 2350 K using a fast optical pyrometer through a quartz guide. The established melting point, 2128 K, served as a calibration point of the temperature at the plateau of melting. Simultaneous measurement of the temperature, enthalpy, and electrical resistivity provided precise determination of the end of melting. Foil thicknesses, density, and dimensions were precisely determined prior to each measurement. Density was determined by weighing the foils in air and in boiled water.

Following control experiments to determine the effects of surface treatment and surface quality on the precise determination of beginning and end of melting, three series of measurements were made using zirconium foils from three different manufacturers. The first series of measurements were made using an annealed foil of zirconium that was 24 microns thick, with a density of 6.53 g/cm^3, from GIREDMET (Russia). In the first series of experiments, some non-coincidence of the instances of the start and end of melting determined from electrical resitivity and from the optical pyrometer temperature indicated non-homogeneity of the surface of this material. Therefore, a second series of measurements were made using a 44.6 micron thick, high-quality zirconium foil, with a density of 6.49 g/cm^3, from Sundwig (Germany). This zirconium foil had a very smooth surface with no apparent traces of rollers. Results from this series are more certain than those of the first series as indicated by the (1) smooth temperature plateau, (2) greater precision of fixing the beginning and ending of melting, and (3) coincidence of the finish of melting as indicated by the temperature plateau and by the electric resistivity. Because a thicker sample has a more uniform cross-section and produces more homogeneous heating and surface temperature, the third series of measurements was made with a thicker foil. This 95.45 microns thick foil with a density of 6.54 g/cm^3, was made of iodide zirconium and manufactured in Russia. It had a very smooth surface (almost unruffled) with only a slight strip-type structure of the surface in the rolling direction.

Enthalpy of fusion results from these ten measurements are shown in Table 2. Additional data such as the enthalpy of transition from the α-phase to the β-phase and the enthalpies of each phase at the phase transition are available in their paper [1] and data report [2]. Both the liquid enthalpy at the melting point based on the pyrometer and based on the electrical resistivity are shown in Table 2. Best agreement between these measurements was obtained for the high quality foil from Sudwig Germany. The last row of Table 2 gives the average values for the solid and liquid enthalpy determined using the pyrometer temperatures and the average enthalpy of fusion. Included with the average values are the statistically determined deviations from the average for a 0.95 confidence level. These deviations for the solid enthalpy, liquid enthalpy and the enthalpy of fusion, expressed as percentages, are respectively, 1.7%, 1.4%, and 2.6%. Maximum deviations from the average solid enthalpy, liquid enthalpy, and heat of fusion are respectively, 3.3%, 3.0%, and 5.2%. The recommended value for the enthalpy of fusion of zirconium is 153 $\pm$ 4 J/g, the average value obtained from these precise measurements.

References

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Table 1. Measurements and Recommendations of the Enthalpy of Fusion of Zirconium

ΔH_f J/g	H_l J/g	H_s J/g	Method	Reference	Year
225			estimated - Richard's rule	Hultgren et al. [3]	1963
229 ± 7%			method of mixing in liquid Mg calorimeter- based on 3 measurements (230, 224, 239 J/g)	Elyutin et al.[4]	1967
156			magnetic levitation in adiabatic calorimeter extrapolated from liquid at 2233-2839 K	Bonnell (Rice University thesis) [5]	1972
185			recommended	Hultgren et al. [6]	1973
236 ± 6%	658	893	pulse heating, heating rate: $5 \cdot 10^6$ K/s, onset of melting & luminescence not recorded	Martynyuk & Tsapkov [7]	1974
206 ± 11%			recommended - average of Hultgren 1973 & Elyutin et al. 1967	Alcock (IAEA publication) [8]	1976
158 ± 2.3%			recommended	Regel & Glazov (Russian only) [9]	1978
150 ± 29%			recommended	Glushko, ed. [10]	1982
161 ± 6%	658	819	magnetic levitation	Kats et al. (Russian only) [11]	1985
230			recommended	Guillermet [12]	1987
				Dinsdale (SGTE) [13]	1991
140 ± 10%	640	780	2 pulse heating measurements (141, 138), rates: $2 \cdot 10^7$ K/s, $1 \cdot 10^8$ K/s	Korobenko & Savvatimskii [14]	1991
225			recommended	MATPRO, Hagrman [15]	1995
153 ± 3%	703	856	10 pulse heating measurements, heating rate: $3 \cdot 10^8$ K/s	Korobenko, Savvatimskii, & Sevostjanov [1,2]	1999

Table 2 Zirconium Enthalpy of Fusion Results for 3 Series of Measurements

Run	Foil source, thickness, density	H(*s*) from pyrometer, J/g	H(*l*) from pyrometer, J/g	H(*l*)from electrical resistivity, J/g	H(*l*)-H(*s*) from pyrometer, J/g
1	Russian annealed, 24 µm, 6.53 g/cm^3	695	840	830	145
2	Russian annealed, 24 µm, 6.53 g/cm^3	690	840	860-880 rounded	150
3	Sudwig Germany, 44.6 µm, 6.49 g/cm^3	710	860	850	150
4	Sudwig Germany, 44.6 µm, 6.49 g/cm^3	680	830	835	150
5	Sudwig Germany, 44.6 µm, 6.49 g/cm^3	700	860	860	160
6	Sudwig Germany, 44.6 µm, 6.49 g/cm^3	700	850	820-860 rounded	150
7	Russian, iodide Zr, 95.45 µm, 6.54 g/cm^3	710	860	840	150
8	Russian, iodide Zr, 95.45 µm, 6.54 g/cm^3	725	880	860	155
9	Russian, iodide Zr, 95.45 µm, 6.54 g/cm^3	705	860	840	155
10	Russian, iodide Zr, 95.45 µm, 6.54 g/cm^3	720	880	850	160
Aver-age	-	**703 $\pm$ 12**	**856 $\pm$ 12**	-	**153 $\pm$ 4**