

Enthalpy and Heat Capacity of Solid Zirconium

Preliminary Recommendation

The preliminary recommendations for the enthalpy and heat capacity of solid zirconium are equations selected by the Scientific Group Thermodata Europe (SGTE) [1]. Enthalpy increments in $\text{J}\cdot\text{mol}^{-1}$ for the α - and β -phases of zirconium relative to the enthalpy at 298.15 K are:

α -phase —

$$H(s, T) - H(s, 298.15) = - 7827.595 + 24.1618T + 4.37791 \times 10^{-3}T^2 + 6.9942 \times 10^4T^{-1} \quad (1)$$

for 298 K \leq T \leq 1139 K ;

β -phase —

$$H(s, T) - H(s, 298.15) = - 525.539 + 25.607406T + 3.40084 \times 10^{-4}T^2 + 1.9457947 \times 10^{-8}T^3 + 2.28428682 \times 10^{-10}T^4 + 5.0466 \times 10^4T^{-1} \quad (2)$$

for 1139 K \leq T \leq 2128 K ;

Temperatures in Eqs. (1-2) are in kelvins. The enthalpy increments calculated with these equations are tabulated in Table 1 in J mol^{-1} and are shown in Figure 1. The atomic weight of zirconium, 91.22 $\text{g}\cdot\text{mol}^{-1}$, may be used to calculate enthalpy increments per gram of zirconium. Estimated uncertainties for the enthalpy increments are 6% for the α - and β -phases.

The recommended heat capacities may be obtained from the temperature derivatives of Eqs.(1-2). The SGTE equations for the heat capacities in $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ for the α - and β -phases are:

α -phase —

$$C_p = 24.1618 + 8.75582 \times 10^{-3}T - 6.9942T^2 \quad (3)$$

for 298 K \leq T \leq 1139 K ;

β -phase —

$$C_p = - 25.607406 + 6.80168T + 5.8373841 \times 10^{-8}T^2 + 9.13714728 \times 10^{-10}T^3 - 5.0466 \times 10^4T^{-2} \quad (4)$$

for 1139 K \leq T \leq 2128 K ;

The recommended heat capacities, in $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, are shown in Figure 2. Heat capacities are tabulated in Table 1 in $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. Estimates of the uncertainties in the recommended heat capacities are 7% for the α -phase and 13% for the β -phase.

Uncertainty

The uncertainties in the preliminary recommendations for the enthalpy increments and heat capacities for the solid-phases have been estimated from the deviations of values given in other assessments from the SGTE recommendations. These uncertainties are smaller than some of the scatter in the experimental data. Scatter between some data are as high as 20%. Based on the deviations of recommendations, the estimated uncertainty for the enthalpy increments for the solid (α - and β -phases) is $\pm 6\%$. Higher uncertainties are estimated for the heat capacities. The uncertainties in the recommended values for the heat capacity are $\pm 7\%$ for the α -phase and $\pm 13\%$ for the β -phase.

Discussion

The SGTE recommended equations for the enthalpy and heat capacity of zirconium are based on the 1987 assessment by Guillermet [2]. Guillermet analyzed available enthalpy and heat capacity measurements on zirconium along with measurements of phase transition temperatures, and other thermodynamic properties to obtain a consistent set of equations to represent the Gibbs energy of the various phases as a function of temperature and pressure. In his analysis, Guillermet used thermodynamic models of the Gibbs energy of individual phases and optimized the model parameters using the computer optimization program PARROT developed by Jansson.[3]. The enthalpy equations and tabulated values given by Cordfunke and Konings [4] are also based on the analysis of Guillermet and are consistent with the SGTE equations.

Although the enthalpy data of Kats et al. [5], which are only available in the Russian literature, were not included in the assessment of Guillermet, the equation recommended by the SGTE for the β -phase is consistent with the data of Kats et al. as shown in Figure 3. In Figure 3, the data of Kats et al. and the enthalpy increments for solid zirconium calculated with the recommended SGTE equations of Guillermet are compared with recommendations from the JANAF Thermochemical Tables [6], Hultgren [7], and the 1976 IAEA review on zirconium by Alcock et al. [8], which is recommended in the book by the Knacke et al.[9] and in the IBRAE on-line database. Deviations of equations for the enthalpy increments of zirconium recommended in the other assessments from the recommended values are shown in Figure 4. The plotted deviations, expressed as percents, are defined by

$$Deviations = \frac{[H(Other) - H(Recommended)]}{H(Recommended)} 100\% , \quad (5)$$

where $H(Other)$ represents the enthalpy increment recommended in the other assessments. These deviations were used in determining the uncertainties. The deviations of the data of Kats et al. from the SGTE equation, defined as in Eq.(5), have been included in Figure 4. Note that the percent deviations of values the assessments from the SGTE values are greater than the deviations between the data of Kats et al. and the SGTE values.

In Figure 2, the heat capacities from the SGTE equations [1] are compared with values from the JANAF Thermochemical Tables [6], Hultgren [7], the 1976 IAEA review by Alcock et al. [8], and the heat capacity data of Cezairliyan and Righini [10]. Differences between the different assessments are more pronounced for the heat capacities than for the enthalpy increments because these are derivatives of the enthalpy increments. Only the SGTE equations and the JANAF Thermochemical Tables are consistent with the data of Cezairliyan and Righini because these data were not included in the other assessments.

Comparison of the JANAF values with the SGTE values for enthalpy increments and heat capacity shows that the agreement is better for the β -phase than for the α -phase. Differences between the SGTE recommended values and the JANAF recommendations are due to (1) Guillermet's inclusion in his analysis of measurements of the $\alpha \rightarrow \beta$ phase transformation temperature and enthalpy of transformation not available at the time of the JANAF assessment and (2) differences in the weights given to the various heat capacity and enthalpy data in the two assessments. For the β -phase, the JANAF analysis was based mainly on the data of Cezairliyan and Righini [10], which was very well reproduced in Guillermet's analysis. Because there is much scatter in the heat capacity data for the α -phase, Guillermet gave higher weights to the enthalpy measurements than to the heat capacity data. The heat capacity data by Scott [11] was not included in Guillermet's analysis because Scott's data have an unphysical inflexion point at 500 K. The JANAF analysis did not include Scott's data below 540 K but gave heavy weight to data from two of the nine sets of Scott's data above 540 K. Guillermet compared his recommended heat capacities with those from the nine runs by Scott and found that Scott's data below 500 K are well reproduced; but above 500 K, Scott's data are low relative to Guillermet's recommended values. This difference between Guillermet's recommendations and Scott's data is consistent with the differences between the JANAF and the SGTE heat capacities in the α -phase.

The analysis given in Hultgren et al.[7], is based on enthalpy and heat capacity data from 1951 through 1962. Both the JANAF analysis and that of Guillermet included more recent data than were analyzed by Hultgren et al.[7]. The assessment by Alcock et al.[8] is based on the 1966 assessment of Hultgren and additional data through 1971 but it does not include the data of Cezairliyan and Righini that was included in the assessments by JANAF and by Guillermet.

References

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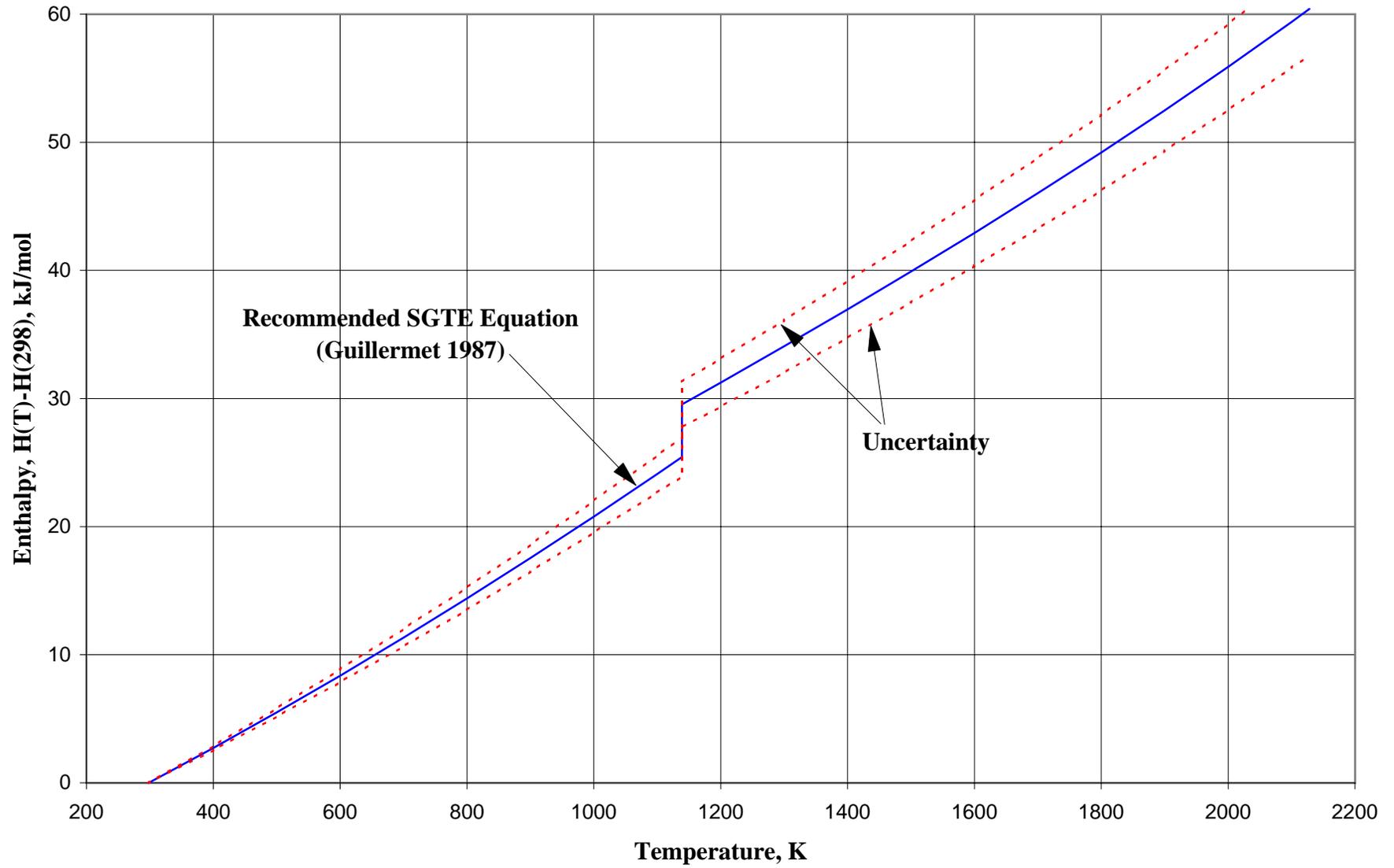
Figure 1 Enthalpy of Solid Zirconium

Figure 2 Zirconium Heat Capacity

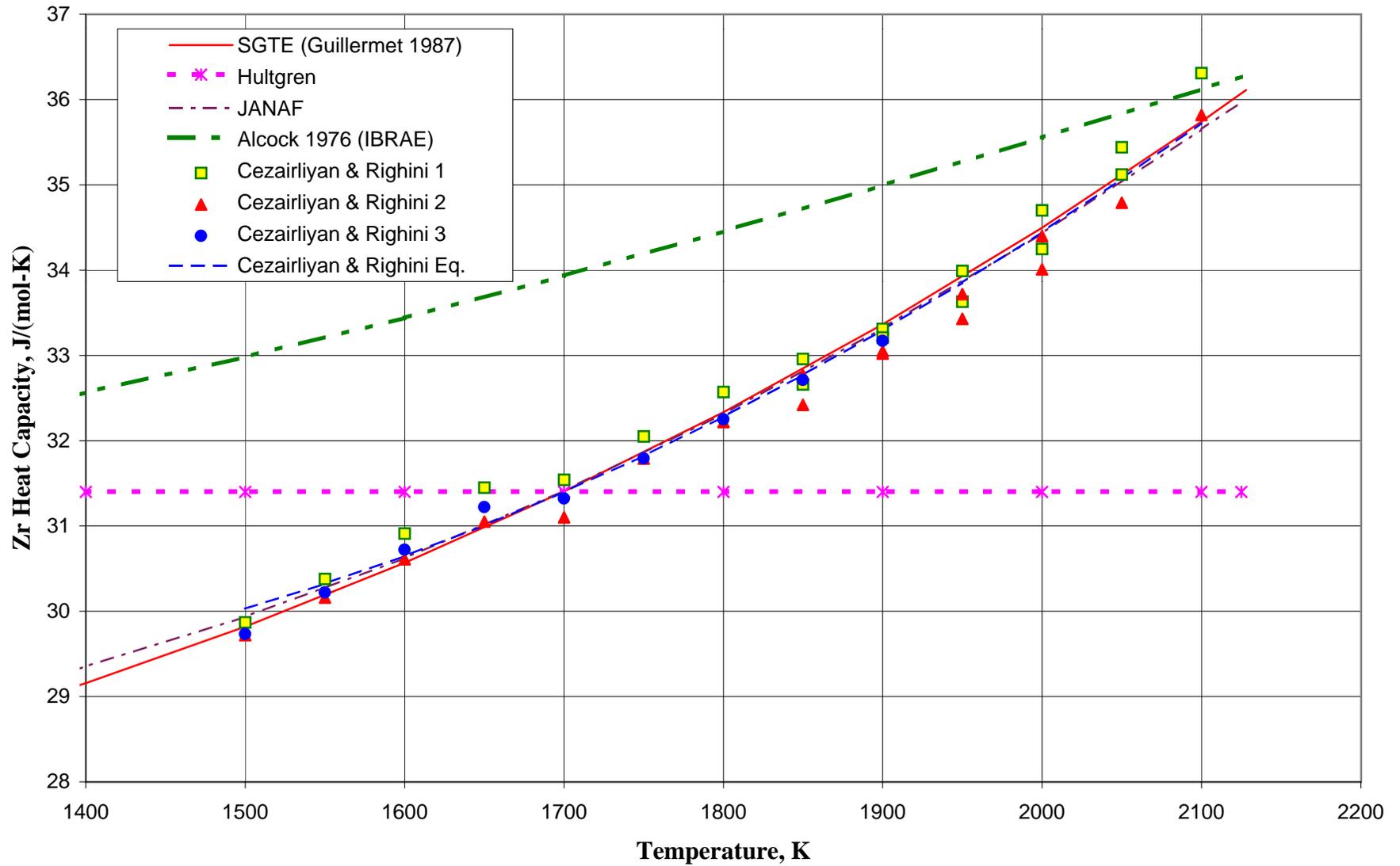


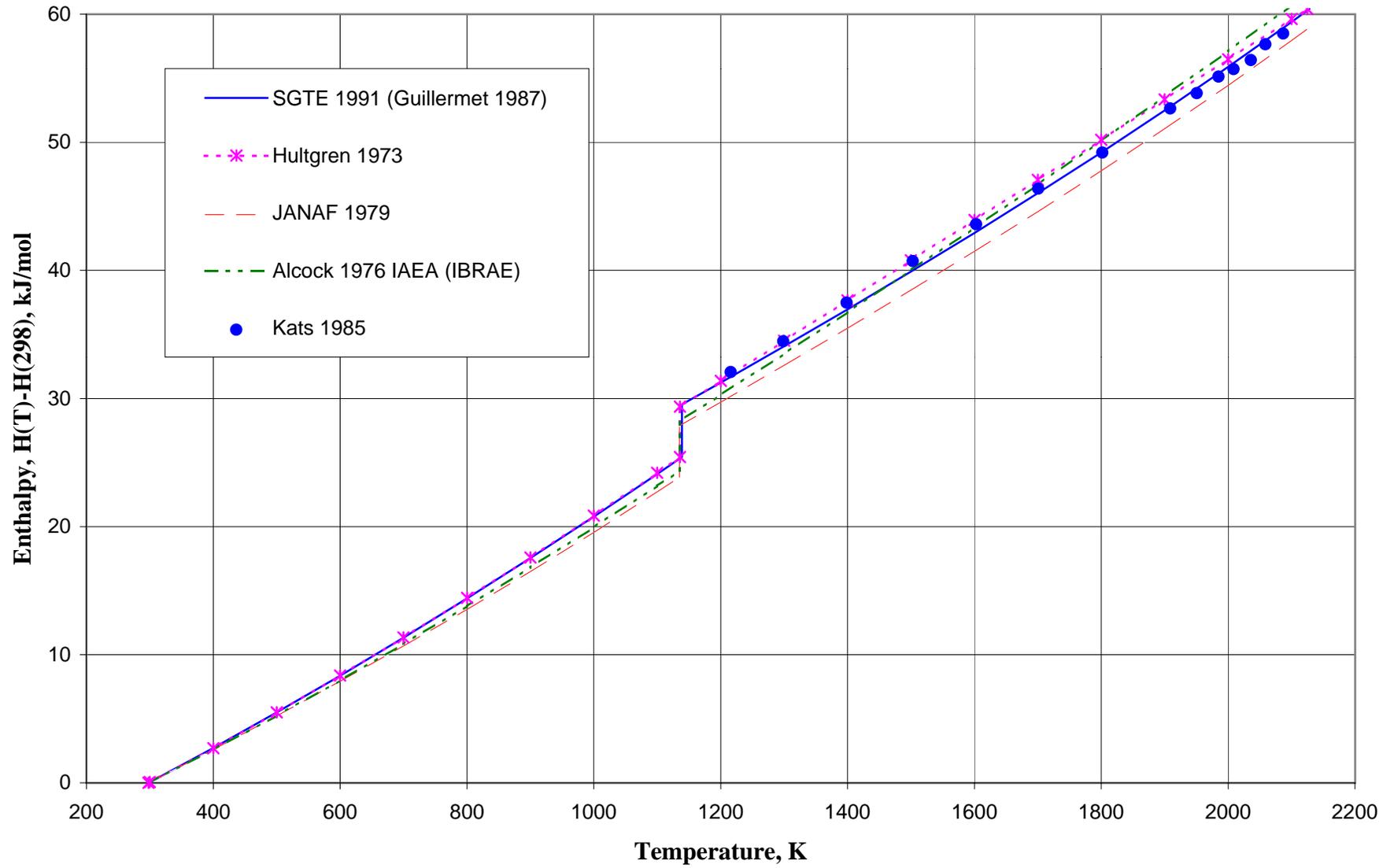
Figure 3 Comparison of Enthalpy Increments for Solid Zirconium

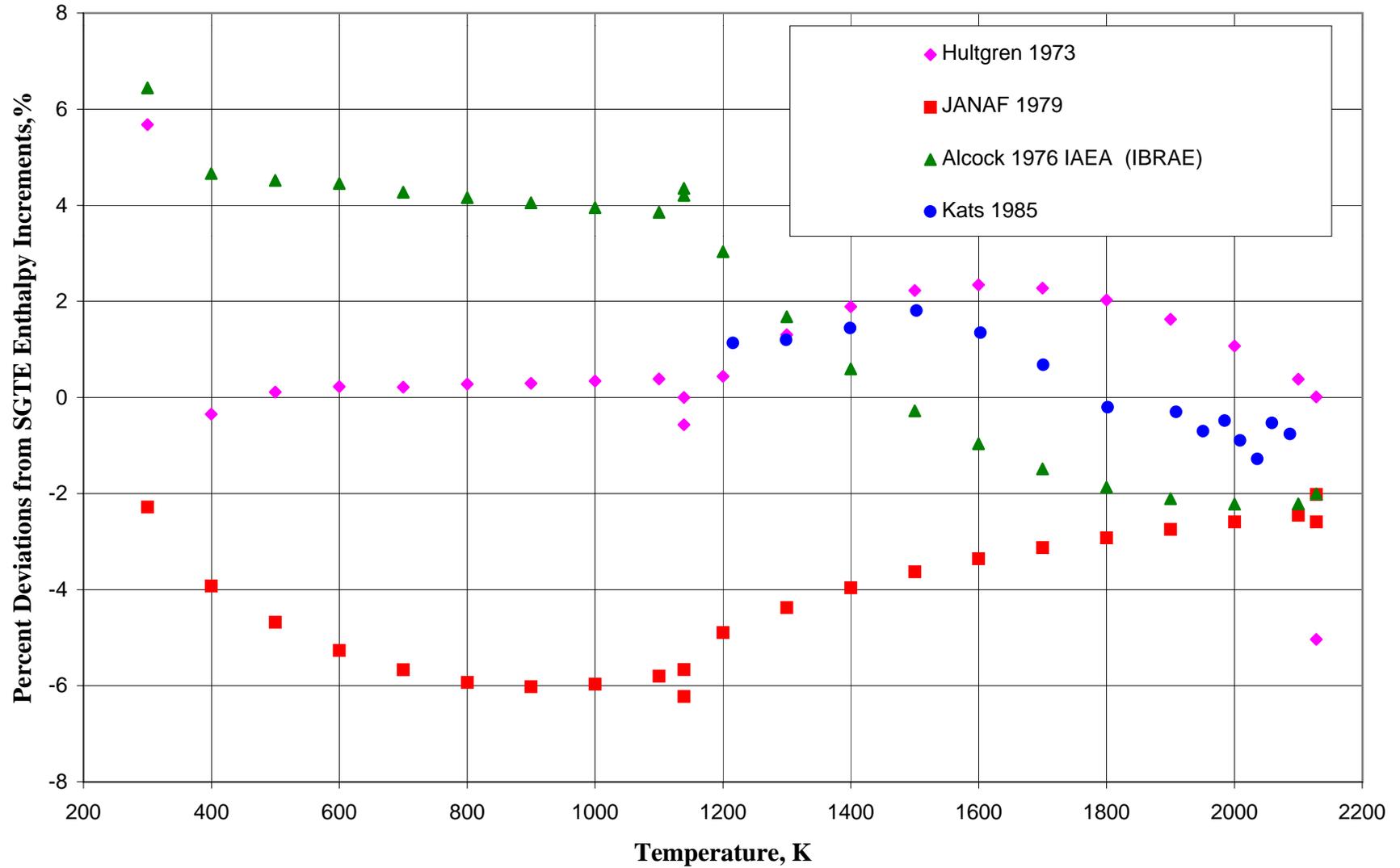
Figure 4 Deviations from SGTE Enthalpy Increments for Solid Zirconium

Table 1 Enthalpy and Heat Capacity of Solid Zirconium

Temperature (K)	H(T) - H(298.15) (J · mol⁻¹)	C_P (J · mol⁻¹ · K⁻¹)
298.15	0	25.99
300	48	26.01
400	2712	27.23
500	5488	28.26
600	8362	29.22
700	11331	30.15
800	14391	31.06
900	17542	31.96
1000	20782	32.85
1100	24111	33.74
1139	25434	34.08
1139	29540	27.77
1200	31242	28.05
1300	34073	28.57
1400	36958	29.16
1500	39906	29.82
1600	42925	30.57
1700	46023	31.40
1800	49209	32.33
1900	52493	33.36
2000	55885	34.50
2100	59397	35.74
2128	60402	36.11

