

## Enthalpy and Heat Capacity of Liquid UO<sub>2</sub>

### Recommendation

The recommended equations for the enthalpy and heat capacity of liquid UO<sub>2</sub> are a least squares fit to the combined enthalpy data from 3173 to 3523 K of Leibowitz et al. [1], the enthalpy data from 3123 to 3260 K of Hein and Flagella [2] and the heat capacity data from 3100 to 4500 K of Ronchi et al. [1]. The data were weighted according to their uncertainties. Although Ronchi et al. made measurements to 8000 K, the data fit were limited to the 3100 to 4500 K temperature range because this is the range of interest for reactor safety calculations and the uncertainties in the determined heat capacities increase significantly with temperature above 4500 K.

For the temperature range 3120 to 4500 K, the recommended equation for the enthalpy increment of liquid UO<sub>2</sub> in J mol<sup>-1</sup> is:

$$H(l,T) - H(s,298.15K) = 8.0383 \times 10^5 + 0.25136T - \frac{1.3288 \times 10^9}{T} \quad (1)$$

The heat capacity at constant pressure is the temperature derivative of the enthalpy. For 3120 to 4500 K, the recommended equation for the heat capacity, C<sub>p</sub>, in J mol<sup>-1</sup> K<sup>-1</sup> is:

$$C_p = + 0.25136 + \frac{1.3288 \times 10^9}{T^2} \quad (2)$$

In Eqs.(1) and (2), the temperature, T, is in K. Recommended values of the enthalpy increment in J mol<sup>-1</sup> and the heat capacity in J mol<sup>-1</sup> K<sup>-1</sup> are tabulated in Table 1 and shown in Figures 1 and 2.

The recommended equations for the enthalpy increment in J kg<sup>-1</sup> and the heat capacity at constant pressure in J kg<sup>-1</sup>K<sup>-1</sup> are:

$$H(T) - H(298.15K) = 2.9768 \times 10^6 + 0.93087T - \frac{4.9211 \times 10^9}{T} \quad (3)$$

and

$$C_p = + 0.93087 + \frac{4.9211 \times 10^9}{T^2} \quad (4)$$

where temperature, T, is in K. Table 2 gives values for the enthalpy increment in J kg<sup>-1</sup> and the heat capacity in J kg<sup>-1</sup>K<sup>-1</sup>.

### Uncertainty

The uncertainty in the recommended values for the enthalpy of liquid UO<sub>2</sub> is 2% from 3120 to 3500 K. It is based on the scatter in the data and deviation of the data from the fit. A 10% uncertainty is estimated for the extrapolated range from 3500 to 4500 K. The uncertainty in the recommended values for the heat capacity of liquid UO<sub>2</sub> is 10% from 3120 through 3400 K and increases linearly from 10% at 3400 K to 25% at 4500 K. Uncertainties have been included in Figure 2, which shows that all the heat capacity data are within the uncertainties except for data at 3370, 3700, and 4370 K.

### Discussion

#### *Enthalpy Experiments*

Both Leibowitz et al.[1] and Hein and Flagella [2] used drop calorimetry to measure the enthalpy increments of molten UO<sub>2</sub> encapsulated in tungsten. Leibowitz et al. made 6 measurements from 3173 to 3523 K; Hein and Flagella made 6 measurements in the temperature range from 3123 to 3264 K but the datum at 3124 K was low relative to other data and discarded by Hein and Flagella. These two sets of data are in excellent agreement even though the samples differed in stoichiometry. The sample of Hein and Flagella had an O/M = 2.003 ± 0.003 at the start of the

measurements and an O/M =  $2.000 \pm 0.003$  at the end of the experiments whereas the sample of Leibowitz et al. had an O/M = 2.015 at the start and an O/M = 1.98 at the end of the experiments. Although the change in O/M was greater in the experiments of Leibowitz et al. than in those of Hein and Flagella, the range in O/M is well within the range expected for variations of O/M in reactor fuel. The greater variation in the O/M in the experiments of Leibowitz et al. is most likely due to reduction from tungsten at high temperatures (~3500 K) because the effect of tungsten would increase as the melting point of tungsten (3685 K) is approached. Four of the six measurements of Leibowitz et al. were above the highest temperature measured by Hein and Flagella. Rand et al. [4] fit the data of Leibowitz et al.[1] and of Hein and Flagella [2] to a linear equation:

$$H(T) - H(298.15K) = 130.95T - 3091 \quad (5)$$

where the enthalpy increment is in  $\text{J mol}^{-1}$  and temperature (T) is in K. This equation fits the data with a standard deviation of 0.41%. This equation has been recommended for the enthalpy of liquid  $\text{UO}_2$  by Fink et al.[5] and by Harding, Martin, and Potter [6]. The data of Leibowitz et al.[1] and of Hein and Flagella [2] and the linear equation of Rand et al. [4] are shown in Figure 3.

### ***Heat Capacity Experiments***

The heat capacity of molten  $\text{UO}_2$  has been determined by Ronchi et al.[3] from the analysis of cooling curves of 0.5- to 1-mm-diameter  $\text{UO}_2$  microspheres heated to 3100-8000 K by four tetrahedrally oriented Nd:YAG lasers. The sintered  $\text{UO}_2$  microspheres were suspended on a tungsten needle in an inert atmosphere autoclave at pressures up to 1000 bar (100 MPa). Analysis of the experiments was based on an energy balance of the rate of input energy and the enthalpy increase of the sample. The determination of the heat capacity is based on the measurement of the sample surface-temperature history during heating and cooling. Since in most cases, the laser-energy deposition rate cannot be assessed with precision, the cooling branch of the curve is used preferentially [7]. Consequently, these difficult experiments required accurate (1) measurements

of the sample temperature during and after laser pulse heating, (2) evaluation of energy loss rates and (3) determination of the heat transport in the sample.

The experimenters took great care to minimize measurement errors as much as possible and to assess all energy losses. In an effort to reduce the errors due to optical absorption by the vapor surrounding the sample [8], temperatures were measured using a six-wavelength optical pyrometer. Melting experiments of oxides and refractory metals, including tungsten, indicated that the accuracy of the temperature measurement was within  $\pm 10$  K. Measurements of the freezing temperature of  $\text{UO}_2$  for various samples indicated that it was in the interval  $3070 \pm 20$  K for samples heated in an inert atmosphere with up to 0.1 bar (0.01 MPa) of oxygen. Higher melting temperatures ( $3140 \pm 20$  K) were obtained for samples in an inert atmosphere without oxygen. This trend is consistent with the effect of change of O/U ratio on the melting temperature. The melting point of stoichiometric  $\text{UO}_2$  is  $3120 \pm 30$  K. This value, recommended by Rand et al.[4] from their analysis of fourteen experimental studies (over a period of 20 years), has been accepted internationally. Although Ronchi et al.[3] cite accurate measurements of lower values [9] ( $3075 \pm 30$  K); Adamson et al.[10] found in their examination of melting behavior of  $\text{UO}_2$  and  $(\text{U,Pu})\text{O}_2$  as a function of stoichiometry and irradiation that these measurements used a V-filament method which yields consistently low melting temperatures. The V-filament method is a measurement on uncontained samples supported on a tungsten needle analogous to the method used for heat capacity measurements by Ronchi et al.[3] Adamson et al.[10] state that in the V-filament method pronounced compositional changes occur in the small uncontained samples as a result of rapid incongruent vaporization and in some cases interactions involving oxygen exchange between either the atmosphere or the tungsten support. These changes lead to surface emissivity changes which cause an error in the temperature measurement. Ronchi et al. did not determine the stoichiometry of the microspheres before or after the heat capacity measurements because of the small size of the samples. They comment that oxidation to stoichiometries of  $\text{O/U} \approx 2.03$  cannot be excluded but no evidence of the formation of  $\text{U}_4\text{O}_9$  was observed in x-ray analysis. Although increases in

stoichiometry may have occurred during heating at high pressure in an atmosphere of an inert gas plus oxygen, reductions could have occurred from heating in contact with tungsten in an inert atmosphere. Diffusion of tungsten from the supporting needle into the  $\text{UO}_2$  was observed above 3000 K. The thickness of the  $\text{UO}_2$ /tungsten interaction region was a function of the pulse time. For a 20 ms pulse creating central melting, the chemical interaction only effected a 10 to 20  $\mu\text{m}$  region near the tungsten needle and was, therefore, negligible. With repeated pulses, the tungsten precipitates migrated to the outside of the microsphere.

Heat losses taken into account during the pulse included radiation losses, evaporation losses, and convective losses. The experimenters observed that the plasma that surrounded their samples was significantly affected by laser excitation (inverse bremsstrahlung and photoeffects). Because the vapor partial pressure of liquid  $\text{UO}_2$  is high and evaporation of atoms presented a serious experimental complication, the experiments had to be done under high pressures to prevent significant vaporization and mass loss. The type and pressure of the gas in the autoclave was selected based on the equation of state of Fischer [11] to reduce losses from vaporization to <1% of the radiative losses. Heat losses due to heat conduction and convection in the buffer gas were determined from similar experiments using tungsten, which has a well known heat capacity. Convective losses were dominant up to 4000 K.

In analysis of the experiments, Ronchi et al. used an iterative numerical method to find the unique heat capacity  $C_p(T)$  that satisfies at any time the heat transport equation with the measured temperature boundary conditions and the one-dimensional unsteady energy conservation equation

$$\frac{dH}{dt} = \int_0^{r_0} 4\pi r^2 \rho(T) C_p(T) \frac{\partial T(r)}{\partial t} dr = \text{losses} \quad (6)$$

where  $H$  is the enthalpy,  $\rho(T)$  is the density as a function of temperature,  $C_p(T)$  is the heat capacity

at constant pressure as a function of temperature,  $T$  is the temperature,  $t$  is the time, and  $r_0$  is the radius of the  $\text{UO}_2$  microsphere. The losses in Eq.(6) are defined by the boundary condition: for  $r = r_0$  and  $t > 0$ ,

$$-k \frac{\partial T}{\partial r} = \varepsilon \sigma (T_S^4 - T_A^4) + D(T_S - T_A) - \phi_L(t) \quad (7)$$

where

$k$  = thermal conductivity of the sphere,

$T_S$  = sphere surface temperature,

$T_A$  = ambient temperature,

$\sigma$  = Stefan-Boltzmann constant,

$\varepsilon$  = total hemispherical emissivity,

$r_0$  = outer radius of the sphere,

$D$  = coefficient of convective and conductive heat losses to the environment,

and  $\phi_L$  = laser energy flux deposited onto the surface.

The quality of the experiments and selection of analyzed pulses was based on posttest metallographic examination of the microsphere to determine the integrity of the zone beneath the measured area. Because severe cracking and large voids influenced temperature measurements, data from samples with defects in the vicinity of the measured area were discarded. Of 120 laser shots, only 20 were considered of sufficient quality for data analysis. Figure 4 shows the heat capacity data and uncertainties which have been obtained from the graph in Figure 14 of reference 3 because the experimenters have not published their tabulated data points. The points designated as “Ronchi (Not Used)” in the legend of Figure 4 indicate data that the experimenters considered to be in error and were discarded in their data analysis. They fit their data to the equation:

$$C_p = 277 + \frac{1.1 \times 10^7}{T^2} \exp\left(\frac{15500 \pm 1000}{T}\right) + \frac{1.0 \times 10^{12}}{T^2} \exp\left(-\frac{35500 \pm 4000}{T}\right) \quad (8)$$

where T is the temperature in K and  $C_p$  is the heat capacity in  $\text{J kg}^{-1} \text{K}^{-1}$ . Heat capacities calculated with this equation are shown in Figure 4 as the curve labeled “RHSB”.

The experimenters comment [3] that the accuracy of the heat capacities obtained from their data analysis depends on the spherical symmetry and the precision of the physical properties used in the analysis. The data reduction and analysis by Ronchi et al.[3] assumed spherical symmetry of the heat pulse, spherical symmetry of the temperature distribution in the microsphere, and maintenance of the spherical shape of the microsphere throughout the measurement. Because the surface temperature was measured on only a small area of the sample, the analysis is only viable if this temperature can be assumed to be homogeneous and if the internal temperature field can be considered spherically symmetric [7]. Although the experimenters commented that posttest examination of their samples showed that the melting front was approximately circular, it is not clear from the paper that all the necessary spherical symmetries were always maintained throughout the measurements. The laser pulse duration ranged from 153 to 10 ms depending on the desired peak surface temperature (3100 to 7850 K) and the input power of the laser. The experimenters commented that the pulse duration was limited because the liquid adheres to the supporting tungsten needle for only a few tens of milliseconds before dropping. It is not clear how long the spherical symmetry of the liquid was maintained because the liquid drop must deform prior to dropping from the needle in tens of milliseconds. The plume of hot gas around the sample during the laser heating, shown in photographs in Figure 6 of Reference 3 and Figure 4 of Reference 7 are not spherical. It is not clear if this departure from spherical symmetry is due to (1) gas flow in the autoclave, (2) nonspherical energy input and heat transfer, (3) change in the sample shape from that of a sphere,

or some combination of these mechanisms.

Because the reliability of the calculated heat capacities depends on the accuracy of the physical properties used in the data analysis, the equations used for thermal conductivity and density have been compared with literature recommendations. Ronchi et al. [3] calculated the density of solid  $\text{UO}_2$  from:

$$\rho^S(T) = 10970[1+2.04 \times 10^{-5}(T-273) + 8.7 \times 10^{-9}(T-273)^2]^{-1} \quad (9)$$

where density  $\rho^S$  is in  $\text{kg m}^{-3}$  and T is in K. Densities calculated with this equation agree within 2% with values recommended in the recent assessment by Martin [12]. The thermal conductivity of solid  $\text{UO}_2$  in  $\text{W m}^{-1} \text{K}^{-1}$  was obtained from the equation of Hyland [13] for  $T > 2000$  K;

$$k(T) = (2.3 \pm 0.4) + \frac{2.25 \times 10^5}{T} \exp\left(-\frac{12410}{T}\right) \quad (10)$$

where T is in K. Melting point values calculated with this equation agree within 8% with the values recommended by Harding and Martin [14] but are 14% higher than the melting point value recommended in this INSC Material Properties Database assessment and analysis that includes the 1999 high-temperature heat capacity and thermal diffusivity data of Ronchi et al. [15].

Ronchi et al. [3] calculated the liquid density of  $\text{UO}_2$  from their least-squares fit to the data of Christensen [16] and Drotning [17]

$$\rho^L(T) = 10970[1+9.30 \times 10^{-5}(T-273)]^{-1} \quad (11)$$

where density is in  $\text{kg m}^{-3}$  and T is in K. The form selected for this equation is the same as that for the solid density. Values calculated with this equation differ significantly from those obtained from

the equation recommended by Drotning and the recent equation of Breitung and Reil [18] which is based on in reactor measurements of the density and thermal expansion from the melting point to 8000 K. The equation of Breitung and Reil [18] is:

$$\rho = 8860 - 0.9285(T - 3120) \quad (12)$$

where density ( $\rho$ ) is in  $\text{kg m}^{-3}$  and T is in K. Densities obtained from the equation by Breitung and Reil are in good agreement with values recommended by Drotning (within 1.2% from 3120 to 7600 K), and within 2.5% of the densities recommended from the melting point to 7600 K in an independent assessment by Harding, Martin, and Potter [6]. In Figure 5, densities calculated with the equation given by Ronchi et al. [3] are compared with the experimental data of Drotning and of Christensen, and with the equation recommended by Breitung and Reil. Densities calculated with the equation used by Ronchi et al. show a systematic deviation compared to densities calculated from the equation of Breitung and Reil. They deviate by -2% at the melting point, +4% at 4500 K, +16% at 6000 K, and +40% at 7600 K. Although the analytical form of equation selected by Ronchi et al. gives decreasing densities with increasing temperature, they do not decrease as fast as the linear equations recommended by Breitung and Reil and by Christensen. Fischer [11] comments that the linear decrease with temperature of the liquid density is well established by existing experiments and the only physical reason for the liquid density to deviate from a straight line is due to the approach of the critical point where the deviation is more negative. The critical temperature and density given by Fischer [11] are respectively 10600 K and  $1560 \text{ kg m}^{-3}$ . The possibility exists that the density equation used by Ronchi et al. includes the increase of density with pressure since experiments at higher temperatures were performed at high pressure. However, Ronchi et al. make no mention of including the effects of pressure in their equation for the liquid density. They simply state that the data of Drotning and of Christensen were fit to Eq. (11). Breitung and Reil have commented that along the saturation line, the change in density due to increasing pressure is much smaller than the change in density due to thermal expansion [18]. Even at 8000 K, the correction of density for saturation pressure is only a few percent [18] so the effects of pressure can be ignored. Thus, it is

unclear why the equation given by Ronchi et al. [3] for the liquid density of  $\text{UO}_2$  deviates so greatly from the expected liquid density behavior and recommended densities at high temperatures.

For the thermal conductivity of liquid  $\text{UO}_2$ , Ronchi et al. used  $2.5 \text{ W m}^{-1} \text{ K}^{-1}$ , which is the value obtained just above the melting point in recent measurements by Tasman [19] at the Institute for Transuranium Elements. This value is in agreement with the average value of  $2.2 \text{ W m}^{-1} \text{ K}^{-1}$  previously obtained by Tasman et al. [20] for the temperature range 3103-3473 K. In these earlier measurements, a thermal conductivity of  $2.4 \text{ W m}^{-1} \text{ K}^{-1}$  was obtained in an experiment in which the maximum top center temperature of the molten pool was 3473 K. In addition to the thermal conductivity measurements of Tasman et al. [19, 20],  $\text{UO}_2$  thermal diffusivity measurements were made by Kim et al. [21] from 3187 to 3310 K and by Otter and Damien [22] in the temperature range of 3133 to 3273 K. The available experimental data on the thermal diffusivity and thermal conductivity [19] of  $\text{UO}_2$  were reassessed in 1985 by Fink and Leibowitz [23] who recommended  $5.6 \text{ W m}^{-1} \text{ K}^{-1}$  for the thermal conductivity from the melting point to 3500 K. In this reassessment, Fink and Leibowitz used  $131 \text{ J mol}^{-1} \text{ K}^{-1}$  ( $485 \text{ J kg}^{-1} \text{ K}^{-1}$ ), the constant heat capacity given by the enthalpy equation of Rand et al. [4]. If the heat capacities given by Ronchi et al. had been used in the reassessment, lower thermal conductivity values ( $3.3$  to  $5.8 \text{ W m}^{-1} \text{ K}^{-1}$ ) would have been obtained in the assessment of these data. Ronchi et al. comment that the existence of a systematic error in the experimental measurements of Tasman et al. cannot be excluded. At low temperatures, their calculated heat capacity is approximately inversely proportional to the thermal conductivity. Thus, selection of a higher thermal conductivity in this low temperature region would give lower heat capacities.

Ronchi et al. have assumed a constant thermal conductivity based on the assumption that thermal conductivity of liquids obey the Lorenz rule and are therefore only a weak function of temperature. Because no temperature dependence was evident in any of the thermal diffusivity data and no information is available on variation of thermal conductivity with temperature from the

measurements of Tasman et al., there is no basis to assess this assumption. Wakeham [24] comments that the thermal conductivities of a number of liquids at high pressure are stronger functions of density change with pressure than functions of temperature. In their analysis, Ronchi et al. have not considered the effects of changes in pressure on the thermal conductivity although the high temperature measurements were done at pressures on the order of 100 MPa (1000 bar). Wakeham [23] found that for pressure variation from 0.1 to 700 MPa, the reduced thermal conductivity decreased as a function of increasing reduced molar volume (inverse reduced density).

***Relationship Between Enthalpy and Heat Capacity Measurements,  $C_p$  and  $C_\sigma$***

The enthalpy measurements by Leibowitz et al. [1] and by Hein and Flagella [2] were performed on encapsulated samples so that the liquid was maintained in equilibrium with a small amount of vapor giving the enthalpy along the saturation curve. The temperature derivative of these enthalpies is the heat capacity along the saturation curve,  $C_\sigma$ , which is related to the heat capacity at constant pressure,  $C_p$ , by:

$$\left( \frac{\partial H}{\partial T} \right)_\sigma = C_\sigma = C_p - \frac{(T\alpha_p - 1)}{\rho} \left( \frac{\partial P}{\partial T} \right)_\sigma \quad (13)$$

where  $P$  is the vapor pressure,  $\rho$  is the density,  $\alpha_p$  is the instantaneous thermal expansion coefficient,  $T$  is the temperature, and the subscript  $\sigma$  designates the saturation curve. For most liquids, the difference between  $C_p$  and  $C_\sigma$  is not significant at temperatures below 75% of the critical temperature. Recent vapor pressure measurements by Breitung and Reil [18] and equation of state calculations by Fischer [11] indicate that the critical temperature for  $\text{UO}_2$  is 10600 K. Thus, differences between  $C_p$  and  $C_\sigma$  are not significant below 7950 K. So for the temperature range of the  $\text{UO}_2$  enthalpy data, the temperature derivative of the equation that fits the enthalpy measurements may be considered as the heat capacity at constant pressure.

The heat capacity measurements of Ronchi et al. were not done at constant pressure because

measurements at constant pressure would have resulted in complete vaporization of the sample as the temperature was increased. Ronchi et al. used the saturated and total pressures from the equation of state of Fischer [11] to determine the pressure needed to prevent large losses from vaporization. However, the extent of increase from the saturation pressure is not clear from the description of the experiment. In the analysis of Ronchi et al. and the analysis below, the heat capacities reported by Ronchi et al. are assumed to be equivalent to  $C_p$ .

### ***Combined Analysis of Enthalpy and Heat Capacity Data***

Ronchi et al.[3] state that the enthalpy data of Hein and Flagella and of Leibowitz et al. are consistent with their equation 20, which will subsequently be referred to as “RHS Eq. 20”:

$$C_p(T) = 277 + \frac{(2370 \pm 290)}{(T/1000)^2} \quad (14)$$

where heat capacity is in  $\text{J kg}^{-1} \text{K}^{-1}$  and temperature is in K. The first term of this equation is the Neumann-Kropp heat capacity value for a harmonic triatomic lattice (9R) which was fixed so that the only free parameter in the fitting procedure was the coefficient for the second term. They fit their heat capacity data from 3200 to 4500 K to an equation of the same form allowing both parameters to vary giving their equation 21, which will be referred to as “RHS Eq. 21”:

$$C_p(T) = 67.7 + \frac{(3831 \pm 300)}{(T/1000)^2} \quad (15)$$

where heat capacity is in  $\text{J kg}^{-1} \text{K}^{-1}$  and temperature is in K.

A weighted chi-squared minimization analysis of has been made of the combined enthalpy and heat capacity data. This analysis included the enthalpy data of Leibowitz et al. [1] from 3173 to 3523 K and of Hein and Flagella [2] from 3123 to 3260 K and the heat capacity data of Ronchi et al. [3] from 3100 to 4500 K. Only the heat capacity at or below 4500 K have been included in this

combined analysis because:

- (1) above 4500 K, the deviations of the densities used by Ronchi et al. increases above 4% from accepted liquid densities;
- (2) at higher temperatures, the pressure in the autoclave was increased significantly to prevent sample vaporization;
- (3) at 4500 K and above, oxygen was added to the gas in an attempt to control the change in sample stoichiometry arising from vaporization so greater uncertainty exists in the stoichiometry of the sample and in the temperature measurements;
- (4) as the temperature increases, sample loss due to laser ablation and ionization effects from the laser heating become more pronounced;
- (5) data above 4500 K are not needed for light water nuclear reactor severe accident analysis because higher temperatures are unlikely in these accident scenarios.

The form of the equation for the heat capacity used in this combined analysis is that suggested by Ronchi et al. in their data analysis in this temperature range. A weighted chi-squared minimization was used to determine the coefficients. In a previous assessment [25], the value of the enthalpy at the melting point had been constrained to equal that given by the enthalpy equation of Rand et al.[4] in order for that analysis to be consistent with the heat of fusion of Rand et al. [4]. No constraint has been made on the enthalpy increment at the melting point in this analysis because the enthalpy of fusion must be redetermined because of changes to the enthalpy and heat capacity of the solid at the melting point. The data have been weighted by the inverse of their uncertainties. Because the enthalpy data are in excellent agreement in the two independent experiments [1, 2] which used standard techniques with calibration standards and the stoichiometry change in these enthalpy experiments were within the variation for reactor fuel, these data were considered to be of higher quality than the heat capacity data. The uncertainty in the enthalpy data has been estimated as 2%. Ronchi et al. state that the uncertainty in the heat capacity data is on the order of 15 to 20% from 3000 to 5000 K. A 15% uncertainty has been assumed for the heat capacity data. Thus, the

enthalpy chi-squared has been weighted by a factor of 50 relative to the heat capacity chi-squared in the combined chi-squared minimization.

Equations (1) and (2) are, respectively, the enthalpy and heat capacity equations obtained from this weighted chi squared minimization. In Figure 6, the enthalpy data are compared with Eq.(1) from this weighted fit, the linear equation of Rand et al., the enthalpies obtained from integration of the heat capacity equation of Ronchi et al. using a constant of integration that gives the enthalpy of Rand et al. at 3120 K (RHSR rel 3120), and the 1997 constrained fit to the enthalpy and heat capacity data [25]. The main difference between this weighted fit and the 1997 constrained fit is the value of the enthalpy increment at 3120 K. Enthalpy increments from these two analysis are within 0.3%, which is less than the uncertainty in the data. Equation (1) fits the data to within 0.7% except for the datum at 3475 K which is fit to 1.3 %. Greater deviation for the higher data may be expected because the stoichiometry variation detected by Leibowitz et al. most likely occurred during these high temperature measurements.

Figure 7 compares the heat capacity data of Ronchi et al. with a number of equations as a function of the square of the inverse temperature. Equations in Figure 7 are the constant heat capacity of Rand et al., RHSR Eq. 20 (the one-parameter enthalpy data fit of Ronchi et al.), RHSR Eq. 21 (the two parameters heat capacity fit of Ronchi et al.), RHSR (the fit by Ronchi et al. to all the heat capacity data) and the recommended equation, Eq.(2), which is the weighted combined fit to the enthalpy and heat capacity data. The equation obtained from this weighted combined analysis fits the heat capacity data as well as the equation suggested by Ronchi et al. for the entire temperature range (RHSR).

Figure 8 shows the heat capacity data with the error bars given by Ronchi et al., the fit by Ronchi et al. to data up to 4500 K (RHSR Eq. 21), the fit by Ronchi et al to the heat capacities for the entire temperature range (RHSR) and the weighted combined fit to the enthalpy and heat

capacities. All but four data are fit to within 10%. Data with error bars that do not intersect this combined fit are also not well represented by the RSH Eq. 21 indicating that they are not consistent with other heat capacity data in this temperature range.

## References

1. L. Leibowitz, M. G. Chasanov, L. W. Mishler, and D. F. Fischer, *Enthalpy of Liquid Uranium Dioxide to 3500 K*, J. Nucl. Mater. **39** 115-116 (1971).
2. R. A. Hein and P. N. Flagella, *Enthalpy Measurements of  $UO_2$  and Tungsten to 3260 K*, General Electric Report **GEMP-578** (February 16, 1968).
3. C. Ronchi, J. P. Hiernaut, R. Selfslag, and G. J. Hyland, *Laboratory Measurement of the Heat Capacity of Urania up to 8000 K: I. Experiment*, Nuclear Science and Engineering **113**, 1-19 (1993).
4. M. H. Rand, R. J. Ackermann, F. Gronvold, F. L. Oetting, A. Pattoret, *The Thermodynamic Properties of the Urania Phase*, Rev. Int. Hautes Temp. Refract. **15**, 355-365 (1978).
5. J. K. Fink, M. G. Chasanov, and L. Leibowitz, *Thermophysical Properties of Uranium Dioxide*, J. Nucl. Mater. **102**, 17-25 (1981); also as ANL Report ANL-CEN-RSD-80-3, Argonne National Laboratory (April 1981).
6. J. H. Harding, D. G. Martin, and P. E. Potter, *Thermophysical and Thermochemical Properties of Fast Reactor Materials*, Commission of the European Communities Report EUR 12402 EN (1989).
7. J.-P. Hiernaut, and C. Ronchi, *Calorimetric Measurements with Acoustic Levitation in High-Temperature Heating Experiments with Pulsed Laser Beams*, High Temps-High Pressures **21**, 119-130 (1989).
8. C. Ronchi, R. Beukers, H. Heinz, J. P. Hiernaut, and R. Selfslag, *Graphite Melting Under Laser Pulse Heating*, Int. J. Thermophys. **13** (1) 107-129 (1992).
9. J. L. Bates, Proc. IAEA Symp. Thermodynamics, Vienna, July 22-27 1965, Vol. II, p. 73, International Atomic Energy Agency, Vienna (1966); as referenced by C. Ronchi, J. P. Hiernaut, R. Selfslag, and G. J. Hyland, *Laboratory Measurement of the Heat Capacity of Urania up to 8000 K: I. Experiment*, Nuclear Science and Engineering **113**, 1-19 (1993).
10. M. G. Adamson, E. A. Aitken, and R. W. Caputi, *Experimental and Thermodynamic Evaluation of the Melting Behavior of Irradiated Oxide Fuels*, J. Nucl. Mater. **130**, 349-365

- (1985).
11. E. A. Fischer, *Evaluation of the Urania Equation of State Based on Recent Vapour Pressure Measurements*, Kernforschungszentrum Karlsruhe GmbH Report **KfK 4084** (September 1987); *Nuclear Science and Engineering* **101**, 97-116 (1989).
  12. D. G. Martin, *The Thermal Expansion of Solid  $UO_2$  and (U,Pu) Mixed Oxides - A Review and Recommendations*, *J. Nucl. Mater.* **152**, 94-101 (1988).
  13. G. J. Hyland, *Thermal Conductivity of Solid  $UO_2$ : Critique and Recommendation*, *J. of Nucl. Mater.* **113**, 125-132 (1983).
  14. J. H. Harding and D. G. Martin, *A Recommendation for the Thermal Conductivity of  $UO_2$* , *J. of Nucl. Mater.* **166**, 223-226 (1989).
  15. C. Ronchi, M. Sheindlin, M. Musella, and G. J. Hyland, *Thermal Conductivity of Uranium Dioxide up to 2900 K from Simultaneous Measurement of the Heat Capacity and Thermal Diffusivity*, *J. Appl. Phys.* **85**, 776-789 (1999).
  16. J. A. Christensen, *Thermal Expansion and Change in Volume of Uranium Dioxide on Melting*, *J. Am. Ceram. Soc.* **46**, 607-608 (1963).
  17. W. D. Drotning, *Thermal Expansion of Molten Uranium Dioxide*, Proceedings of the Eighth Symp. On Thermophysical Properties, Gaithersburg, Maryland, June 15-18, 1981, J. V. Sengers, Ed., ASME, New York, Vol. II, pp 245-249 (1981).
  18. W. Breitung and K. O. Reil, *The Density and Compressibility of Liquid (U,Pu)-Mixed Oxide*, *Nuclear Science and Engineering* **105**, 205-217 (1990).
  19. H. A. Tasman, *Thermal Conductivity of Liquid  $UO_2$* , Commission of the European Communities Joint Research Centre Annual Report **TUAR88**, Karlsruhe, Germany EUR-12385, p. 80 (1989), as referenced by C. Ronchi in *On the Thermal Conductivity and Diffusivity of Solid and Liquid Uranium Dioxide*, *J. Phys. Condens. Matter* **6**, L561-L567 (1994) .
  20. H. A. Tasman, D. Pel, J. Richter, and H. E. Schmidt, *Measurement of the Thermal Conductivity of Liquid  $UO_2$* , *High Temp.-High Pressures* **15**, 419-431 (1983).

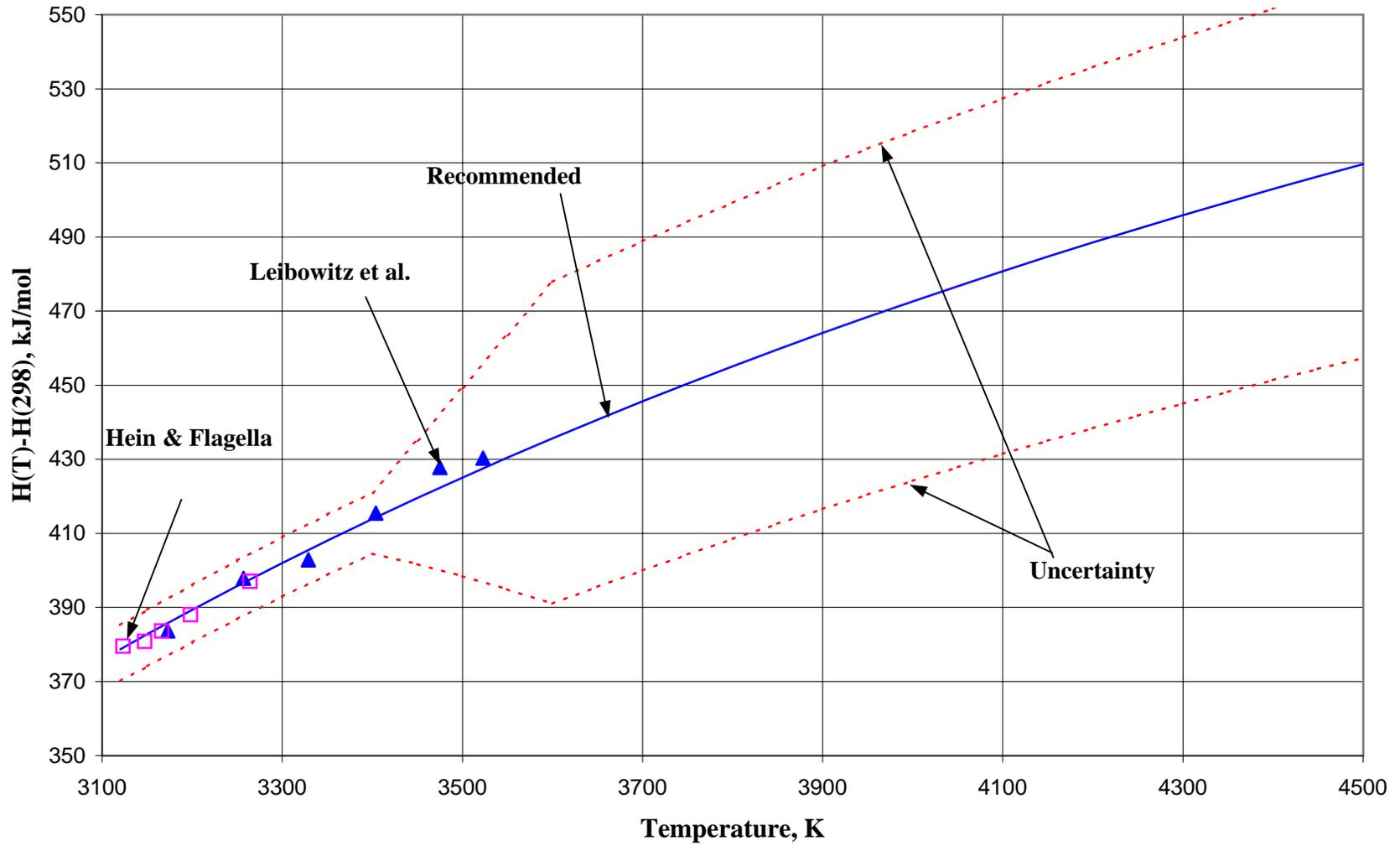
21. C. S. Kim, R. A. Haley, J. Fischer, M. G. Chasanov, and L. Leibowitz, *Measurement of Thermal Diffusivity of Molten UO<sub>2</sub>*, Proc. Seventh Symp. On Thermophysical Properties, A. Cezairliyan, Ed., ASME, New York, p. 338-343 (1977).
22. C. Otter and D. Damien, *Mesure de la Diffusivite Thermique de UO<sub>2</sub> Fondu*, High Temp.- High Pressures **16**, 1-6 (1984).
23. J. K. Fink and L. Leibowitz, *An Analysis of Measurements of the Thermal Conductivity of Liquid Urania*, High Temp.- High Pressures **17**, 17-26 (1985).
24. W. A. Wakeham, *Thermal Conductivity of Liquids Under Pressure*, High Temp.- High Pressures **21**, 249-259 (1989).
25. J. K. Fink and M. C. Petri, *Thermophysical Properties of Uranium Dioxide (Version 0 for Peer Review)*, Argonne National Laboratory Report **ANL/RE-97/2** (February 1997).

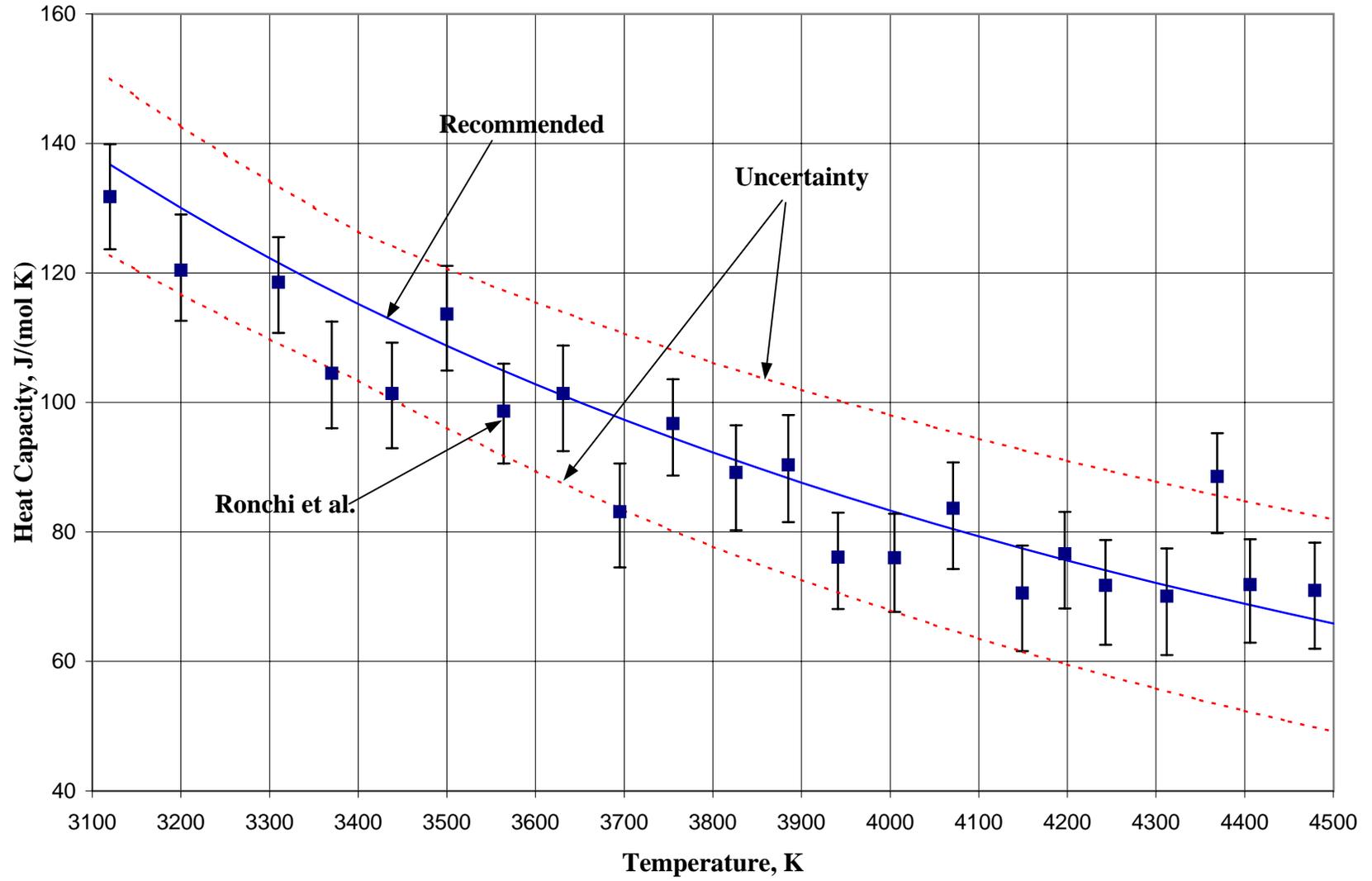
**Table 1 Enthalpy and Heat Capacity of Liquid UO<sub>2</sub> per mole of UO<sub>2</sub>**

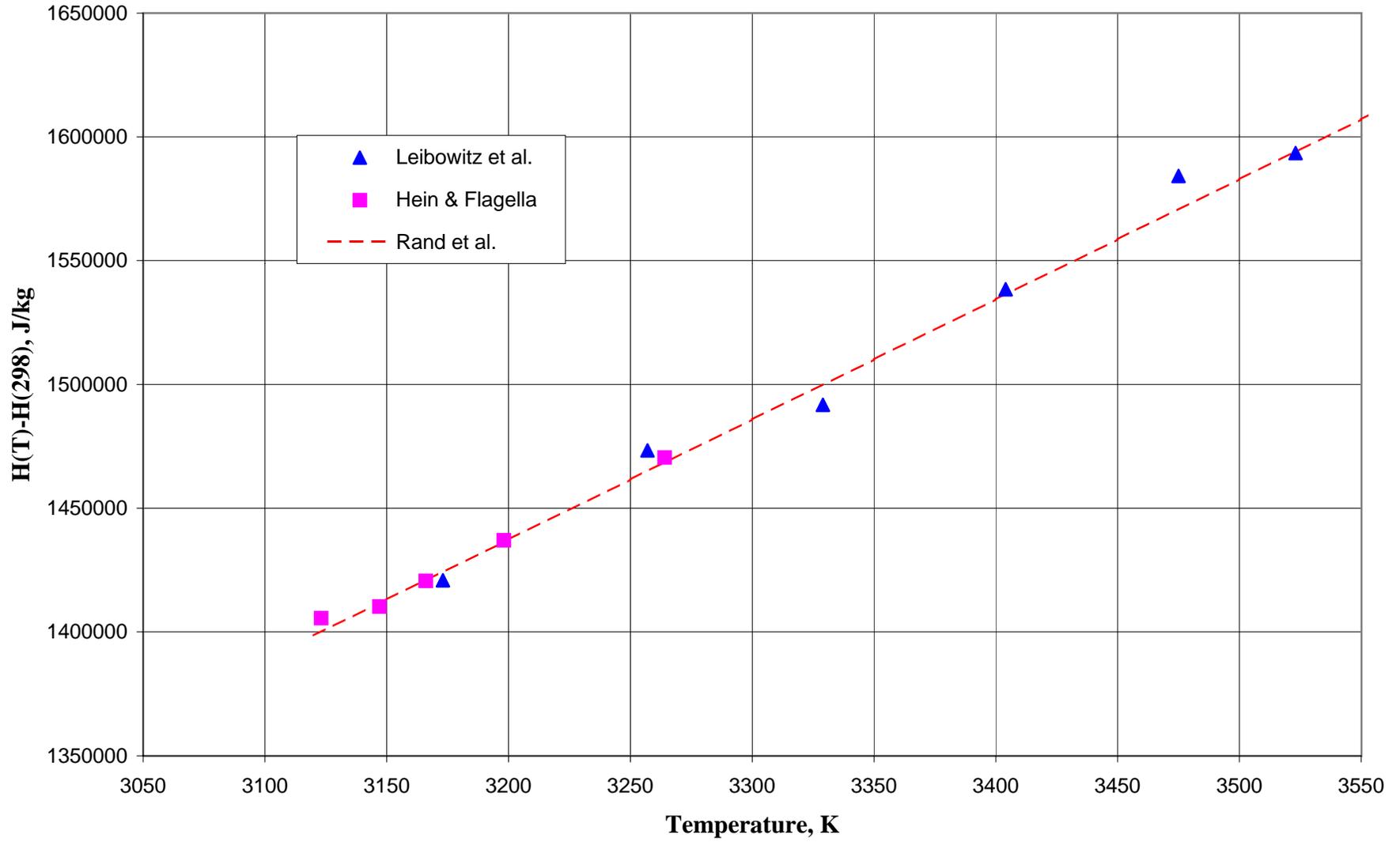
<b>Temperature K</b>	<b>Enthalpy H(T)-H(298.15 K) kJ mol<sup>-1</sup></b>	<b>Heat Capacity C<sub>P</sub> J mol<sup>-1</sup> K<sup>-1</sup></b>
3120	379	137
3150	383	134
3200	389	130
3250	396	126
3300	402	122
3350	408	119
3400	414	115
3450	420	112
3500	425	109
3550	430	106
3600	436	103
3650	441	100
3700	446	97.3
3750	450	94.7
3800	455	92.3
3850	460	89.9
3900	464	87.6
3950	468	85.4
4000	473	83.3
4050	477	81.3
4100	481	79.3
4150	485	77.4
4200	488	75.6
4250	492	73.8
4300	496	72.1
4350	499	70.5
4400	503	68.9
4450	506	67.4
4500	510	65.9

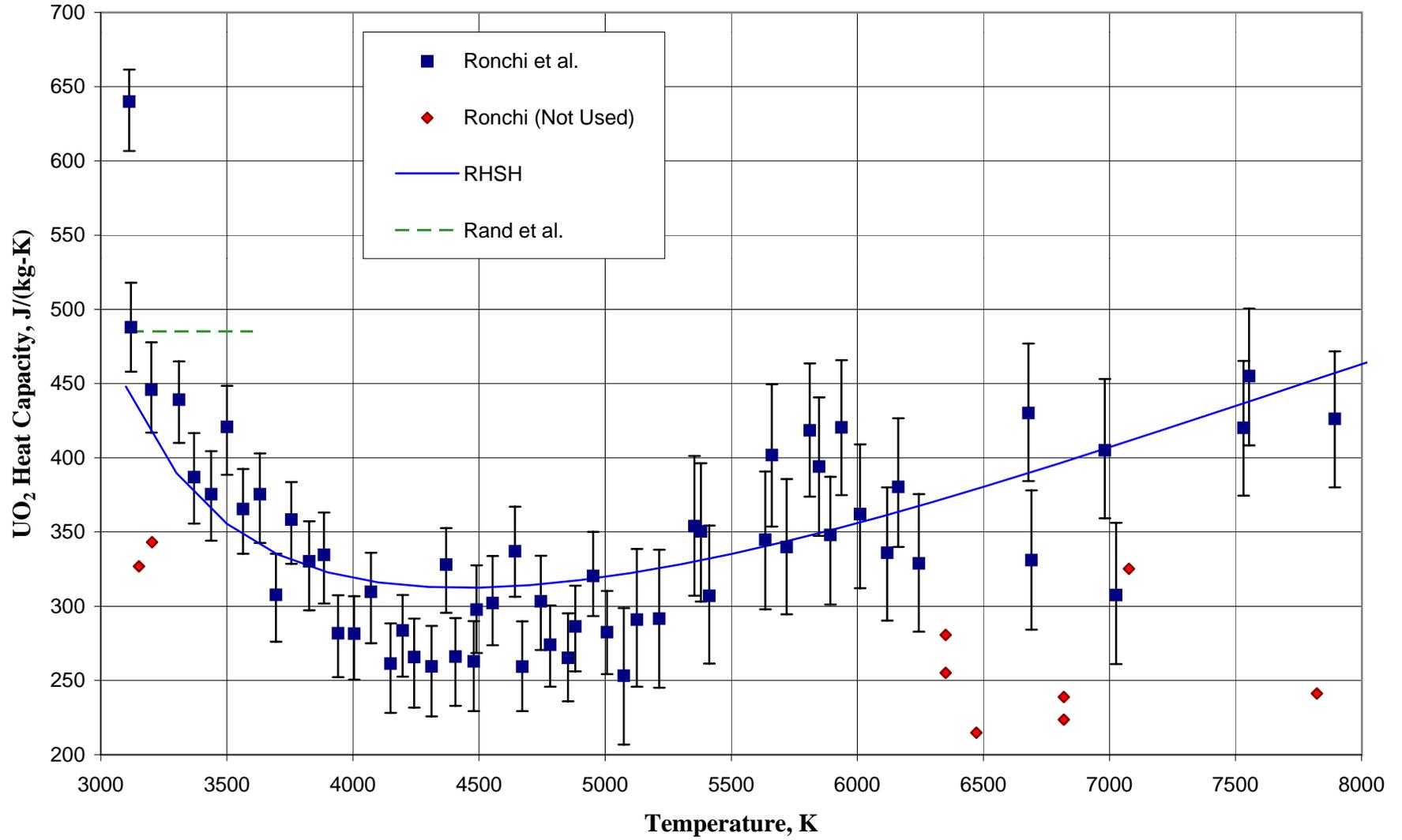
**Table 2 Enthalpy and Heat Capacity of Liquid UO<sub>2</sub> per kg of UO<sub>2</sub>**

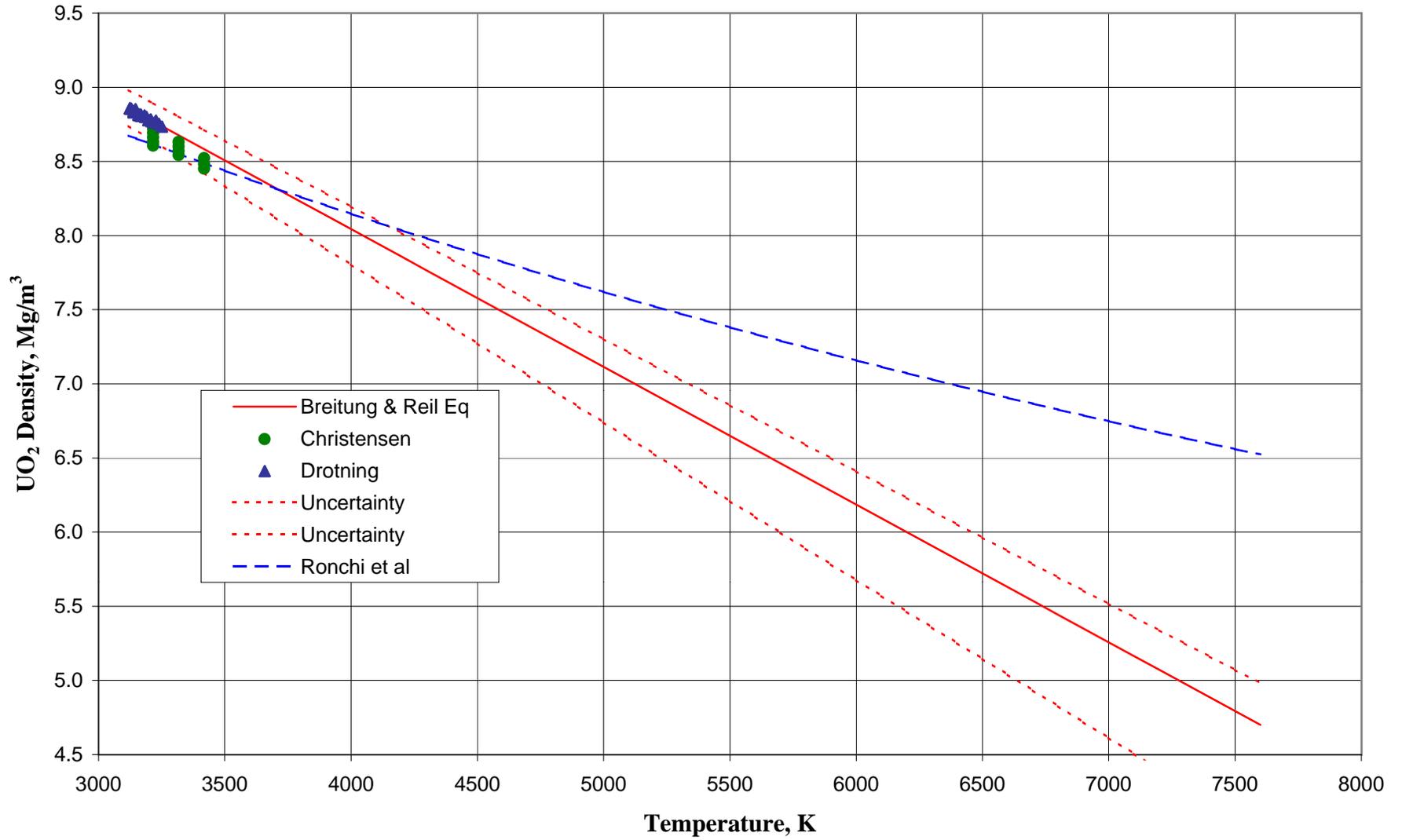
<b>Temperature K</b>	<b>Enthalpy H(T)-H(298.15 K) kJ kg<sup>-1</sup></b>	<b>Heat Capacity C<sub>P</sub> J kg<sup>-1</sup> K<sup>-1</sup></b>
3120	1403	507
3150	1418	497
3200	1442	482
3250	1466	467
3300	1489	453
3350	1511	439
3400	1533	427
3450	1554	414
3500	1574	403
3550	1594	391
3600	1613	381
3650	1632	370
3700	1650	360
3750	1668	351
3800	1686	342
3850	1702	333
3900	1719	325
3950	1735	316
4000	1750	309
4050	1766	301
4100	1781	294
4150	1795	287
4200	1809	280
4250	1823	273
4300	1837	267
4350	1850	261
4400	1863	255
4450	1875	249
4500	1888	244

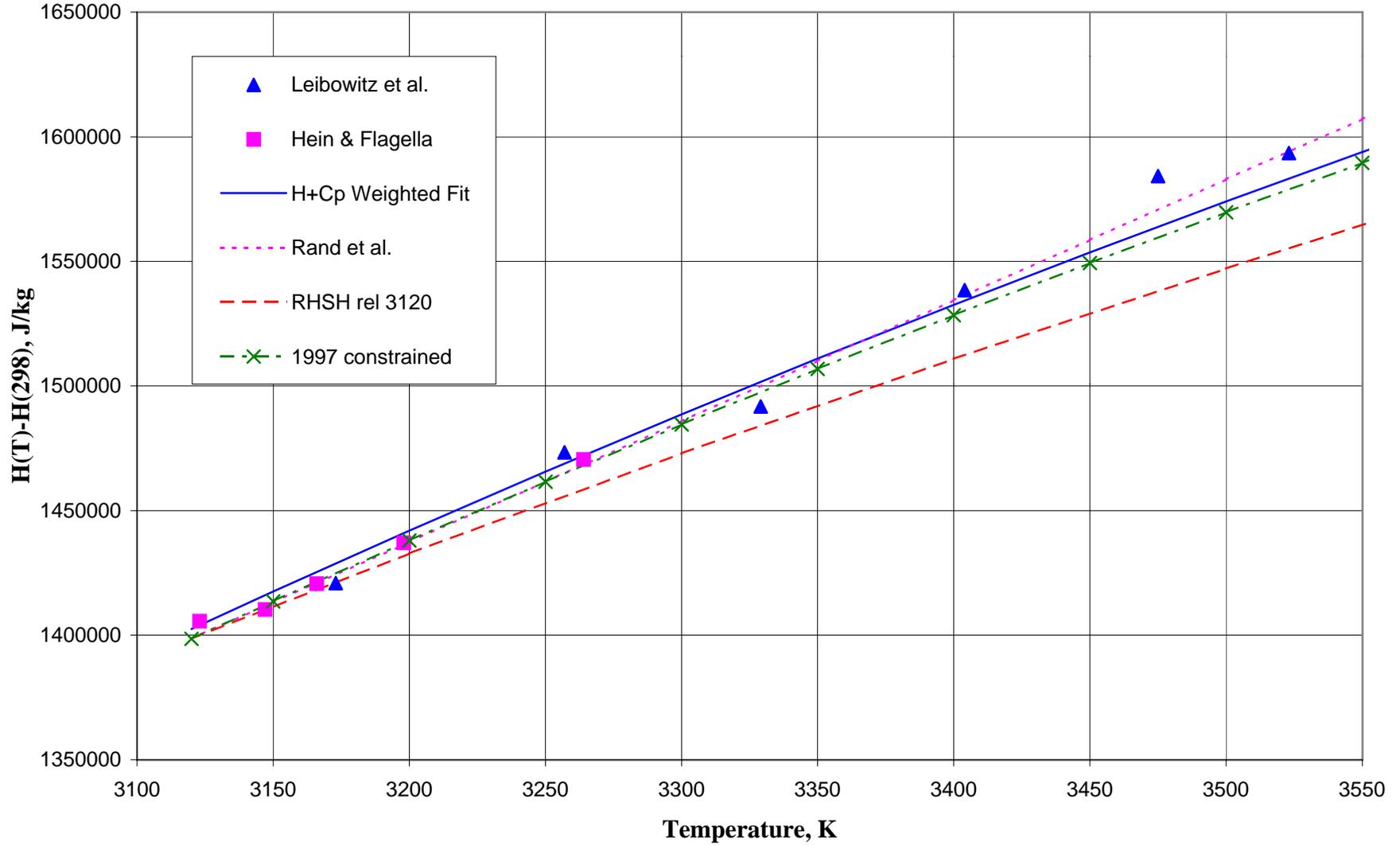
**Figure 1 Recommended Values for the Enthalpy of Liquid  $\text{UO}_2$** 

**Figure 2 Liquid UO<sub>2</sub> Heat Capacity**

**Figure 3 Fit of the Enthalpy of Liquid  $\text{UO}_2$  by Linear Equation of Rand et al.**

**Figure 4 Liquid UO<sub>2</sub> Heat Capacity Measurements of Ronchi et al.**

**Figure 5 Liquid Density of UO<sub>2</sub>**

**Figure 6 Comparison of Equations for the Enthalpy of Liquid  $\text{UO}_2$** 

**Figure 7 Comparison of Equations for the Heat Capacity of Liquid  $\text{UO}_2$**

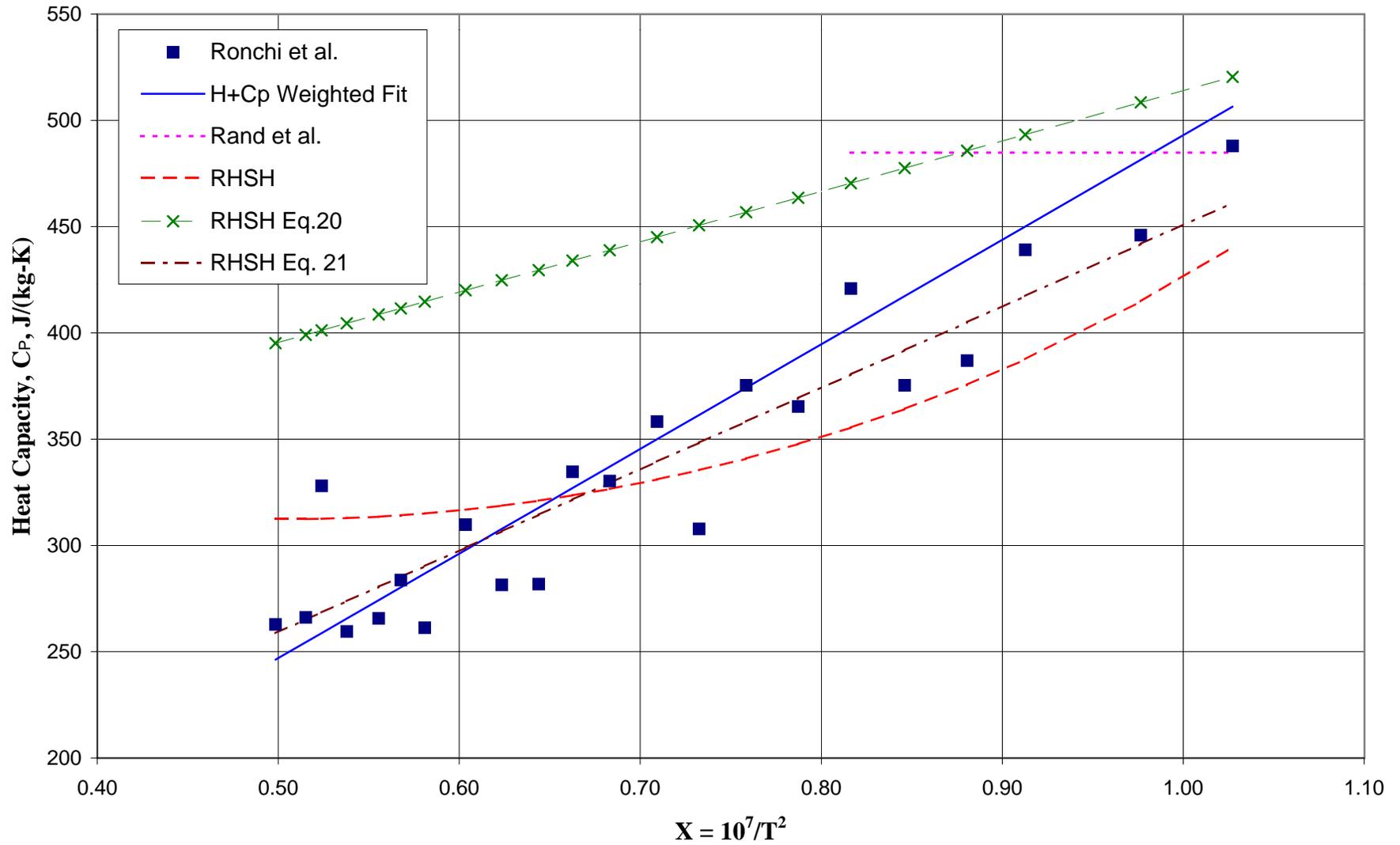


Figure 8 Liquid UO<sub>2</sub> Heat Capacity