Distribution Category:
General, Miscellaneous, and
Progress Reports (Nuclear)
(UC-2)

ANL-CEN-RSD-81-2

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

THE ENTHALPY AND HEAT CAPACITY OF SOLID UO_2

by

J. K. Fink, M. G. Chasanov, and L. Leibowitz

Chemical Engineering Division

May 1981

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Re 4

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	1
I. INTRODUCTION	1
II. DATA SELECTION AND ANALYSIS	2
III. RESULTS AND RECOMMENDATIONS	4
ACKNOWLEDGMENTS	7
REFERENCES	8

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Measured Values of $H(T) - H(298.15)$ and the Recommended Enthalpy Function to Fit These Values	6
2.	Experimental Heat Capacity Data and Plot of Recommended Equation to Fit Data	7

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Data on Enthalpy of Solid UO_2	3
2.	Data on Heat Capacity of Solid UO_2	3
3.	Standard Deviations for the Enthalpy and Heat-Capacity Data Using Different Approaches	4

THE ENTHALPY AND HEAT CAPACITY OF SOLID UO_2

by

J. K. Fink, M. G. Chasanov, and L. Leibowitz

ABSTRACT

Equations have been derived based upon a reevaluation of the enthalpy and heat-capacity data of UO_2 . We recommend a three-term nonlinear equation below 2670 K, with terms representing contributions from phonons, volumetric thermal expansion, and electrons, and a linear equation above 2670 K.

I. INTRODUCTION

Kerrisk and Clifton¹ and Rand *et al.*² have undertaken the most recent evaluations of the experimental data for the enthalpy and heat capacity of solid UO_2 . To correlate these data, Kerrisk and Clifton employed a modified Einstein relationship. The equation used by them to fit the enthalpy data consists of three terms,

$$\begin{aligned} H(T) - H(298) = & C_1 \theta \left[\left(e^{\theta/T} - 1 \right)^{-1} - \left(e^{\theta/298} - 1 \right)^{-1} \right] \\ & + C_2 \left[T^2 - (298)^2 \right] \\ & + C_3 e^{-E_D/RT} \end{aligned} \quad (1)$$

The first term, which dominates at low temperatures, is due to phonons. The second term is a contribution related to volumetric thermal expansion. The third term takes into account an anomalous contribution not included in the first two terms. The form of this last term in the Kerrisk-Clifton treatment was chosen to account for Frenkel defects. In the above equation, E_D is the activation energy for formation of an anion Frenkel defect.

Rand *et al.* analyzed the enthalpy and heat-capacity data for solid UO_2 and concluded that the Bredig³ proposal of a diffuse phase transition in UO_2 at 2670 K is reasonably supported. As a result, they fit the data to the Kerrisk-Clifton equation below 2670 K and a linear equation above that temperature.

Young,⁴ MacInness *et al.*,⁵ and Harding *et al.*⁶ have pointed out that it is more appropriate to attribute the anomalous contribution in enthalpy and heat capacity to electron effects rather than to Frenkel defects. Young suggests that the third term for enthalpy should be of the form:

$$\frac{-E_a/kT}{CkTe} \quad (2)$$

where k is Boltzmann's constant and E_a is the energy gap between the conduction and valence bands. The importance of the electronic contribution in thermal conductivity and thermal diffusivity^{4,7,8} suggests that, from a phenomenological point of view, the recommendation of Young, MacInness *et al.*, and Harding *et al.* is reasonable.

Motivated by this recommendation, we have reexamined the enthalpy and heat-capacity data for UO_2 . Comparisons were made of the data fits to the following types of equations: (1) a Kerrisk-Clifton (K-C) equation over the temperature range from 298 to 3120 K (the melting point), (2) a K-C equation with an electronic term for the anomalous contribution, (3) the Rand formulation using a K-C equation to 2670 K and a linear equation above that temperature, and (4) the Rand formulation with an electronic term in the low-temperature equation to represent the anomalous contribution.

The heat capacity at constant pressure was used as a check of the validity of the enthalpy expression selected. Heat capacity at constant pressure and enthalpy are related by the thermodynamic relation:

$$C_p = \left(\frac{\partial H}{\partial T} \right)_\sigma - V\gamma_\sigma + VT\alpha_p\gamma_\sigma \quad (3)$$

where H is the enthalpy, C_p is the heat capacity at constant pressure, V is the volume, α_p is the instantaneous volumetric thermal expansion coefficient, and $\gamma_\sigma = \left(\frac{\partial P}{\partial T} \right)_\sigma$ where P is the pressure. The subscript σ means that the derivative is defined along the saturation curve. For UO_2 , the term $-V\gamma_\sigma + VT\alpha_p\gamma_\sigma$, which distinguishes C_p from $\left(\frac{\partial H}{\partial T} \right)_\sigma$, is so small (on the order of $10^{-6} \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ compared to values of C_p on the order of $10^2 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) that it makes no contribution to Eq. 3 within the error of experimental data. Thus, for UO_2 heat capacity at constant pressure is very well approximated by

$$C_p \approx \left(\frac{\partial H}{\partial T} \right)_\sigma \quad (4)$$

II. DATA SELECTION AND ANALYSIS

Experimental measurements have been made for enthalpy⁹⁻¹³ and heat capacity at constant pressure¹⁴⁻¹⁹. In Table 1, the enthalpy data considered are listed according to date along with the temperature range and number of points of each experimental set. The heat capacity of solid uranium dioxide has been measured from 5 to 3150 K. Table 2 lists the heat-capacity data considered in this analysis. All data were converted to the 1968 International Practical Temperature Scale. The heat capacity data of Affortit and Marcon¹⁸ and Affortit¹⁹ from 350 to 3150 K were clearly at variance with those of other workers and, therefore, were not included in this analysis.

Since the enthalpy data cover a larger temperature range than the heat-capacity data, the enthalpy data were investigated first. Each of the four methods given above were used to fit the data. The K-C equation from 298 to 3120 K and the Rand formulation using the K-C equation below 2670 K are from

Table 1. Data on Enthalpy of Solid UO_2

Experimenter	Temperature Range, K	No. of Points	Year	Reference
Moore and Kelly	483-1464	14	1947	9
Ogard and Leary	1339-2306	13	1968	10
Hein and Flagella	1174-3112	33	1968	11
Leibowitz, Mishler, and Chasanov	2561-3088	12	1969	12
Fredrickson and Chasanov	674-1436	24	1970	13

Table 2. Data on Heat Capacity of Solid UO_2

Experimenter	Temperature Range, K	No. of Points	Year	Reference
Popov, Gal'chenko, and Seniv	433-876	28	1958	14
Engel	300-1000	8	1969	15
Gronvold, Kveseth, Sveen, and Tichy	304-1006	88	1970	16
Hunzicker and Westrum	5-346	109	1971	17

references 20 and 2, respectively. A nonlinear least-squares method described by Bevington²¹ was used (1) to determine the coefficients for the K-C equation with an electronic term for the anomalous contribution and (2) to determine the coefficients for Rand's two equations with the electronic term. The constraints

$$H(T) - H(298.15) = 0 \quad (5)$$

and

$$dH/dT(T = 298.15 \text{ K}) = 15.20 \text{ cal/mol} \quad (6)$$

were placed on the fitting functions. The enthalpy expression selected was substituted into Eq. 4 to obtain the heat capacity at constant pressure, which was compared with the experimental heat capacity.

Examination of the experimental data sets indicated that not all of them should be included in the final analysis. In the region from room temperature to 1500 K, the measurements of Moore and Kelly⁹ and Ogard and Leary¹⁰ do not agree well with those of Fredrickson and Chasanov.¹³ Because of the good agreement of the measured values of Fredrickson and Chasanov¹³ with those of Hein and Flagella,¹¹ which in turn agree well at high temperatures with the data of Leibowitz, Mishler, and Chasanov,¹² the data of Fredrickson and Chasanov¹³ were selected for use in the moderate temperature range. For each form of enthalpy equation, the parameters determined by a least-square fit of the experimental data do not differ appreciably whether or not the data of Ogard and Leary and Moore and Kelly are included in the analysis. However, all fits of the data were consistently better when the smaller data set was used. The selection of data set did not affect the relative closeness of any of the fits.

Because the heat-capacity data of Popov *et al.*¹⁷ are high and those of Engel¹⁶ appear to have a systematic error (they differ from data of other experimenters by a normalization), these two sets of data have not been included in the final assessment of the equation obtained to fit the enthalpy data. The resulting heat-capacity data set is the same considered by Rand *et al.*² in their analysis.

III. RESULTS AND RECOMMENDATIONS

Table 3 gives the standard deviations of the four approaches from the data sets for enthalpy (Table 1) and heat capacity (Table 2). The standard deviations given in Table 3 show that Rand's two equations with a phase transition at 2670 K fit the data better than does the single K-C equation for the entire temperature range, 298.15 to 3120 K. In addition, plots of the difference between experimental and calculated values at each data point and statistical analysis indicate that the use of the two-equation approach is justified.

Table 3. Standard Deviations for the Enthalpy and Heat-Capacity Data Using Different Approaches

	Standard Deviation, %	
	Enthalpy	Heat Capacity
(1) Kerrisk-Clifton (K-C)	0.94	0.95
(2) Rand (two equations)	0.68	0.92
(3) Modified K-C with electronic term	0.87	1.42
(4) Rand with electronic term (two equations)	0.63	0.88

Rand's two equations with an electronic term are the best fit for both the heat-capacity and enthalpy data, but are not significantly better than the Rand formulation with a Frenkel defect term. Nevertheless, the former approach is recommended because it is phenomenologically consistent with the well-accepted electronic contribution to thermal conductivity and thermal diffusivity and because theoretical studies^{4,5,6} have shown that the electronic contribution to enthalpy and heat capacity is significantly larger than the contribution due to Frenkel defects. In addition, the use of the two-equation form with an electronic term eliminates discontinuities that exist when the two equations originally proposed by Rand *et al.* are used. At the 2670 K phase transition, Rand's equations result in a change in enthalpy of 1.82 kJ/mol (0.8%) and a change in heat capacity of 16.88 J·mol⁻¹·K⁻¹ (10%). No such discontinuity is evident experimentally in other properties such as density, thermal conductivity, or thermal diffusivity. Thus, the original Rand equations introduce consistency problems in the calculation of thermodynamic and transport properties related to heat capacity. Our recommended equations (see below) give a 0.3 kJ/mol (0.13%) change in enthalpy at 2670 K and a 0.6 J·mol⁻¹·K⁻¹ (0.36%) change in heat capacity at 2670 K. These differences are within the relative standard deviation of the fit and are sufficiently small so as not to introduce discontinuities.

The recommended equations for enthalpy and heat capacity are given below. For 298.15 ≤ T ≤ 2670 K,

$$\begin{aligned}
 H(T) - H(T^*) &= C_1 \theta \left[\left(e^{\theta/T} - 1 \right)^{-1} - \left(e^{\theta/T^*} - 1 \right)^{-1} \right] \\
 &+ C_2 \left[T^2 - T^{*2} \right] \\
 &+ C_3 k (T - T^*) e^{-E_a/kT}
 \end{aligned} \tag{7}$$

and

$$\begin{aligned}
 C_p &= \frac{C_1 \theta^2 e^{\theta/T}}{T^2 \left(e^{\theta/T} - 1 \right)^2} + 2C_2 T \\
 &+ C_3 k e^{-E_a/kT} \left(1 + \frac{(T - T^*) E_a}{kT^2} \right)
 \end{aligned} \tag{8}$$

where $C_1 = 78.212 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$

$C_2 = 3.8616 \times 10^{-3} \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-2}$

$C_3 = 3.3993 \times 10^8 \text{ J} \cdot \text{mol}^{-1} \cdot \text{eV}^{-1}$

$\theta = 516.11 \text{ K}$

$$E_a = 1.8815 \text{ eV}$$

$$T^* = 298.15 \text{ K}$$

$$k = 8.6144 \times 10^{-5} \text{ eV/K (Boltzmann constant)}$$

In addition, H is in J mol^{-1} , C_p is in $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, and T is in kelvins. For $2670 \leq T \leq 3120 \text{ K}$,

$$H(T) - H(298.15) = 167.04T - 218342 \quad (9)$$

and $C_p = 167.0 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. In Eq. 9, H is in J/mol and T is in kelvins. Equation 9 is identical with the linear equation given by Rand *et al.*² The factor $(T - T^*)$ in the third term of Eq. 7, which differs slightly from that suggested by Young (Eq. 2), was included to satisfy the constraint given in Eq. 5.

Figures 1 and 2 show the enthalpy and heat-capacity data along with a graphical representation of our recommended equations. The shaded area above the curve in Figure 2 indicates the data of Gronvold *et al.*¹⁶ which they believe are high due to contamination of their sample by U_4O_9 .

Fig. 1.

Measured Values of $H(T) - H(298.15)$ and the Recommended Enthalpy Function to Fit These Values (Solid Curve)

Fig. 2.

Experimental Heat Capacity Data and Plot of Recommended Equation to Fit Data (Solid Curve). Shaded area designates the data of Gronvold *et al.*¹⁴ which they believe to be high due to contamination of their sample by U_4O_9 .

ACKNOWLEDGMENTS

We greatly appreciate the advise of Dr. R. A. Young on the theoretical basis of the electronic contribution to the enthalpy and heat capacity. The helpful comments, interest, and assistance of Dr. C. L. Fink in data fitting using nonlinear least-squares methods are gratefully acknowledged. Thanks are given to Pamela Dalman for typing this manuscript.

REFERENCES

1. J. F. Kerrisk and D. G. Clifton, Nucl. Technol. 16, 531 (1972).
2. M. H. Rand, R. J. Ackermann, F. Gronvold, F. L. Oetting, and A. Pattoret, Int. Rev. Hautes Temp. et Refract. 15, 355 (1978).
3. M. A. Bredig, Coll. Int. sur l'etudes des transformations cristalline à haute temperature, Odeillo, p. 183 (1971).
4. R. A. Young, J. Nucl. Mater. 87, 283 (1979).
5. D. A. MacInnes and C. R. A. Catlow, J. Nucl. Mater. 89, 354 (1980).
6. J. H. Harding, P. Masri, and A. M. Stoneham, J. Nucl. Mater. 91, 73 (1980).
7. P. Browning, J. Nucl. Mater. 92, 33 (1980).
8. J. C. Killeen, J. Nucl. Mater. 92, 136 (1980).
9. G. E. Moore and K. K. Kelley, J. Am. Chem. Soc. 69, 2105 (1947).
10. A. E. Ogard and J. A. Leary, *Thermodynamics of Nuclear Materials 1967*, IAEA, Vienna, p. 651 (1969).
11. R. A. Hein and P. N. Flagella, *Enthalpy Measurements of UO₂ and Tungsten to 3260 K*, General Electric Report GEMP-578 (February 16, 1968).
12. L. Leibowitz, L. W. Mishler, and M. G. Chasanov, J. Nucl. Mater. 29, 356 (1969).
13. D. R. Fredrickson and M. G. Chasanov, J. Chem. Thermodynamics 2, 263 (1970).
14. M. M. Popov, G. L. Gal'chenko, and M. D. Seniv, Zh. Neorg. Khim. 3, 1734 (1958); Trans. J. Inorganic Chem., USSR, 3, 18 (1958).
15. T. K. Engel, J. Nucl. Mater. 31, 211 (1969).
16. F. Gronvold, N. J. Kveseth, A. Sveen, and J. Tichy', J. Chem. Thermodyn. 2, 665 (1970).
17. J. J. Hunzicker and E. F. Westrum, J. Chem. Thermodyn. 3, 61 (1971).
18. C. Affortit and J. Marcon, Rev. Int. Hautes Temp. et Refract. 7, 236 (1970).
19. C. Affortit, High Temperature-High Pressure 1, 27 (1969).
20. L. Leibowitz, ed., *Properties for LMFBR Safety Analysis*, Argonne National Laboratory Report ANL-CEN-RSD-76-1 (April 1976).
21. Philip R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences*, McGraw-Hill, New York, NY (1969).