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Enthalpy and Heat Capacity of the Actinide Oxides

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The available enthalpy data on UO_2, ThO_2, PuO_2, $(Th, U)O_2$, and $(Pu, U)O_2$ have been analyzed and equations have been derived to fit the data. Phase transitions were found in UO_2, ThO_2, $(Th, U)O_2$, and $(Pu, U)O_2$. The high temperature PuO_2 data were too scattered to determine whether a phase transition exists. Above the phase transition temperature, the enthalpy data were fit with a linear equation. Enthalpy data for PuO_2 and ThO_2 below the phase transition temperature were fit with two-term equations whose contributions are due to phonons and thermal expansion. For UO_2 below its phase transition, a term for an electronic contribution was added to this basic equation. Below the phase transitions for $(Th, U)O_2$, enthalpy data were fit by a mole average of the equations used to fit the ThO_2 and UO_2 data below their phase transitions; however, the mole average equation was not valid for 90 and 92% ThO_2 in the mixed oxide. Since it was found that mole averages of the PuO_2 and UO_2 data do not fit the $(Pu, U)O_2$ data, these data were fit with an equation of the same form as that that used for UO_2.

KEY WORDS: actinide oxides; enthalpy; heat capacity; plutonium dioxide; thorium dioxide; thorium-uranium dioxide; uraniun dioxide; uraniun-plutonium dioxide.

1. INTRODUCTION

The enthalpy and heat capacity of the actinide oxides UO_2, ThO_2, PuO_2, $(Th, U))_2$, and $(Pu, U)O_2$ are needed for reactor safety calculations. The Kerrisk–Clifton equation [1] previously used to fit the enthalpy data of UO_2 consists of three terms, two of which are due to phonons and volumetric thermal expansion. The third term is a contribution that takes into account anomalous effects not included in the other two. Kerrisk and Clifton [1] attributed this anomalous term to Frenkel defects. Recently,

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there have been many papers [2–6] discussing whether this anomalous contribution is electronic in origin. Theoretical evidence strongly suggests that an electronic contribution is important in UO_2 [2–4]. Browning [6] has made a detailed analysis of the magnitude of contributions to the enthalpy of UO_2 from all possible mechanisms and has concluded that the anomalous contribution is electronic. However, since the data are equally well fit by an equation with a Frenkel defect term in place of the electronic term [7, 8], analysis of the UO_2 data alone does not give definitive proof that this anomalous contribution is electronic [4].

Analysis of enthalpy data for UO_2, ThO_2, and PuO_2 gives strong support for the proposal that the origin of the anomalous term in UO_2 is electronic. Solid-solid phase transitions for UO_2 and ThO_2 but not for PuO_2 have been incorporated in this analysis. In Section 3, the UO_2 enthalpy data below the phase transition at 2670 K are fit by an equation with an electronic term. The enthalpy data of ThO_2 below the phase transition at 2950 K and the enthalpy data of PuO_2 are fit in Section 4 by an equation similar to that used for UO_2 without an electronic term.

In an attempt to understand completely the enthalpy of the actinide oxide systems, the enthalpy data of $(Th, U)O_2$ and of $(Pu, U)O_2$ have also been analyzed. As in UO_2 and ThO_2, solid-solid phase transitions were also found for $(Th, U)O_2$ and $(Pu, U)O_2$. These two mixed oxides are discussed in Sections 5 and 6, respectively. Because of the limited amount of data available, a complete mathematical model to calculate the enthalpy of the entire $(Th, U)O_2$ and $(Pu, U)O_2$ systems has not been formulated. Nevertheless, methods to calculate the enthalpy of the $(Th, U)O_2$ system in the regions of experimental data are given, and equations that fit the $(Pu, U)O_2$ data and are consistent with those used for UO_2, ThO_2, and PuO_2 are presented. The next section gives a brief discussion of the theoretical basis for the equations selected to represent these data.

2. THEORY

In this analysis, the heat capacity of the actinide oxides is described by the equation

$$C_p = C_L + 2C_T T + C_A(T) \qquad (1)$$

where C_P is the heat capacity at constant pressure. C_L represents the lattice contribution to the constant volume heat capacity. The second term on the right-hand side of the equation represents the contribution from thermal expansion and also includes the anharmonic contributions, which are small in the cases under consideration. The last term is the anomalous contribution, which is attributed to electrons in this analysis.

The form chosen to describe the lattice contribution to the heat capacity at constant volume is the Einstein harmonic oscillator model of the lattice heat capacity, which is represented [9] by

$$C_L = 3Nk\left(\frac{\theta}{T}\right)^2 \frac{e^{\theta/T}}{\left(e^{\theta/T} - 1\right)^2} \tag{2}$$

where N is the number of oscillators, k is the Boltzmann constant, and θ is the Einstein temperature. In this equation, $\theta = \hbar\omega/k$ where ω is the frequency and $\hbar$ is Planck's constant, h, divided by 2π. The Einstein model on which Eq. (2) is based has been chosen instead of the Debye model [9], in order to obtain a relatively simple equation for use in reactor safety calculations.

The second term in Eq. (1) consists mainly of the thermal expansion contribution arising from the thermodynamic relation [10]

$$C_P = C_V + \frac{\alpha_P^2 VT}{\beta_T} \tag{3}$$

where α_P is the thermal expansion coefficient, V is the molar volume, and β_T is the isothermal compressibility. The representation of the thermal expansion contribution by a constant times temperature is not strictly correct because α_P, β_T, and V are functions of temperature. However, examination of the temperature dependence of these properties for solid uranium dioxide in the temperature range 298.15–1600 K, where experimental data are available [11], indicates only a small increase in $\alpha_P^2 V/\beta_T$ with temperature. The values obtained for $2C_T$ by fitting the experimental enthalpy data of UO_2 and ThO_2 are consistent with the calculated values.

Browning [6] included in his analysis of the heat capacity of UO_2 an anharmonic contribution, which he described by

$$C_{\text{anh}} = 2B^2kRT/K^3 \tag{4}$$

where $K = 7.15 \times 10^{-12}$ erg · Å^{-2} and $B = -10.8 \times 10^{-12}$ erg · Å^{-3}. Since this contribution has a linear temperature dependence, it may be assumed to be included in the second term of Eq. (1). However, the anharmonic contribution is so small, on the order of 1% of the enthalpy from 298.15 to 2670 K, that it is of the same order of magnitude as the error in the experimental data. The contribution from thermal expansion is of the order of 4.5% of the enthalpy at 298.15 K and 8.9% at 2670 K. Thus this anharmonic contribution, while only a small contribution to the total enthalpy, is significant compared to the thermal expansion contribution, and the second term in Eq. (1) may be described as containing the thermal expansion and anharmonic contributions.

The last term in Eq. (1) is the contribution due to electrons. The form that has been chosen to describe this term is the one suggested by Young [2]. The form of this last term is

$$C_3 k e^{-E_a/kT}\left(1+\frac{E_a}{kT}\right) \tag{5}$$

where k is the Boltzmann constant, and the quantity E_a is the electron activation energy.

In his analysis of the heat capacity of UO_2, Browning [6] also includes a Schottky or crystal field contribution. His analysis has shown that this contribution is small compared to those due to phonons and thermal expansion. For simplicity in formulation of analytic expressions to describe the enthalpy and heat capacity, the Schottky contribution has not been included explicitly in this analysis. This exclusion may be the origin of small differences between the two analyses in the contributions attributed to the phonon and thermal-expansion terms.

In this analyis, the heat capacity of uranium dioxide is described by Eq. (1), and the heat capacities of thorium dioxide and of plutonium dioxide are described by only the first two terms of Eq. (1). No additional term is needed to fit the experimental enthalpy data of ThO_2 and PuO_2.

3. ENTHALPY OF UO_2

Experimental measurements of the enthalpy of solid UO_2 have been made from 483 to 3112 K [12–18]; measurements of heat capacity at constant pressure have been made from 5 to 1006 K [19–24]. All data were converted to the 1968 International Practical Temperature Scale. Motivated by the theoretical basis for an electronic contribution to the enthalpy and heat capacity of UO_2 [2–5], the enthalpy data below the phase transition at 2670 K [25] were fit using a nonlinear least-squares method [26] by the equation

$$\begin{aligned} H_T^0 - H_{298.15}^0\,(\mathrm{J\cdot mol^{-1}}) = {} & C_1\theta\left[\left(e^{\theta/T}-1\right)^{-1} - \left(e^{\theta/298.15}-1\right)^{-1}\right] \\ & + C_2\left[T^2-(298.15)^2\right] \\ & + C_3 k\left(Te^{-E_a/kT} - 298.15e^{-E_a/k(298.15)}\right) \end{aligned} \tag{6}$$

where T is in K and k is the Boltzmann constant $= 8.6144 \times 10^{-5}\ \mathrm{eV \cdot K^{-1}}$. The three terms in Eq. (6) represent contributions due to phonons,

Table I. Parameters in the equation

$$H_T^0 - H_{298.15}^0 = C_1\theta\left[(e^{\theta/T} - 1)^{-1} - (e^{\theta/298.15} - 1)^{-1}\right]$$
$$+ C_2[T^2 - (298.15)^2] + C_3k(Te^{-E_a/kT} - 298.15e^{-E_a/k(298.15)})$$

to fit the UO_2, ThO_2, $(Th, U)O_2$ and $(Pu, U)O_{2-x}$ Enthalpy Data

Oxide	θ (K)	C_1 ($J \cdot mol^{-1} \cdot K^{-1}$)	$C_2 \times 10^3$ ($J \cdot mol^{-1} \cdot K^{-2}$)	C_3 ($J \cdot mol^{-1} \cdot eV^{-1}$)	E_a (eV)
UO_2	516.12	78.215	3.8609	3.4250×10^8	1.9105
ThO_2	408.14	68.654	4.8174		
PuO_2	587.41	87.394	3.9780		
$(Th_{0.92}U_{0.08})O_2$	268.87	62.072	6.4546		
$(Th_{0.90}U_{0.10})O_2$	438.35	71.759	3.0214		
$(Pu, U)O_{2-x}$	585.49	87.104	0.80048	2.6863×10^6	0.75748

thermal expansion, and electrons, respectively.[2] The values used for the parameters, θ, C_1, C_2, C_3, and E_a are given in Table I. Equation (6), which is the integral of Eq. (1), is constrained by the conditions

$$H_T^0 - H_{298.15}^0 = 0\big|_{T=298.15\ K} \tag{7}$$

and

$$\left(\frac{\partial H}{\partial T}\right)_P\bigg|_{T=298.15} = C_P(298.15\ K) = 63.6\ J \cdot mol^{-1} \cdot K^{-1} \tag{8}$$

The above value for the heat capacity at 298.15 K is from experimental measurements by Huntzicker and Westrum [20]. Further details of the selection of experimental data and the analysis itself can be found in ref. [8].

Above the phase transition of 2670 K and below the melting point of 3120 K, the data were fit to the linear equation recommended by Rand et al. [7]: For $2670 \leqslant T \leqslant 3120$ K,

$$H_T^0 - H_{298.15}^0\ (J \cdot mol^{-1}) = 167.04T - 218{,}342 \tag{9}$$

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[2] The form of the third term of Eq. (6) has been modified from that used in previous publications of the author at the suggestion of C. Roderick who recommended this form of invoking the constraint of zero at 298.15 K since it results in a simpler expression for the heat capacity. The calculated values by the two forms are essentially unchanged and the nonlinear-least squares fits to the data are identical.

Table II. Standard Deviations of Enthalpy and Heat Capacity Data from Equations Using Different Methods

	Standard deviation (%)		
	Enthalpy	Heat capacity	Ref.
Two equations with electronic terms	0.63	0.88	This report
Two equations with Frenkel defect term	0.68	0.92	[7]
One equation with electronic term	0.87	1.42	[8]
One equation with Frenkel defect term	0.94	0.95	[1]

In this analysis of the enthalpy of UO_2, a phase transition at 2670 K as predicted by Bredig [25] has been incorporated. Statistical analysis of the data show that the use of two equations with a phase transition at 2670 K is justified. Table II compares the standard deviations to the UO_2 enthalpy data [14, 17, 18] and the heat capacity data [19, 20] for equations using both electronic and Frenkel defect terms with and without a phase transition. The equation with a Frenkel-defect contribution but without a phase transition is that given by Kerrisk and Clifton [1].

Table II shows that the exclusion of a phase transition at 2670 K gives a significantly poorer fit to the enthalpy data for both descriptions of the anomalous contribution. An F test on the χ^2 for the different fits indicated that the difference in the standard deviations (0.63% versus 0.87%) is sufficient to justify statistically the use of two equations. The two-equation formulation is further supported by the pronounced phase transition at 2950 K in the recent experimental data for ThO_2 enthalpy obtained by Fischer et al. [27]. The ratio of phase-transition temperature to melting point is approximately the same for both of these actinide oxides. This observation of a phase transition in ThO_2 supports the Bredig theory and lends credence to the existence of an analogous phase transition in UO_2.

Table II also shows that the enthalpy data are fit equally well by Eqs. (6) and (9) as by equations recommended by Rand et al. [7] in which a Frenkel defect term replaces the electronic term in Eq. (6). Equations (6) and (9) have been selected over the equations suggested by Rand et al. [7] for the following reasons: (a) there is theoretical evidence [2–4] of an electronic contribution to the enthalpy and heat capacity of UO_2; (b) enthalpy data on ThO_2 and PuO_2, which show no Frenkel defect contribution, support an electronic contribution to UO_2 since it is expected that a Frenkel defect contribution would also affect ThO_2 and PuO_2, whereas theory predicts an electronic contribution for UO_2 alone; (c) consistency with our treatment of thermal conductivity of UO_2 [28, 29] is desired.

The curve in Fig. 1 shows the enthalpy of UO_2 relative to 298.15 K, calculated from Eqs. (6) and (9); also shown are the experimental data [14, 17, 18] fit by these equations. The heat capacity of UO_2 can be calculated by differentiation of Eqs. (6) and (9). For $298.15 \leqslant T \leqslant 2670$ K,

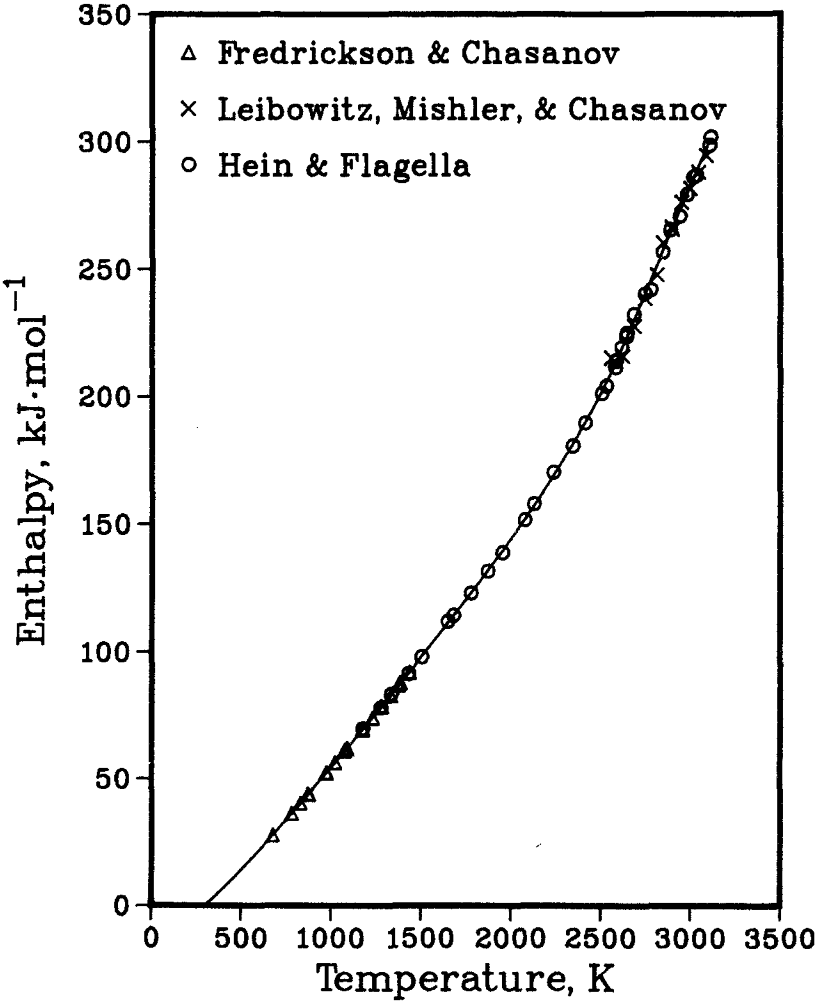

Fig. 1. Measured values of $H_T^0 - H_{298.15}^0$ for UO_2 and the equations to fit these data.

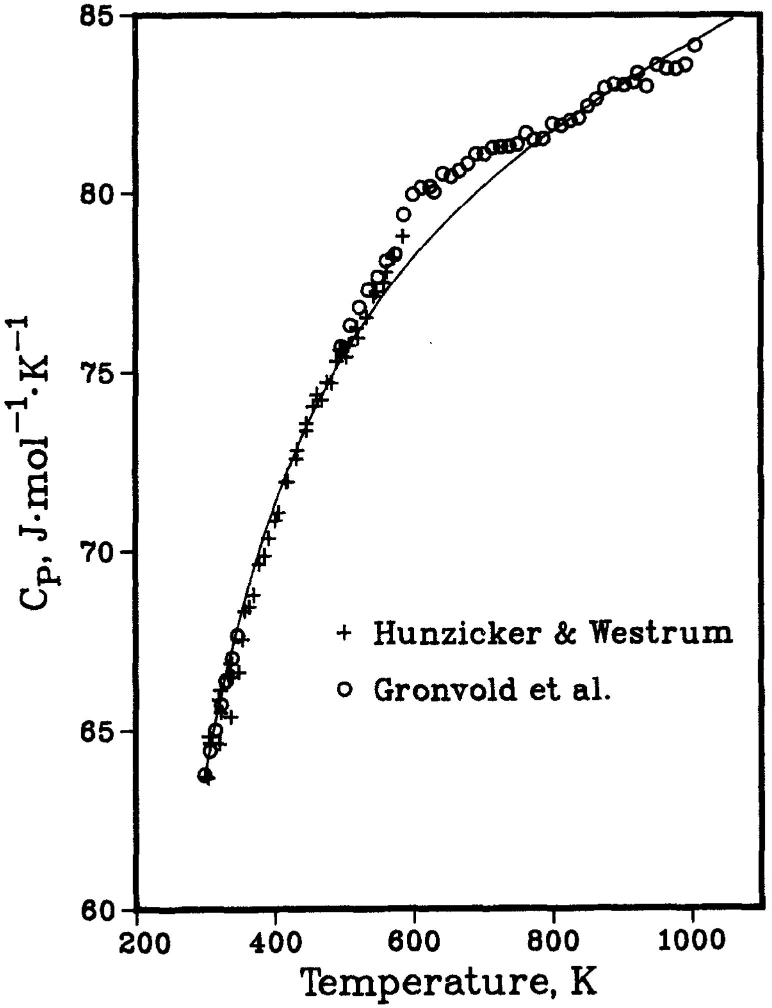

Fig. 2. Comparison of experimental and calculated heat capacity of UO_2.

this yields

$$C_P\ (\mathrm{J \cdot mol^{-1} \cdot K^{-1}}) = \frac{C_1\theta^2 e^{\theta/T}}{T^2\left(e^{\theta/T}-1\right)^2} + 2C_2T + C_3ke^{-E_a/kT}\left(1+\frac{E_a}{kT}\right) \qquad (10)$$

where k is the Boltzmann constant = 8.6144×10^{-5} eV · K^{-1}. The values used for the parameters in Eq. (10) are given in Table I. The three terms in Eq. (10) are attributed, respectively, to phonons, thermal expansion with an anharmonic contribution, and electrons. For $2670 \leqslant T \leqslant 3120$ K,

$$C_p = 167.04 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \tag{11}$$

Figure 2 shows the heat capacity calculated with Eq. (10) as well as the experimental data [19, 20]. Gronvold et al. [19] state that their data in the temperature region 600–775 K, which is located above the curve, is believed to be high because of contamination of their sample by U_4O_9.

4. ENTHALPY OF ThO_2 AND PuO_2

The enthalpy of ThO_2 from 323 to 3400 K has been measured [7, 30–34]. Table III provides information about the available experimental data. The only heat capacity measurements on ThO_2 were obtained at low temperatures, from 10 to 305 K, by Osborne and Westrum [35]. The available enthalpy data were converted to the 1968 International Practical Temperature Scale. The recent experimental data of Fischer et al. [27] show a pronounced phase transition for ThO_2 in the neighborhood of 2950 K. Slagle [36] also identified a phase transition at this temperature region in thoria creep data. While Bredig [25] predicted the existence of a phase transition in ThO_2, he did not suggest a temperature for this transition as he did for the transition in UO_2. The temperature 2950 K was selected for this phase transition by examination of the slopes of the curve defined by the data points in the region of the suspected phase transition followed by minimization of both the nonlinear least-squares fit to the data below the possible transition temperature and the linear least-squares fit above this temperature. At temperatures below the phase transition of 2950 K [27],

Table III. Measurements of the Enthalpy of ThO_2

Experimenter/ref.	Temperature range (K)	Number of points	Deviation from fit (%)	Year
Jaeger and Veenstra [31]	671–1666	12	1.25	1934
Southard [32]	905–1594	6	0.46	1941
Southard [32]	523–1789	16	1.35	1941
Hoch and Johnston [30]	1458–2758	9	0.87	1961
Victor and Douglas [33]	323–1174	27	1.21	1961
Springer et al. [34]	374–2261	17	1.76	1967
Fischer et al. [27]	2415–3400	13	0.62	1981

these data were fit, by a nonlinear least-squares method [26], to an equation of the form of Eq. (6) without the electronic term. The parameters used in this fit are given in Table I. This modified Eq. (6) was constrained by Eq. (7) and by the heat capacity given by Osborne and Westrum at 298.15 K:

$$\left(\frac{\partial H}{\partial T}\right)_P\Bigg|_{T=298.15} = C_P(298.15\text{ K}) = 61.74\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} \tag{12}$$

Above the phase transition at 2950 K, the enthalpy data were fit to the linear equation

$$H_T^0 - H_{298.15}^0\,(\text{J}\cdot\text{mol}^{-1}) = 142.33T - 192{,}920 \tag{13}$$

The standard deviation of the data from the fit using these two equations is 1.24%. Table III gives the standard deviation of each set of experimental data from the fit. Figure 3 gives the fit to the experimental data.

The enthalpy of PuO_2 has been measured by Kruger and Savage [37] from 298 to 1404 K, by Ogard [38] from 1500 to 2715 K, and by Oetting and Bixby [39] from 353 to 1610 K. The five points of Ogard above 2370 K were not included in this analysis since they appear to be measurements of the enthalpy of substoichiometric plutonium dioxide in the two-phase region. The partial melting of the samples of Ogard above 2370 K is most likely a consequence of the reaction between plutonium dioxide and the tungsten container [40]. Ogard also recommends the exclusion of these five data. The PuO_2 data were fit by a nonlinear least-squares method [26] to an equation of the form of Eq. (6) without the electronic term. This equation was constrained by Eq. (7) and by the condition

$$\left(\frac{\partial H}{\partial T}\right)_P\Bigg|_{T=298.15} = C_P(298.15\ K) = 66.24\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} \tag{14}$$

The heat capacity at 298.15 K was obtained from measurements by Flotow et al. [41]. Table I gives the parameters used in the fit. The data are fit by Eq. (6) without an electronic term with a standard deviation of 2.15%. The standard deviations for this enthalpy equation are 1.45% for the data of Kruger and Savage [37], 3.02% for the data of Ogard [38], and 2.24% for the data of Oetting and Bixby [39].

Although the occurrence of phase transitions in UO_2 might lead to the expectation of a similar transition in PuO_2, no phase transition has been used in this fit to the PuO_2 data. The reasons for not including a phase transition are (a) the scatter in the four points in the region where a phase transition may be expected (2160–2370 K) is large, and (b) the lack of any higher temperature data make it impossible to determine the presence or

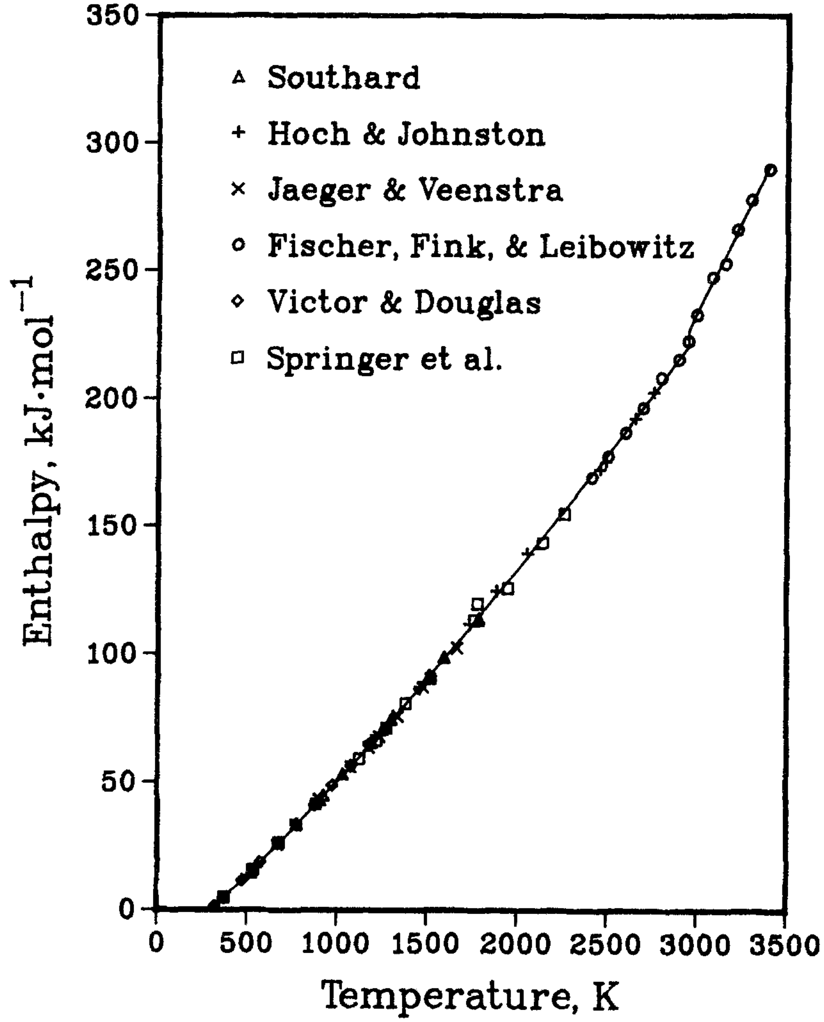

Fig. 3. Experimental enthalpy of ThO_2 and the calculated fit to the data.

absence of a phase transition from the available enthalpy data. Examination of Fig. 4, which gives this fit to the experimental data, shows that the scatter of the high temperature data is too great to draw any definite conclusions via data analysis and statistical methods. Thus while this analysis provides a reasonable equation for the calculation of the enthalpy of PuO_2, it also indicates that more accurate high-temperature enthalpy measurements of PuO_2 are greatly needed.

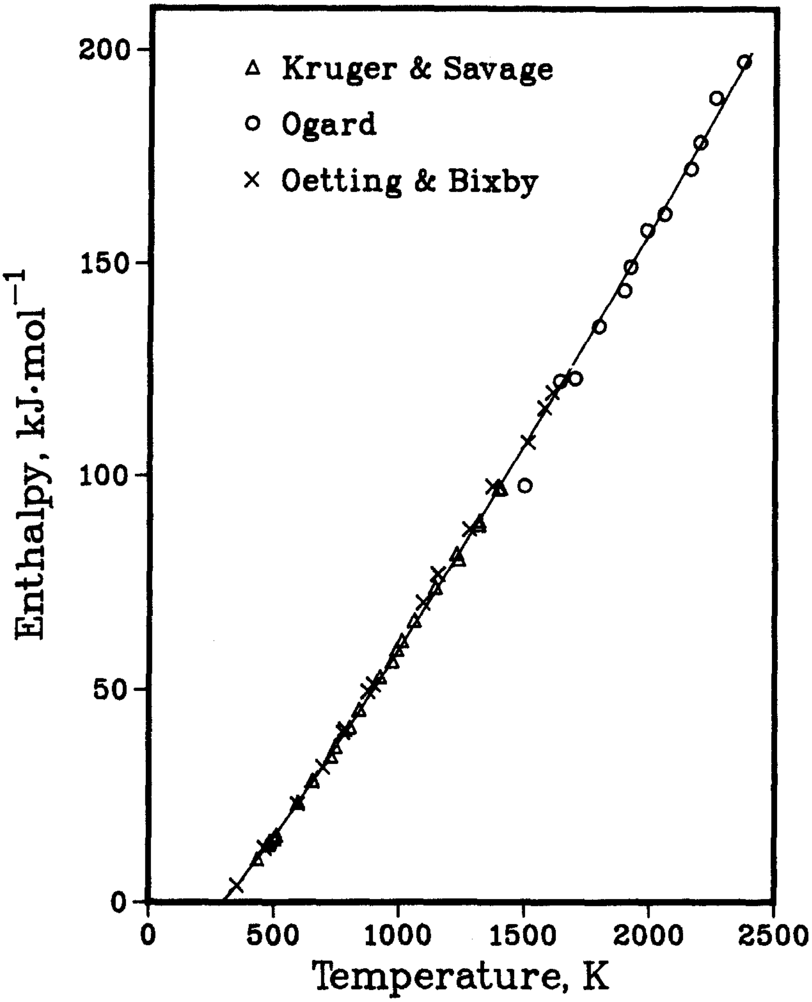

Fig. 4. PuO_2 enthalpy measurements and fit to these data.

The heat capacity of ThO_2 and of PuO_2 may be calculated from the first two terms of Eq. (10), using the parameters given in Table I. No heat capacity data above 298.15 K exist for these two oxides for comparison with calculated values. The calculated heat capacity of these two actinide oxides as well as the heat capacity of UO_2 are illustrated in Fig. 5 and given in Table IV. Table IV gives the thermodynamic functions of UO_2, PuO_2, and ThO_2. Note the large increase in the heat capacity of ThO_2 at the phase transition, 2950 K.

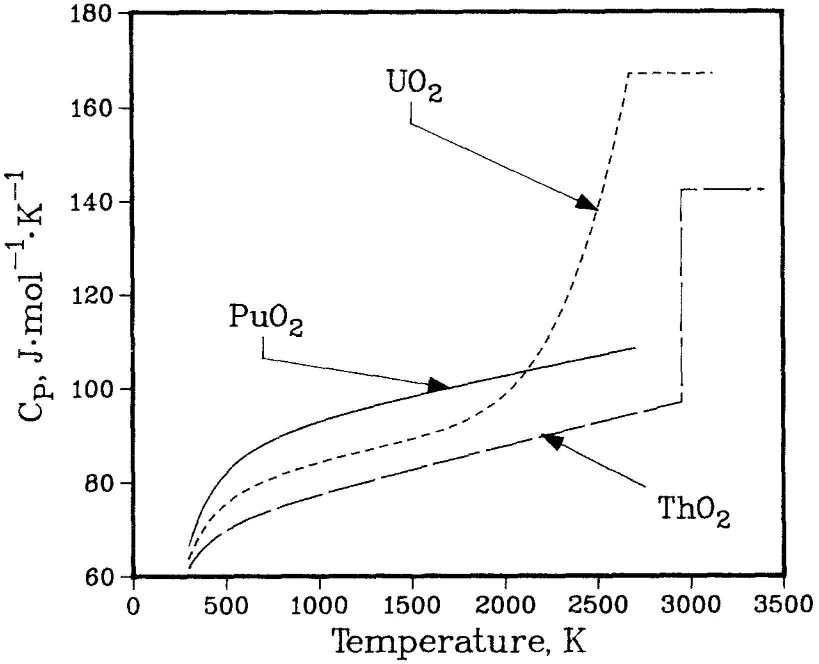

Fig. 5. Heat capacity of UO_2, PuO_2, and ThO_2 calculated by differentiation of the enthalpy equations.

This difference between UO_2 and ThO_2 at the phase transition is also evident in the entropy of transition. For UO_2, the entropy of transition is 0.1 $J \cdot mol^{-1} \cdot K^{-1}$; for ThO_2, the entropy of transition is 2.1 $J \cdot mol^{-1} \cdot K^{-1}$. If the phase transitions are identical, one would expect the entropy of transition to be similar. The reasons for this large increase (47%) in the heat capacity of ThO_2 at the phase transition and the difference in entropy of transition between UO_2 and ThO_2 are presently not known since the cause of the phase transition is uncertain. While Bredig predicted the existence of a phase transition in UO_2 and ThO_2, he did not explicitly define its origin and stated only that Frenkel defects alone are not sufficient to explain the phase transition in UO_2. He attributed the transition to a disordering of the oxygen ions and suggested that some cooperative process such as destruction of long-range order may be occurring [25].

An interesting observation from Table IV is that the thermodynamic functions of ThO_2 are closer to those of UO_2 following the phase transition than before. Since UO_2 has an electronic contribution to enthalpy before and after its phase transition, it is possible that ThO_2 has undergone sufficient structural change during the solid-solid phase transition to de-

Table IV. Comparison of Thermodynamic Functions for Solid UO_2, ThO_2, and PuO_2[a]

T	C_P^0			S^0			$-(G^0 - H_{298}^0)/T$			$H_T^0 - H_{298}^0$		
(K)	UO_2	ThO_2	PuO_2	UO_2	ThO_2	PuO_2	UO_2	ThO_2	PuO_2	UO_2	ThO_2	PuO_2
0	0.0	0.0	0.0	0.0	0.0	0.0	∞	∞	∞	− 11.3	− 10.6	− 10.8
298.15	63.6	61.74	66.24	77.0	65.2	66.1	77.0	65.2	66.1	0.0	0.0	0.0
500	75.48	69.78	81.98	113.3	99.4	104.9	84.8	72.6	74.4	14.3	13.4	15.3
1000	84.22	77.34	92.88	168.9	150.4	165.8	114.3	100.0	106.3	54.6	50.4	59.5
1500	89.21	82.68	98.22	204.0	182.8	204.6	138.7	122.5	133.0	98.0	90.5	107.4
2000	98.68	87.69	102.68	230.6	207.3	233.4	158.4	140.8	154.6	144.4	133.1	157.6
2500	138.13	92.59	106.88	256.0	227.4	256.8	175.4	156.1	172.8	201.5	178.1	210.0
2670(α)	166.40	94.25	108.29	265.9	233.5	263.8	180.8	160.8	178.3	227.2	194.0	228.3
2670(β)	167.04			266.0			180.8			227.5		
2701(s)	167.04	94.55	108.54	267.9	234.6	265.1	181.7	161.7	179.4	232.8	196.9	231.7
2950(α)		96.97			243.1			168.2			220.8	
2950(β)	167.04	142.33		282.7	245.2		189.7	168.2		274.4	227.0	
3000	167.04	142.33		285.5	247.6		191.2	169.5		282.8	234.1	
3120(s)	167.04	142.33		292.0	253.1		195.0	172.6		302.8	251.2	
3500		142.33			269.5			182.3			305.2	
3643(s)		142.33			275.2			185.8			325.6	

[a] Heat capacity, entropy, and the free energy functions are in $J \cdot mol^{-1} \cdot K^{-1}$. Enthalpy is in $kJ \cdot mol^{-1}$.

velop an electronic contribution to enthalpy. Unfortunately, the absence of electrical conductivity measurements on ThO_2 at temperatures in the phase transition region make it impossible to support or deny this conjecture.

The fact that only phonon and thermal expansion terms are needed to fit the experimental enthalpy data of ThO_2 and PuO_2 confirms the theoretical models of Young [2] and MacInnes and Catlow [4], which imply that the anomalous contribution to the enthalpy of UO_2 is electronic. If the origin of the anomalous contribution were Frenkel defects, then a Frenkel-defect term would be required to fit the enthalpy data of ThO_2 and PuO_2 since the Frenkel-defect contribution to all three actinide oxides would be similar. Young [2] has shown that the difference in the electronic energy levels of the three actinide oxides makes the electronic contribution energetically favorable for UO_2 but unfavorable for both ThO_2 and PuO_2. The electronic structure of UO_2 resembles a semiconductor. The $5f$ level in UO_2 is between the $2p$ valence band and the $6d$ conduction band. The valence band is located about 6 eV below the conduction band, but the $5f$ levels are only about 2 eV below the conduction band. In ThO_2, the band structure is similar to that of UO_2 except that the $5f$ electron state is located at the same energy level as the conduction band. The band structure in PuO_2 is similar to that of UO_2 and ThO_2, except that for PuO_2 the $5f$ electron levels are located in the valence band. Thus for PuO_2 and ThO_2, there exists a large gap between the valence and conduction bands. For UO_2, the presence of the 5*f* level in this gap only 2 eV below the conduction band leads to an electronic contribution at high temperatures ($T > 1500$ K). This difference in location of the 5*f* electron states in these three actinide oxides accounts for the experimentally observed differences in enthalpy.

5. ENTHALPY OF (TH, U)O_2

Measurements of the enthalpy of (Th, U)O_2 have been made by Springer et al. [34] and by Fischer et al. [42]. Table V lists the mixed oxide compositions and the temperature range of the measurements. The enthalpy data of Fischer et al., which are for higher temperatures than those of Springer et al., reveal phase transitions as observed in UO_2 and ThO_2. Below the phase transitions for 70, 80, and 85% ThO_2, the (Th, U)O_2 data are well fit by the mole average of the equations used to fit the ThO_2 and UO_2 data below their phase transitions [Eq. (6)] with parameters given in Table I. Above the phase transitions, the data are fit by a linear equation of the form $A + BT$. Table VI gives the coefficients for this linear equation and the temperatures of the phase transition. The standard deviations of

Table V. Measurements of the Enthalpy of (Th, U)O_2

Oxide	Temperature range (K)	Number of points	Deviation of fit (%)	Experimenter/ref.
$(Th_{0.70}U_{0.30})O_2$	2400–3437	21	1.02	Fischer et al. [42]
$(Th_{0.80}U_{0.20})O_2$	324–2270	19	1.34	Springer et al. [34]
$(Th_{0.85}U_{0.15})O_2$	2401–3401	16	0.77	Fischer et al. [42]
$(Th_{0.90}U_{0.10})O_2$	340–2271	23	0.51	Springer et al. [34]
$(Th_{0.92}U_{0.08})O_2$	2303–3302	12	0.52	Fischer et al. [42]

Table VI. Phase Transition Temperatures and Parameters A and B for the Linear Equation $A + BT$ for the (Th, U)O_2 System

% UO_2	Phase transition temperature (K)	A ($J \cdot mol^{-1}$)	B ($J \cdot mol^{-1} \cdot K^{-1}$)
100	2670	− 218,342	167.04
30	2900	− 148,640	131.85
15	2950	− 219,310	152.37
8	2850	− 155,710	128.11
0	2950	− 192,920	142.33

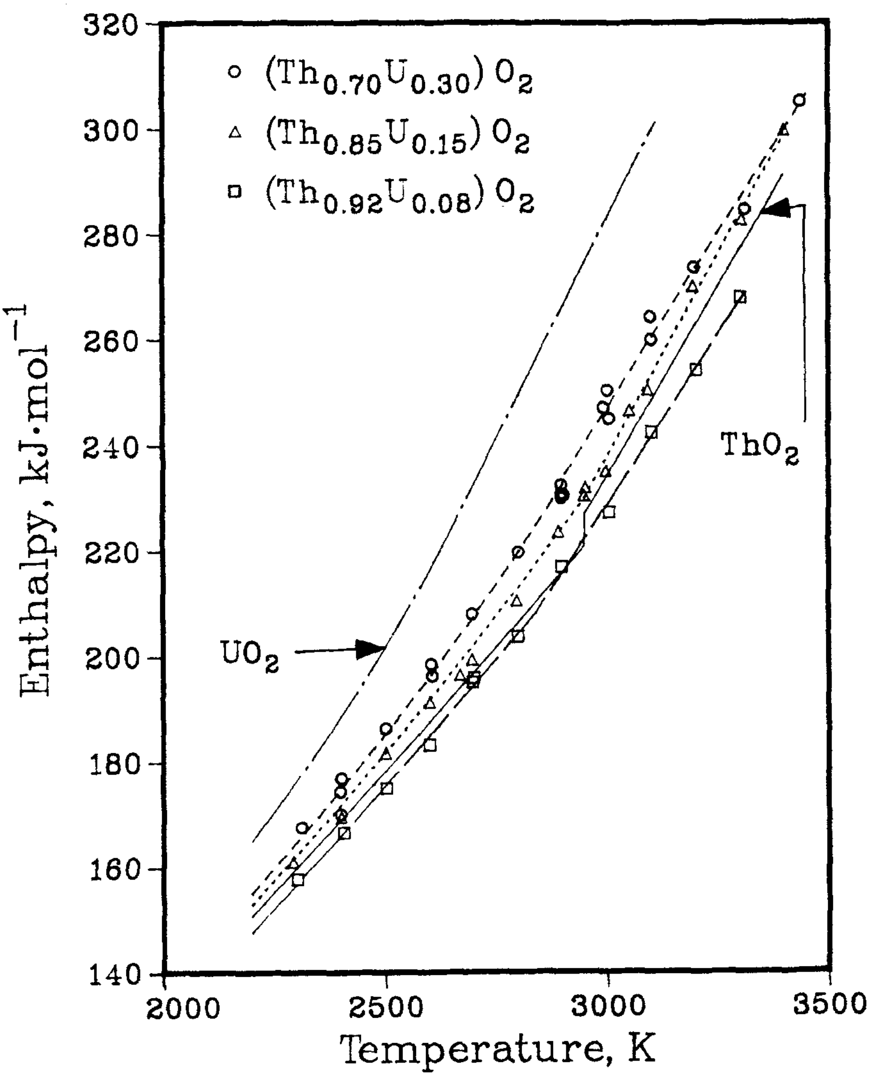

Fig. 6. Experimental enthalpy data of $(Th_{0.70}U_{.030})O_2$ and $(Th_{0.85}U_{0.15})O_2$ compared with the mole average of the equations that fit the UO_2 and ThO_2 data below the phase transitions; experimental enthalpy data of $(Th_{0.92}U_{0.08})O_2$ and fit to the data; the linear equations to fit the data above the phase transitions.

the data from the fit to the mole-average and linear equations are given in Table V. Figures 6 and 7 show the fits of these two equations to the experimental enthalpy data for 70, 80, and 85% thoria in the mixed oxides.

The $(Th_{0.92}U_{0.08})O_2$ data of Fischer et al. and the $(Th_{0.90}U_{0.10})O_2$ data of Springer et al. could not be fit by the mole average method because these

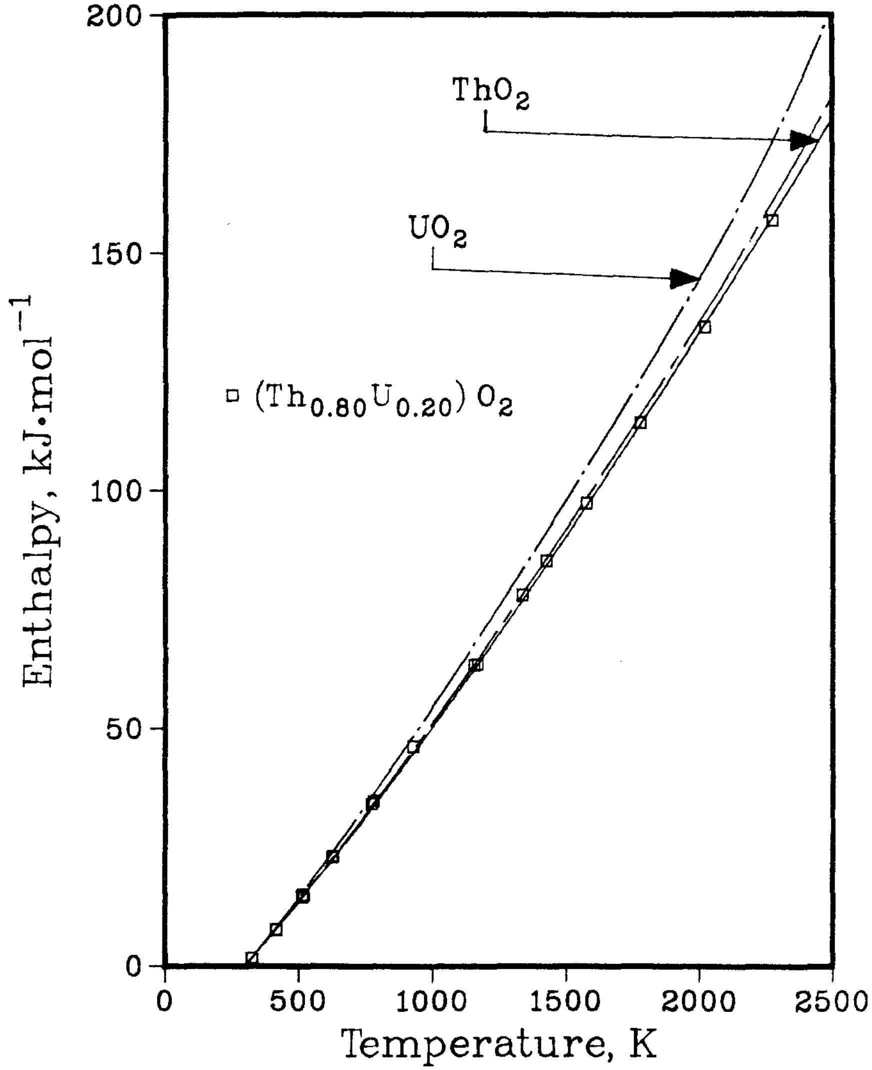

Fig. 7. Experimental $(Th_{0.80}U_{0.20})O_2$ enthalpy data compared with the mole average of the UO_2 and ThO_2 enthalpy equations.

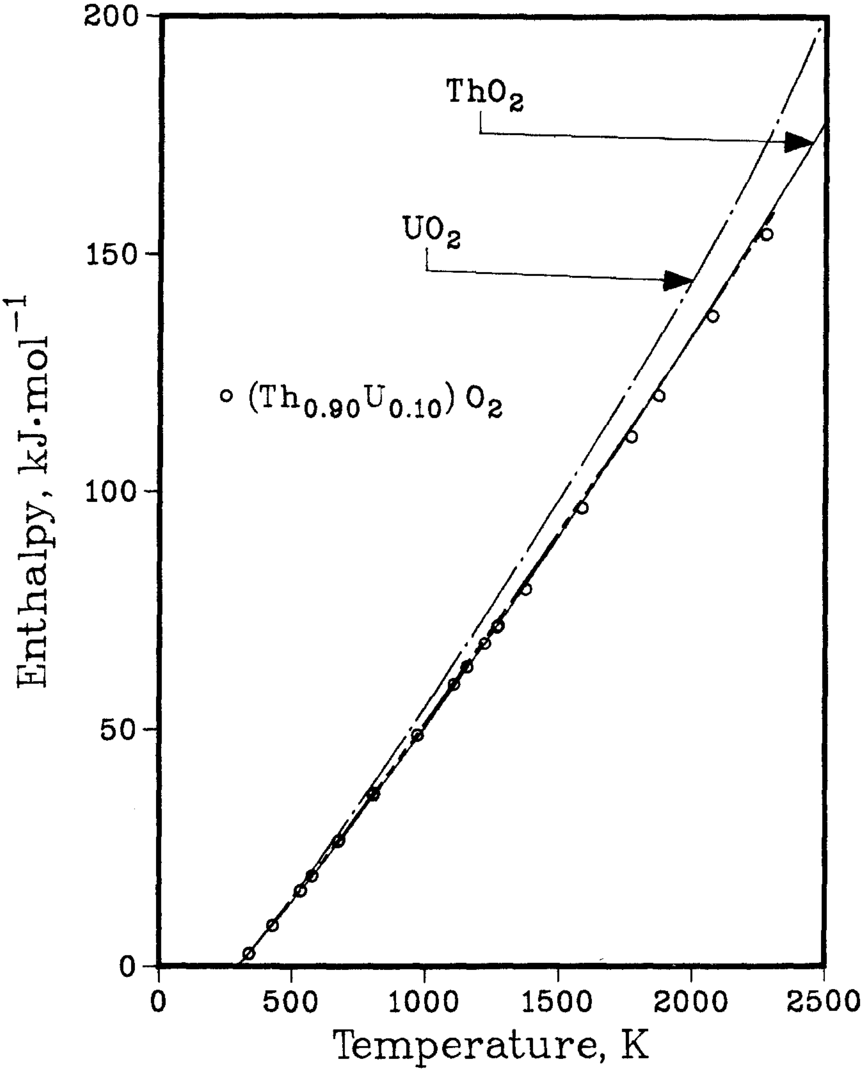

Fig. 8. Experimental enthalpy of $(Th_{0.90}U_{0.10})O_2$ and the equation used to fit this data.

data do not lie between the ThO_2 and UO_2 data. This is illustrated in Figs. 6 and 8. Consequently, the $(Th_{0.92}U_{0.08})O_2$ data below the phase transition at 2850 K and the $(Th_{0.90}U_{0.10})O_2$ data were fit by Eq. (6) without the electronic term. Equation (7) and the mole-average heat capacities at 298.15 K were used to constrain the fitting equations. The parameters found to fit the data for these two oxides are given in Table I. The inconsistently low value of θ for $(Th_{0.92}U_{0.08})O_2$ is the result of the fitting procedure. Only data above 2300 K exist for $(Th_{0.92}U_{0.08})O_2$. However, theoretically, the term involving θ dominates in the temperature region below 1500 K. Thus using the nonlinear least-squares fitting procedure to determine θ, which should be determined by data below 1500 K, gives low values which have no physical significance. Application of this fitting procedure to the ThO_2 data between 2400 and 2950 K resulted in similarly low values for θ, confirming this hypothesis of effect of the temperature region of the data on θ. Consequently the parameters in Table I for $(Th_{0.92}U_{0.08})O_2$ should only be used between 2300 and 2850 K, where experimental data exist.

Measurements of the low-temperature enthalpy of $(Th_{0.92}U_{0.08})O_2$ are needed in order to obtain an equation that accurately represents the enthalpy from room temperature to the phase transition and that has parameters with physical significance. Above the phase transition at 2850 K, the $(Th_{0.92}U_{0.08})O_2$ data were fit by a linear equation. The standard deviation of the $(Th_{0.92}U_{0.08})O_2$ data from this two-equation fit is 0.5%, as is the standard deviation of the $(Th_{0.90}U_{0.10})O_2$ data from Eq. (6) without an electronic term. At this time the reason for the unusual behavior for 90% ThO_2 and 92% in $(Th, U)O_2$ is not understood.

In summary, for percentages of ThO_2 between 70 and 85%, the enthalpy and heat capacity of the $(Th, U)O_2$ system below the phase transition may be calculated by a mole average of the equations for UO_2 and ThO_2. Above the phase transition temperature, a linear equation should be used to calculate the enthalpy of the $(Th, U)O_2$ system. There are insufficient data at this time to formulate a generalized model to obtain the coefficients for the linear equation. Table VI gives the coefficients of this linear equation for the oxide compositions where experimental data exist, and these values show no simple dependence on mole fraction.

The heat capacities for the $(Th, U)O_2$ system have been calculated from differentiation of the equations used to calculate the enthalpies; i.e., the mole average equations for 70, 80, and 85% ThO_2 below their phase transitions, Eq. (6) for 90 and 92% ThO_2 below their phase transitions, and the linear equations given in Table VI above the phase transitions. Figure 9 shows these calculated heat capacities with the heat capacities of UO_2 and ThO_2 for comparison. The heat capacity of $(Th_{0.92}U_{0.08})O_2$ is not given below 2300 K because the absence of low temperature experimental data gives unphysical values for the low temperature dependent parameters making extrapolation to low temperatures unjustified. Similarly, the temperature limit of the $(Th_{0.80}U_{0.20})O_2$ and $(Th_{0.90}U_{0.10})O_2$ enthalpy data

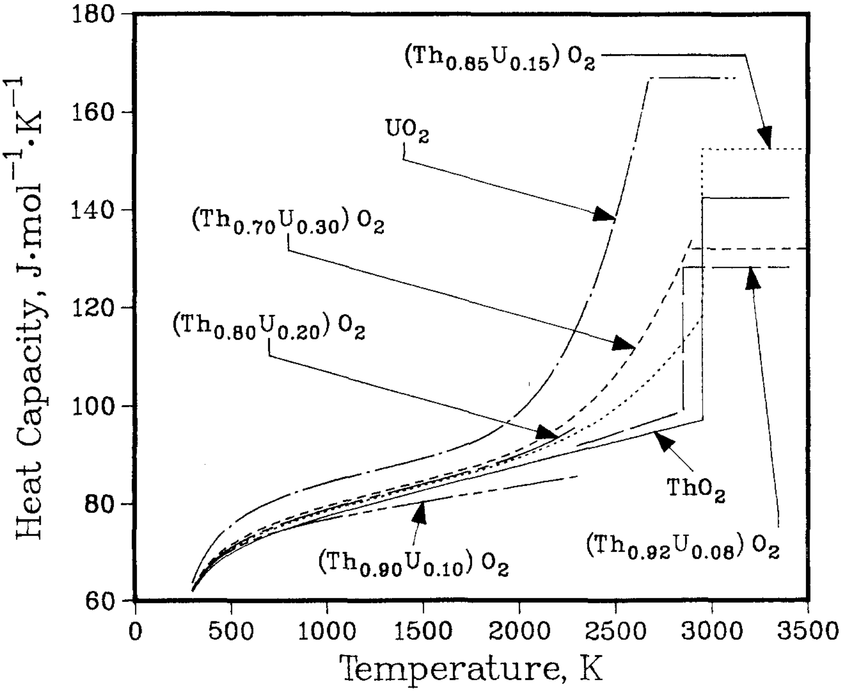

Fig. 9. Calculated heat capacities of the (Th, U)O_2 system.

of Springer, et al. prevents extrapolation of these heat capacities above 2300 K.

6. ENTHALPY OF (Pu, U)O_2

As shown in Table VII, measurements of the enthalpy of (Pu, U)O_{2-x} have been made [13, 43–46] for a range of oxygen to metal ratios (O/M)for both $(Pu_{0.20}U_{0.80})O_{2-x}$ and $(Pu_{0.25}U_{0.75})O_{2-x}$. Examination of the data indicated that variation with O/M is small. A data point at 3041 K was obtained by Leibowitz et al. [43], but was not included in the analysis because the experimenters observed that the sample was partially molten at this temperature. Leibowitz et al. [44] made two sets of measurements using $(Pu_{0.20}U_{0.80})O_{1.92}$. The measured enthalpy of $(Pu_{0.20}U_{0.80})O_{1.92}$ from one set of experiments deviates from the enthalpy of $(Pu_{0.20}U_{0.80})O_{1.97}$ measured by Leibowitz et al. [43], while the enthalpy from the other set of experiments gives reasonable agreement with the latter enthalpy data. This finding is not understood by the experimenters. Since the experimenters have no basis

Table VII. Measurements of the Enthalpy of (Pu, U)O_{2-x} and Standard Deviations from Eq. (6) with Coefficients from Table I and from the Linear Equation $161.90T - 205{,}940$ in $J \cdot mol^{-1}$

Oxide	Temperature range (K)	Number of points	Deviation of fit (%)	Year	Experimenter/ref.
$(Pu_{0.25}U_{0.75})O_{1.98}$	353–1761	27	1.71	1973	Gibby [45]
$(Pu_{0.25}U_{0.75})O_{1.95}$	351–1761	25	1.45	1973	Gibby [45]
$(Pu_{0.20}U_{0.80})O_{1.97}$	2348–3041	16	0.85	1974	Leibowitz et al. [43]
$(Pu_{0.20}U_{0.80})O_{1.92}$[a]	2550–3312	24	2.82	1974	Leibowitz et al. [44]
$(Pu_{0.198}U_{0.802})O_{2.00}$	1168–2450	21	1.72	1968	Ogard and Leary [13]
$(Pu_{0.198}U_{0.802})O_{1.98}$	1176–2470	21	1.47	1968	Ogard and Leary [13]
$(Pu_{0.2}U_{0.8})O_2$	1518–2496	9	2.59	1971	Clifton [46]
$(Pu_{0.2}U_{0.8})O_2$ (irradiated)	1468–2416	12	1.37	1971	Clifton [46]

[a] This result not included in the fit.

upon which to decide which set of $(Pu_{0.20}U_{0.80})O_{1.92}$ data to reject, neither set has been included in this assessment.

Mole averages of the equations used to fit the UO_2 and PuO_2 enthalpy data [Eq. (6) with parameters given in Table I] give values that are below those of most of the (Pu, U)O_{2-x} enthalpy measurements except above 2720 K, where the mole average gives values that are greater than the data. This is illustrated in Figs. 10a and 11a, which show the calculated mole-averaging enthalpy along with the measured data for $(Pu_{0.20}U_{0.80})O_{2-x}$ and $(Pu_{0.25}U_{0.75})O_{2-x}$; the differences of the mole-average value from the measured data expressed as a percent are presented in Figs. 10b (20% PuO_{2-x}) and 11b (25% PuO_{2-x}).

The evidence for an electronic term in UO_2 implies that an electronic contribution to the mixed oxide (Pu, U)O_{2-x} may also be expected. Therefore, an equation of the form of Eq. (6) was used to fit all of the (Pu, U)O_{2-x} enthalpy data, which could be fit together because there appears to be only a small variation with O/M and small variation between the 20 and 25% PuO_{2-x} data. This equation was constrained by the condition given in Eq. (7) and the constraint that the derivative of the enthalpy equals the mole-average heat capacity at 298.15 K, i.e.,

$$\left(\frac{\partial H}{\partial T}\right)_P\Bigg|_{T=298.15\text{ K}} = C_P(298.15\text{ K}) = 64.26\ \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \qquad (15)$$

The value 64.26 $J \cdot mol^{-1} \cdot K^{-1}$, the mole average of the heat capacity of $(Pu_{0.25}U_{0.75})O_{2-x}$ at 298.15 K was chosen to constrain the heat capacity

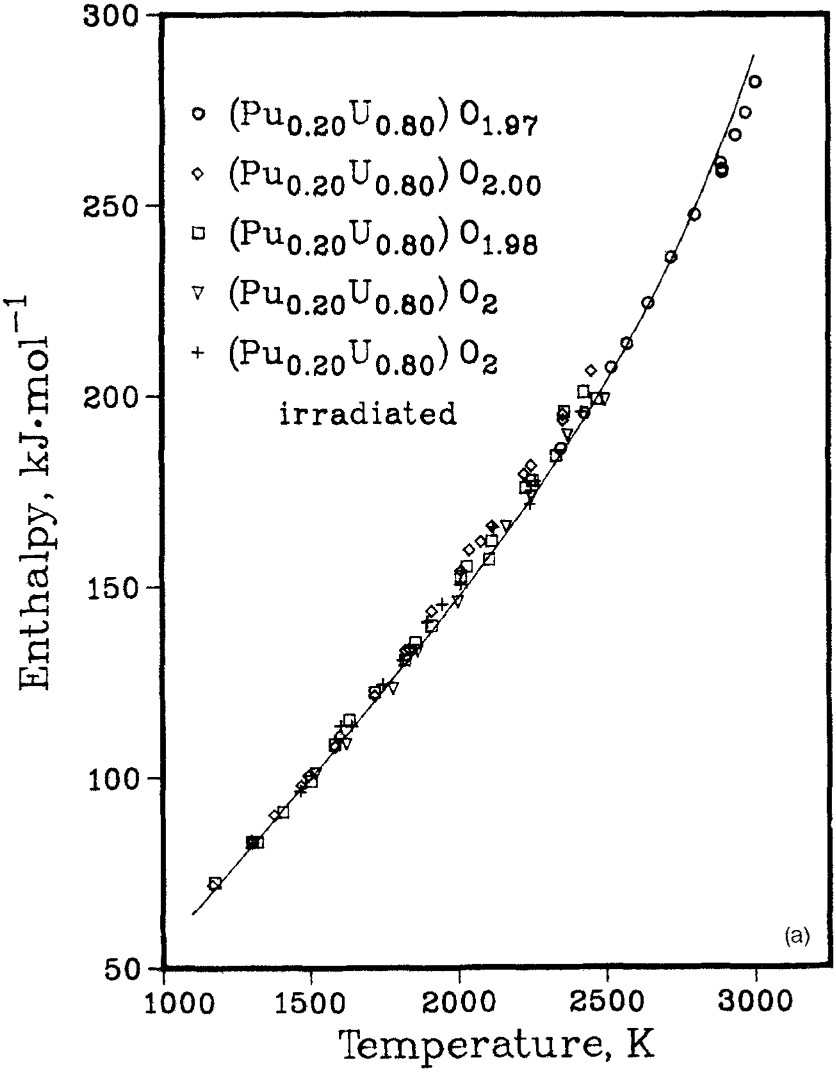

Fig. 10(a). Mole average of the equations that fit the UO_2 and PuO_2 enthalpy data compared with the $(Pu_{0.20}U_{0.80})O_{2-x}$ enthalpy data.

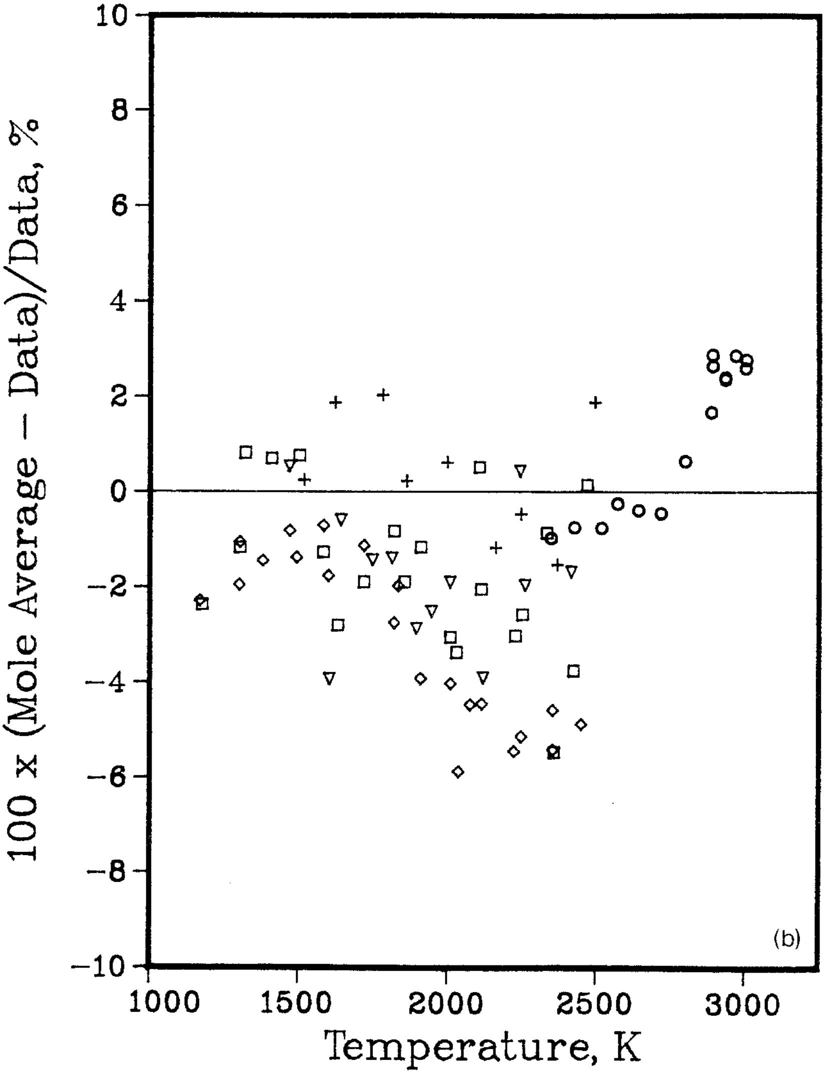

Fig. 10(b). Plot of the differences 100% (mole average-data)/data as a function of temperature for the $(Pu_{0.20}U_{0.80})O_{2-x}$ enthalpy data.

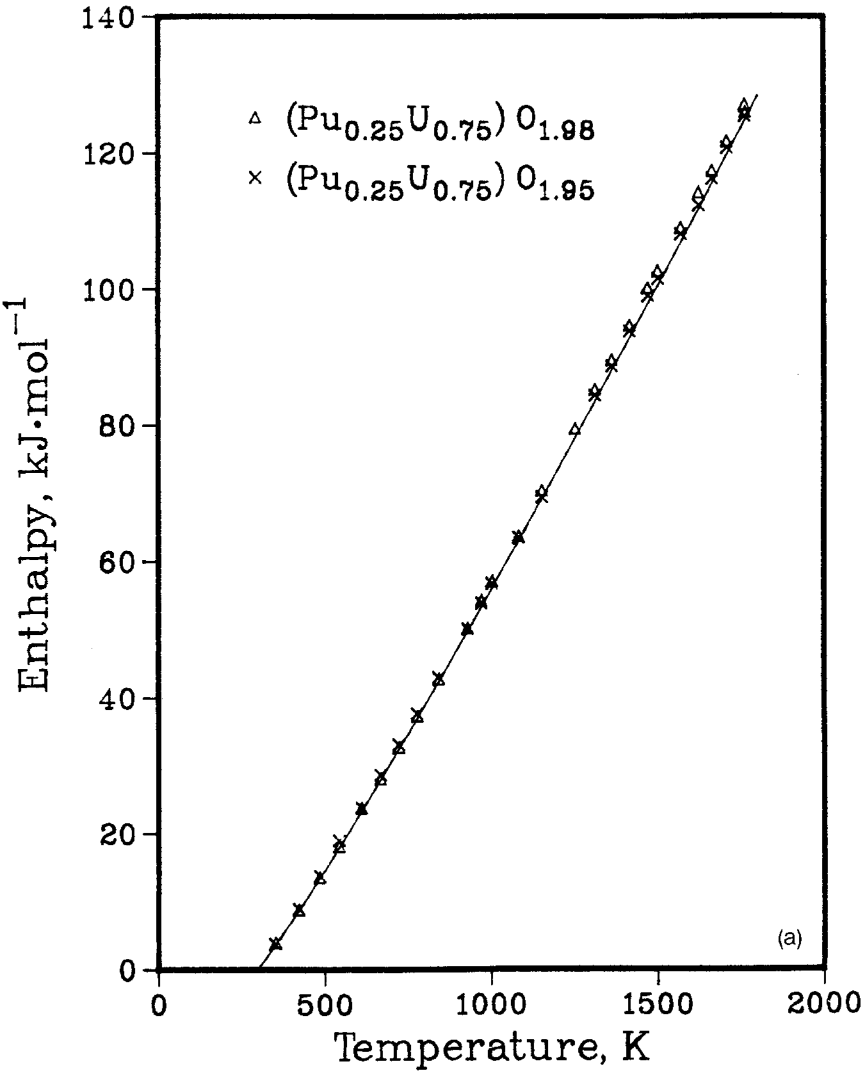

Fig. 11(a). The $(Pu_{0.25}U_{0.75})O_{2-x}$ enthalpy data plotted with the mole average of the enthalpy equations that fit the UO_2 and PuO_2 data.

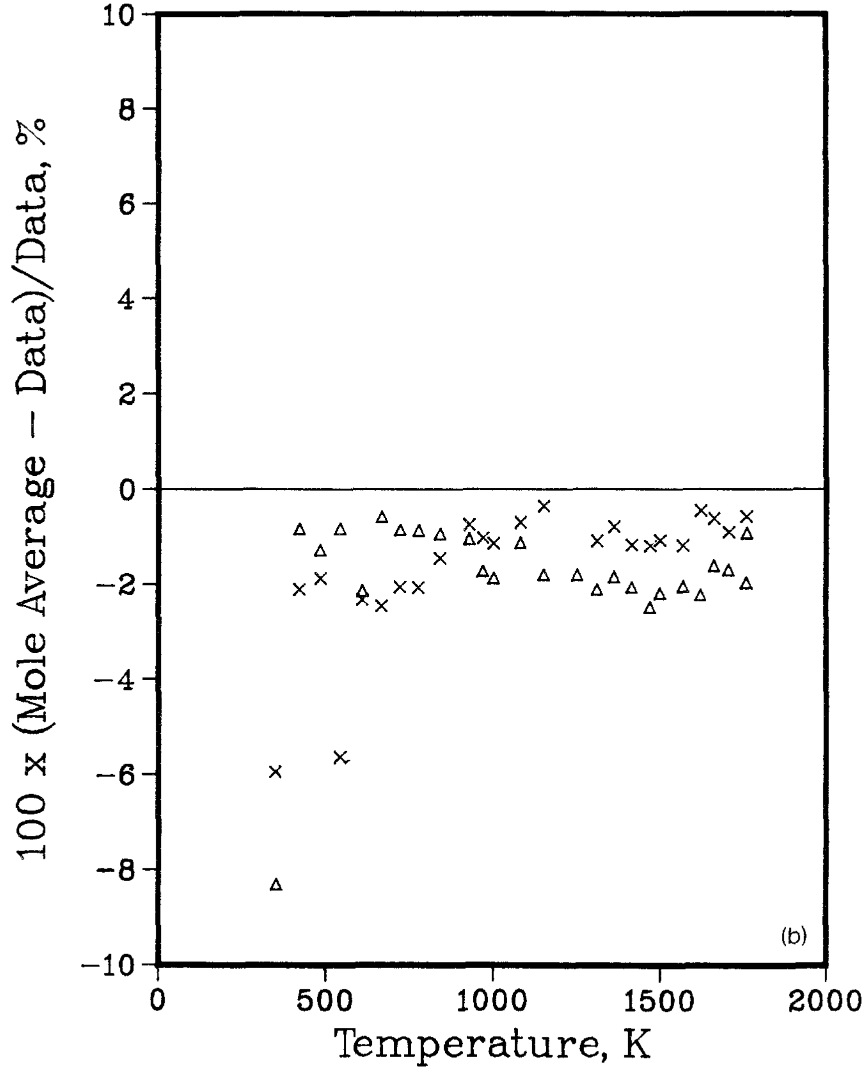

Fig. 11(b). Plot of the differences 100% (mole average-data)/data as a function of temperature for the $(Pu_{0.25}U_{0.75})O_{2-x}$ enthalpy data.

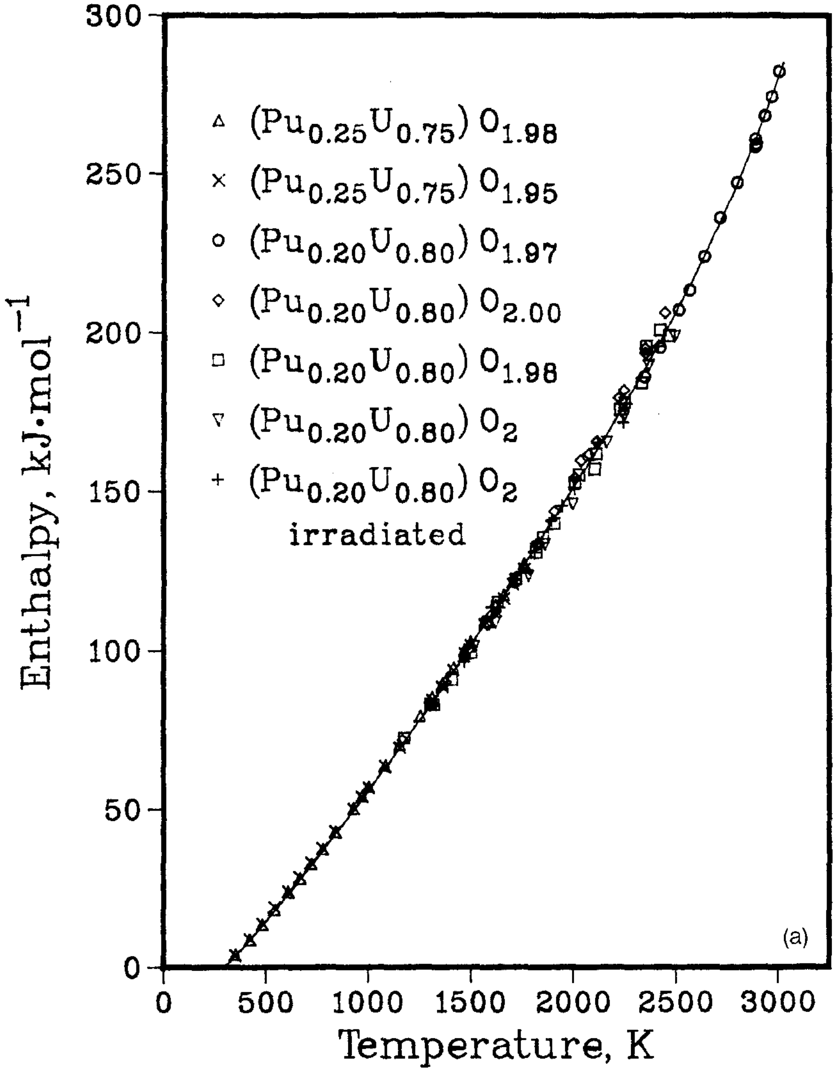

Fig. 12(a). Experimental enthalpy data of $(Pu, U)O_{2-x}$ and fit to those data using Eq. (6).

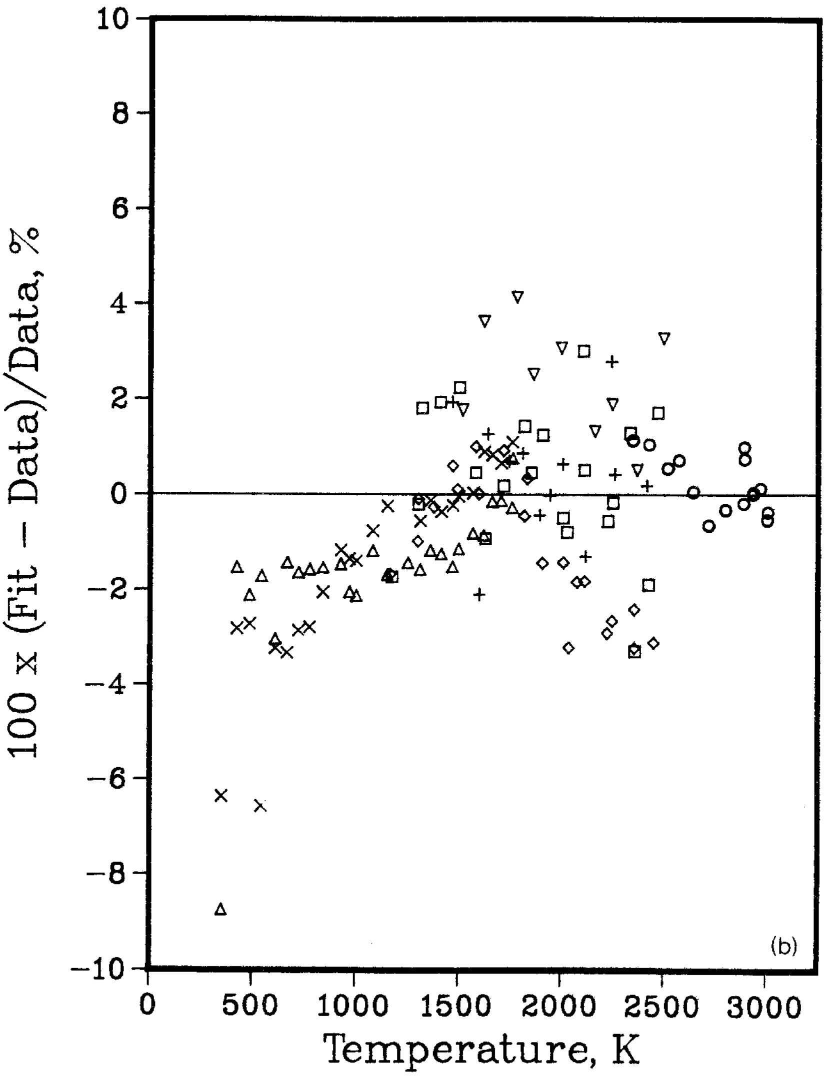

Fig. 12(b). Difference plot of enthalpy data of (Pu, U)O_{2-x} and fit to those data using Eq. (6).

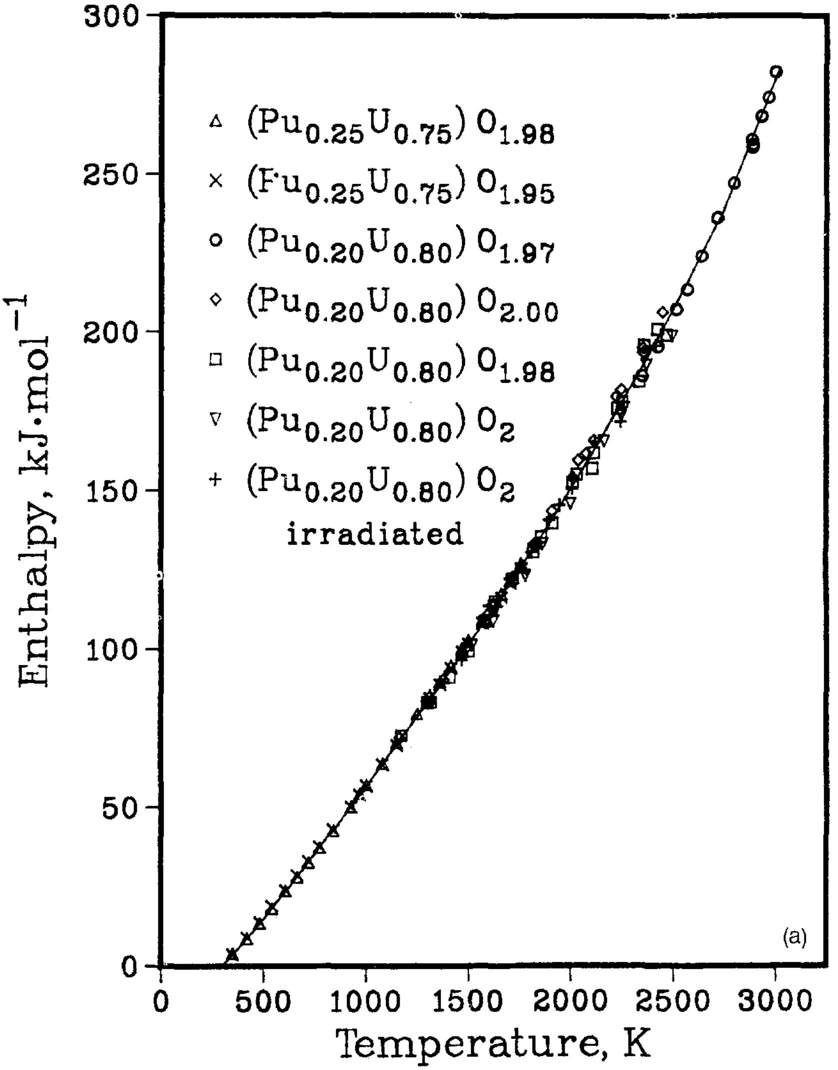

Fig. 13(a). Experimental enthalpy data of $(Pu, U)O_{2-x}$ and fit to those data with a phase transition at 2750 K. Equation (6) is used to fit the data below the transition; a linear equation is used above the transition.

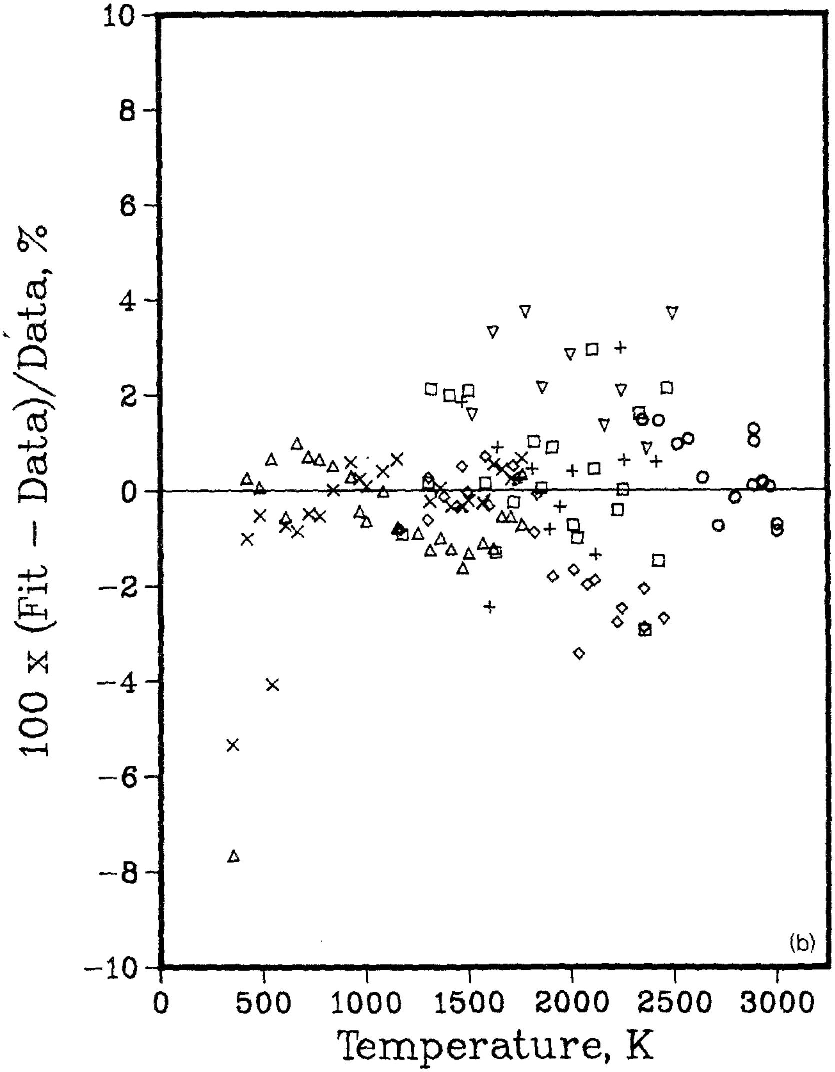

Fig. 13(b). Difference plot of 100% (fit-data)/data for (Pu, U)O_{2-x} where the fit has a phase transition at 2750 K.

because most of the low temperature data are for $(Pu_{0.25}U_{0.75})O_{2-x}$. The standard deviation of the data from this nonlinear least-squares fit is 1.97%. Figure 12a shows the fit of this equation to the experimental data. Percent differences of the data from the fit are given in Fig. 12b. The consistently negative deviations at low temperature imply that this form of equation is not adequate to fit the low temperature data of Gibby [45] simultaneously with the higher temperature data using a nonlinear least-squares technique.

Gibby et al. [47], fit the $(Pu_{0.25}U_{0.75})O_{1.98}$ enthalpy data of Gibby [45], $(Pu_{0.20}U_{0.80})O_{1.97}$ enthalpy data of Leibowitz et al. [43], and the $(Pu_{0.20}U_{0.80})O_{1.98}$ enthalpy data of Ogard and Leary [13] to an equation of similar form to Eq. (6) with a Frenkel defect term for the anomalous contribution. This equation is

$$\begin{aligned} H_T^0 - H_{298.15}^0\,(\mathrm{J\cdot mol^{-1}}) = {} & C_1\theta\left[\left(e^{\theta/T}-1\right)^{-1} - \left(e^{\theta/298}-1\right)^{-1}\right] \\ & + C_2\left(T^2 - (298)^2\right) \\ & + C_3' e^{-E_d/RT} \end{aligned} \tag{16}$$

where E_d is the defect formation energy.

Only these three sets of data were selected for the fit because Gibby et al. thought that variations in O/M may cause significant differences in the enthalpy data. Equation (16) was also used to fit the complete set of available data [13, 43, 45, 46] fit above using the heat capacity of 64.26 $\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$ to constrain the data at 298 K. Gibby et al. [47] used the value 64.978 $\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$ for the heat capacity to constrain their equation. This value used by Gibby et al. is the mole average based on the heat capacity of PuO_2 calculated from the enthalpy measurements of Kruger and Savage [37], whereas the value 64.26 $\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$ is the mole average based on the more recent low-temperature heat capacity measurements of Flotow, et al. [41]. Both mole averages used the heat capacity measurements of Huntzicker and Westrum [20] for the heat capacity of UO_2 at 298.15 K. Fitting all data simultaneously using a nonlinear least-squares method [26] to an equation of the form of Eq. (16) gives a standard deviation of 1.95%. Examination of the deviation of the data from the fit indicates the same problem in fitting the low temperature data that was found with the fit which has an electronic term for the anomalous contribution.

Recently Slagle [36] has observed a phase transition in the neighborhood of 2720 K in $(Pu,U)O_{2-x}$ creep data. He suggested that the enthalpy data be examined to see if there is also some indication of a phase transition in it. Examination indicated that inclusion of a phase transition at 2750 K eliminates the systematic deviation of the fit from the low temperature data. The $(\mathrm{Pu, U})\mathrm{O}_{2-x}$ enthalpy data have been fit using an equation of the form of Eq. (6) to 2750 K and a linear equation above this temperature with a standard deviation of 1.60%. Table I gives the parameters used to fit the data using a nonlinear least-squares method. The linear equation used to fit the data for $T \geqslant 2750$ K is

$$H_T^0 - H_{298.15}^0\,(\mathrm{J \cdot mol^{-1}}) = 161.80T - 205{,}940 \tag{17}$$

Figure 13a shows this fit to the data. A difference plot of the fractional deviation of the data from the fit expressed as a percent is given in Fig. 13b. Comparison of this difference plot with Fig. 12b shows that inclusion of a phase transition around 2750 K makes it possible to fit all the data below the phase transition with a single equation and no systematic deviation. Statistical examination of the χ^2 of the fits indicates that inclusion of a second equation is justified.

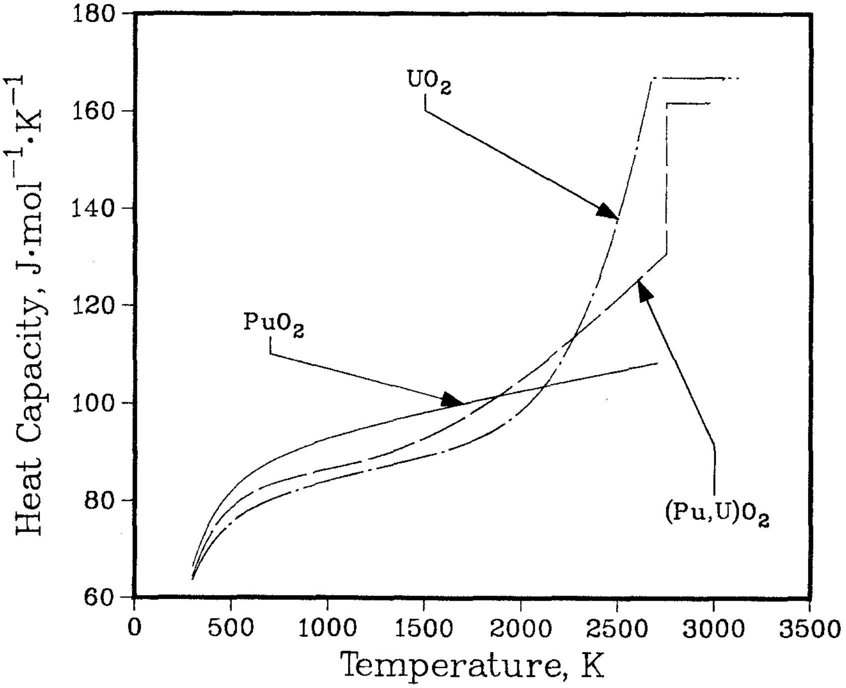

Fig. 14. Heat capacity of $(\mathrm{Pu, U})\mathrm{O}_2$ compared with the heat capacities of UO_2 and PuO_2.

The ratio of phase transition temperature to melting point for (Pu, $O)_{2-x}$ is higher (0.92) than observed for UO_2 (0.86) and for ThO_2 (0.81). Analysis of the enthalpy data indicated that there could be no transition below 2700 K. The phase transition temperature 2750 ± 50 K was selected by a minimization method similar to that used for ThO_2. The error limits on the transition temperature indicate the uncertainty in its value which results from the limited data in the temperature region of the transition. Additional experimental data in this temperature region are needed to determine the exact transition temperature. Evidence of a phase transition in $(Pu, U)O_{2-x}$ creep data in the temperature region of 2720 K [36], fission gas experiments which indicate that the mixed oxide fuel pins undergo extensive swelling in the temperature region of 2770 K [48], as well as the ability to fit all the enthalpy data with no systematic deviations by the inclusion of a phase transition, gives confidence of the existence of a phase transition in the neighborhood of 2750 K.

The heat capacity of $(Pu_{0.80}U_{0.20})O_{2-x}$ has been measured by Affortit and Marcon [23]. No comparison was made between values calculated from differentiation of the recommended enthalpy equations and their experimental data because heat capacity measurements on UO_2 made in the same set of experiments are inconsistent with experimental measurements of heat capacity of UO_2 by other investigators [19–22]. Figure 14 shows the heat capacity calculated from the fit to the enthalpy data of $(Pu, U)O_{2-x}$ using Eq. (6). The heat capacities of PuO_2 and UO_2 are included for comparison.

7. CONCLUSIONS

As a result of this analysis, equations based on theory as well as experimental measurements have been derived for the calculation of the enthalpy and heat capacity of UO_2, ThO_2, PuO_2, $(Th, U)O_2$, $(Pu_{0.75}U_{0.25})O_{2-x}$, and $(Pu_{0.80}U_{0.20})O_{2-x}$. Not only do these equations represent the experimental data well, but the values of their parameters in most cases agree with accepted solid state theory.

According to theory, the coefficient C_1 tabulated in Table I for the different actinide oxides should be approximately $9R = 75\ J \cdot mol^{-1} \cdot K^{-1}$. The value of C_1 for $(Th_{0.92}U_{0.08})O_2$ is lower than the theoretical value, and the values of C_1 for PuO_2 and $(Pu, U)O_{2-x}$ are somewhat higher than the theoretical value. The low value for C_1 of the $(Th_{0.92}U_{0.08})O_2$ data is due to the fact that only high-temperature data are available in the literature. The phonon term is determined mainly by low-temperature data, so parameters in this term found from fits to solely high-temperature data have no physical significance. The high value for C_1 for PuO_2 may be related to the existence of a phase transition which has not been included in the calculations. Since the nonlinear least-squares method used fits all the data simultaneously, inclusion of additional high-temperature data that theoretically should not be included in the fit would affect parameters that are mainly sensitive to low temperatures. Examination of the available thermal expansion, density, and compressibility data of UO_2 [11] reveals that the value of C_2 for UO_2 is consistent with calculated values of $\alpha_P^2 V/\beta_T$. This comparison is limited to 1600 K since data for the calculation of C_2 are only available from room temperature to 1600 K. At 1600 K, C_2 calculated from thermodynamic properties is 3.6×10^{-3} J · mol^{-1} · K^{-2} compared to 3.86×10^{-3} J · mol^{-1} · K^{-2} obtained for C_2 from the fit to the enthalpy data. Except for ThO_2, which shows good agreement, insufficient data make it impossible to calculate $\alpha_P^2 V/\beta_T$ for the other actinide oxides, but their values for C_2 seem reasonable since they do not vary appreciably from the value obtained for UO_2. There is no theoretical prediction for C_3.

Experimental determinations of the Einstein temperature for UO_2 give 542 K [49–51]. The Einstein temperature of UO_2 determined by the nonlinear least-squares fitting technique is 516 K, which is in reasonable agreement with the experimental value. The values for the Einstein temperature given in Table I for the other actinide oxides are in accordance with this value for UO_2 with the exception of the 269 K value for $(Th_{0.92}U_{0.08})O_2$. As for the coefficient C_2, this low value for $(Th_{0.92}U_{0.08})O_2$ is due to the absence of low-temperature data. Consequently, it has no physical significance and should not be identified as an Einstein temperature.

The value for E_a is expected to be about 1.00 eV for UO_2 [2,4], but was found by the fitting procedure to equal 1.88 eV for UO_2 and 0.73 eV for $(Pu, U)O_{2-x}$. This deviation of almost a factor of 2 from theory for UO_2 is not understood. Since $(Pu, U)O_{2-x}$ cannot be represented as a mole average of UO_2 and PuO_2, an ideal solution model is not adequate to describe it; thus there is no basis to determine how the energy levels would be changed in the solid solution of UO_2, which has an electronic contribution, and of PuO_2, which does not. Therefore, it is not surprising that E_a for $(Pu, U)O_2$ differs from the value found for UO_2. In conclusion, with the exception of the value for the electron excitation energy in UO_2, the parameters listed in Table I are in reasonable agreement with theoretical values.

Analyses of the enthalpy and heat-capacity data for all these actinide oxides give insight into the experimental basis for an electronic contribution to the enthalpy and heat capacity of UO_2. The ThO_2 enthalpy data below the phase transition at 2950 K and the PuO_2 data are well fit with only phonon and thermal expansion terms in the enthalpy equation. No Frenkel defect or anomalous contributions are needed. Furthermore, additional terms are not statistically justified. If a significant Frenkel defect contribution to UO_2 were to exist, a corresponding Frenkel defect contribution would be observed in ThO_2 and PuO_2 [2,4]. The absence of a Frenkel defect term in ThO_2 or in PuO_2 implies that there is no significant Frenkel defect contribution to UO_2. In addition, the difference in the electronic structure of ThO_2, UO_2, and PuO_2 indicates that an electronic contribution to UO_2 is energetically favorable, while none could be expected for ThO_2 and PuO_2 [2].

Analyses of these enthalpy data have indicated that phase transitions occur in UO_2, ThO_2, $(Th,U)O_2$, and $(Pu,U)O_2$. One may expect the existence of a similar transition in PuO_2. However, conclusions regarding a phase transition in PuO_2 cannot be drawn because there are presently too few experimental data, with too much scatter in the region where a phase transition may be expected.

For 70–85% of ThO_2 in $(Th,U)O_2$, the enthalpy of $(Th,U)O_2$ below the phase transition may be calculated by a mole average of the equations used for UO_2 and ThO_2 below their phase transitions. The success of this mole-average technique lends confidence in the equations used to describe the enthalpy of UO_2 and ThO_2. Above the phase transition, a linear equation may be used to represent the enthalpy. Insufficient data exist to formulate a theory by which the coefficients of the linear equation can be obtained. For 90 and 92% of ThO_2 in $(Th,U)O_2$, the mole-average technique is not applicable since at a given temperature, the enthalpies of these percentages of ThO_2 in $(Th,U)O_2$ are less than the enthalpies of ThO_2. At present, the cause for this is unknown.

The experimental data needed to obtain a complete understanding of the enthalpy for ThO_2, UO_2, PuO_2, $(Th,U)O_2$, and $(Pu,U)O_2$ have been identified. Data on the enthalpy of PuO_2 between 1800 and 2701 K are needed to determine whether or not a phase transition exists in PuO_2. To better determine the temperature of the phase transition in $(Pu,U)O_{2-x}$, more data in the temperature region 2700–2800 K are required. Additional $(Pu,U)O_2$ data for different ratios of Pu to U are needed to formulate a description of this system. Measurements of the enthalpy of $(Th,U)O_2$ at around 90% ThO_2 at high and low temperatures are necessary in order to confirm the past experiments, to derive an equation with physically significant parameters that describes this high percent ThO_2 mixture, and to aid in understanding what happens to the mixture when large amounts of ThO_2 are present. Measurements of the electrical conductivity of ThO_2 in the temperature region of the phase transition, 2950 K, would help resolve the question of origin of the large increase in heat capacity at the phase transition.

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