



Calorimetric measurements on plutonium rich (U,Pu)O₂ solid solutions

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ABSTRACT

Enthalpy increments of U_(1-y)Pu_yO₂ solid solutions with $y=0.45, 0.55$ and 0.65 were measured using a high-temperature differential calorimeter by employing the method of inverse drop calorimetry in the temperature range 956–1803 K. From the fit equations for the enthalpy increments, other thermodynamic functions such as heat capacity, entropy and Gibbs energy function have been computed in the temperature range 298–1800 K. The results are presented and compared with the data available in the literature. The results indicate that the enthalpies of U_(1-y)Pu_yO₂ solid solutions with $y=0.45, 0.55$ and 0.65 obey the Neumann–Kopp's molar additivity rule.

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1. Introduction

Uranium–plutonium mixed oxides containing about 13–30 wt.% PuO₂ have been used as fuels for fast reactors in many countries. Uranium–plutonium mixed oxides containing 40 wt.% and higher amounts of PuO₂ are being considered as potential fuels for the plutonium burner reactors [1]. Uranium–plutonium mixed oxides containing 21 wt.% and 28 wt.% PuO₂ have been chosen as fuels for the Prototype Fast Breeder Reactor (PFBR) of India which is under construction. Uranium–plutonium mixed oxide containing 45 wt.% PuO₂ along with the mixed carbide has been proposed as the fuel for the expanded hybrid core for the Fast Breeder Test Reactor (FBTR) at Kalpakkam, India. The heat capacity is an important thermodynamic property, which is required for understanding the various chemical interactions likely to occur during the irradiation of the fuel as well as for modeling the behavior of the fuel.

Experimental determination of the heat capacity and enthalpy increments of uranium–plutonium mixed oxides containing 20 wt.% and 25 wt.% PuO₂ have been reported in the literature [2–9] by several authors. In general, there is agreement among different sets of experimental enthalpy increment data within $\pm 3\%$ though the compositions, O/M ratios and temperature ranges are different. The only exception is the data of Leibowitz et al. [5,6], which are

higher than all the others. There exist correlations by Fink [10,11], Cordfunke and Konings [12], MATPRO [13] and Carbajo et al. [14] for the enthalpy increment and heat capacity data for UO₂, PuO₂ and (U,Pu)O₂. In the latest correlation, Carbajo et al. [14] recommended the calculation of enthalpy and heat capacity of solid MOX fuel, U_(1-y)Pu_yO₂ by using the Neumann–Kopp's molar additivity rule, since the solid solutions formed in the system UO₂–PuO₂ are almost ideal. They recommended the use of the equations given by Fink for UO₂ [11] and that given by Cordfunke and Konings for PuO₂ [12] because the results are in very good agreement with the experimental data.

We have earlier reported the thermodynamic functions for U_{0.79}Pu_{0.21}O₂, U_{0.72}Pu_{0.28}O₂ and U_{0.60}Pu_{0.40}O₂ from our calorimetric measurements [15]. No experimental data are in the literature for the mixed oxides of U_{0.55}Pu_{0.45}O₂, U_{0.45}Pu_{0.55}O₂ and U_{0.35}Pu_{0.65}O₂. Further, the conclusion of Carbajo et al. [14] that the solid solutions of mixed oxides obey Neumann–Kopp's law was arrived at from the experimental data of oxides containing 20–30 wt.% PuO₂. With a view to verify whether the conclusion holds good also for the solid solutions with higher amounts of plutonium oxides, measurements on the U_(1-y)Pu_yO₂ solid solutions with higher amounts of plutonium oxides (with $y=0.45, 0.55$ and 0.65) were taken up. In the present study, the enthalpy increment measurements on U_{0.55}Pu_{0.45}O₂, U_{0.45}Pu_{0.55}O₂ and U_{0.35}Pu_{0.65}O₂ were carried out in the temperature ranges 993–1803 K, 960–1782 K and 956–1797 K, respectively, by inverse drop calorimetry using a high-temperature differential calorimeter. Thermodynamic functions such as heat capacity, entropy and Gibbs

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energy functions were computed from the measured enthalpy increments.

2. Experimental

2.1. Sample preparation

The $U_{0.55}Pu_{0.45}O_2$, $U_{0.45}Pu_{0.55}O_2$ and $U_{0.35}Pu_{0.65}O_2$ samples used for the enthalpy increment measurements were prepared, characterised and supplied by Radiometallurgy Division, BARC, Mumbai, India. The experimental procedure used for the preparation and characterisation of uranium–plutonium mixed oxide fuel pellets have been described elsewhere [16]. The lattice parameters are in agreement with the literature data [17]. The total amount of impurities was less than 3000 ppm. Though the O/M ratios of the as prepared samples were less than 2.00, they were used several days after the preparation and hence the mixed oxide samples were equilibrated at 1073 K with an Ar–H₂/H₂O gas mixture having an oxygen potential of $-418.4 \text{ kJ mol}^{-1}$ in a gas equilibration set up, prior to the calorimetric measurements, to make them stoichiometric. No change in the weights of the samples was observed after the measurements and hence the samples have been presumed to maintain an O/M ratio of 2.00 during the measurements. Further, the enthalpy increment and heat capacity of the mixed oxides do not vary much with the O/M ratio [14] and inaccuracies in heat capacity due to variation of O/M are expected to be negligible.

2.2. Drop calorimeter

The high-temperature differential calorimeter (Model HT 1500 of M/s. SETARAM, France) used in the present study and the argon atmosphere radioactive glove box to which the calorimeter is attached have been described elsewhere [18,19].

2.3. Experimental procedure

Enthalpy increments of $U_{0.55}Pu_{0.45}O_2$, $U_{0.45}Pu_{0.55}O_2$ and $U_{0.35}Pu_{0.65}O_2$ were determined by inverse drop calorimetric technique employing sandwich method. Dropping of each uranium–plutonium mixed oxide sample was sandwiched between dropping of two references α -alumina (SRM 720) reference samples supplied by NIST, USA. The experimental procedure adopted for measuring the enthalpy increment of the sample by the sandwich method has been described earlier [18].

3. Results

Enthalpy increments of $U_{0.55}Pu_{0.45}O_2$, $U_{0.45}Pu_{0.55}O_2$ and $U_{0.35}Pu_{0.65}O_2$ were measured in the temperature range of 993–1803 K, 960–1782 K and 956–1797 K, respectively. The measured enthalpy values were fitted to 4-term polynomial functions in temperature of the following form by using the least-squares method:

$$H_T - H_{298} (\text{kJ mol}^{-1}) = A(T/K) + B(T/K)^2 + C(K/T) + D$$

The following constraints were used for fitting the data: (a) $H_T - H_{298} = 0$ at 298 K and (b) the derivative of the function at 298 K is equal to the value of heat capacity of the solid solutions at 298 K ($C_{p,298}$) which was estimated from the literature data [14] for $C_{p,298}^0$ of pure UO_2 and PuO_2 by using Neumann–Kopp's molar additivity rule. However, for the estimation of S_{298} values needed for computing entropy and Gibbs energy functions the contribution of ideal entropy of mixing besides the molar additivity of the S_{298}^0 values of UO_2 and PuO_2 from literature [14] was taken into account. The

Table 1

Heat capacity and entropy values of (U,Pu) O_2 solid solutions employed in this study for computations

Solid solution	$C_{p,298}$ ($\text{J K}^{-1} \text{mol}^{-1}$)	S_{298} ($\text{J K}^{-1} \text{mol}^{-1}$)
$U_{0.55}Pu_{0.45}O_2$	64.835	77.816
$U_{0.45}Pu_{0.55}O_2$	65.089	75.636
$U_{0.35}Pu_{0.65}O_2$	65.343	75.298

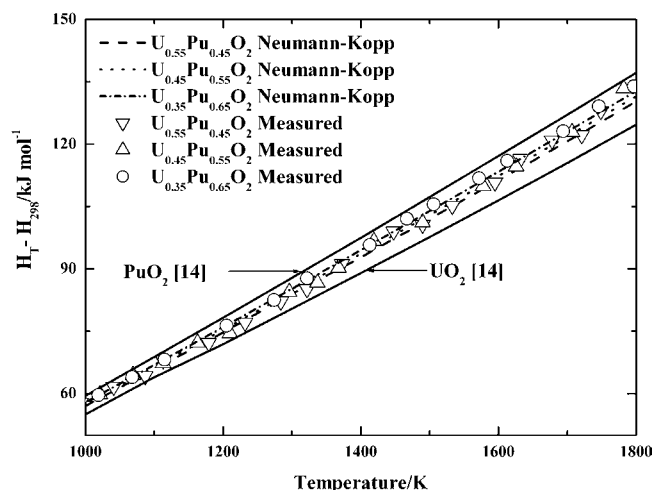


Fig. 1. Comparison of measured enthalpy increments of (U,Pu) O_2 solid solutions with the values computed by Neumann–Kopp's rule.

calculated heat capacity ($C_{p,298}$) and entropy (S_{298}) values at 298 K for the solid solutions and used for further computation of thermodynamic functions are given in Table 1.

The values of the constants of the fit equations obtained for the measured enthalpy increment values of $U_{0.55}Pu_{0.45}O_2$, $U_{0.45}Pu_{0.55}O_2$ and $U_{0.35}Pu_{0.65}O_2$ are given in Table 2. The equations fit the enthalpy increment data very well. The standard errors of the fit were 1.36%, 1.43% and 0.41% for $U_{0.55}Pu_{0.45}O_2$, $U_{0.45}Pu_{0.55}O_2$ and $U_{0.35}Pu_{0.65}O_2$, respectively. The estimates of the standard deviations for the fit were 1279 J mol^{-1} , 1268 J mol^{-1} , 386 J mol^{-1} respectively. The measured values of the enthalpy increments and the fit values for $U_{0.55}Pu_{0.45}O_2$, $U_{0.45}Pu_{0.55}O_2$ and $U_{0.35}Pu_{0.65}O_2$ are given in Tables 3–5. The values of other thermodynamic functions, namely, heat capacity, entropy and Gibbs energy function in the temperature range 298–1800 K were computed from the fit equations and are given in Tables 3–5.

4. Discussion

In Fig. 1, the present experimentally determined enthalpy increment values are compared with polynomial fits of UO_2 , PuO_2 and U–Pu-mixed oxides calculated using Neumann–Kopp's rule. In Fig. 2, computed heat capacity values from our fit equations for U–Pu-mixed oxides are compared with the values calculated using Neumann–Kopp's rule as well as UO_2 and PuO_2 values. As seen from the Fig. 1 the enthalpy increments for $U_{(1-y)}Pu_yO_2$ solid solutions with $y = 0.45, 0.55$ and 0.65 are indistinguishable within the

Table 2

Constants for the fit equations of the enthalpy increments $H_T - H_{298}$ (kJ mol^{-1}) = $A(T/K) + B(T/K)^2 + C(K/T) + D$

Solid solution	A	$B \times 10^3$	$C \times 10^{-4}$	D	Temperature (K)
$U_{0.55}Pu_{0.45}O_2$	77.983	6.121	149.325	-28803	298–1803
$U_{0.45}Pu_{0.55}O_2$	77.419	6.537	144.257	-28502	298–1782
$U_{0.35}Pu_{0.65}O_2$	79.757	6.051	160.203	-29691	298–1797

Table 3
Thermodynamic functions of $U_{0.55}Pu_{0.45}O_2$

T (K)	$H_T - H_{298}$ (kJ mol ⁻¹)		$100 \times (\Delta H_F - \Delta H_M) / \Delta H_F$ (%)	T (K)	$H_T - H_{298}$ (kJ mol ⁻¹)	C_p (J K ⁻¹ mol ⁻¹)	S_T (J K ⁻¹ mol ⁻¹)	$-(G_T - H_{298})/T$ (J K ⁻¹ mol ⁻¹)
	(ΔH_M) measured	(ΔH_F) fit						
993	57.76	56.17	-2.83	298	0	64.84	77.82	77.82
1041	61.66	60.45	-2.01	300	0.12	65.06	78.22	77.82
1087	64.26	64.57	0.48	400	7.11	73.55	98.25	80.49
1113	68.06	66.92	-1.71	500	14.71	78.13	115.19	85.78
1179	72.21	72.91	0.97	600	22.68	81.18	129.72	91.92
1232	77.09	77.77	0.88	700	30.92	83.51	142.42	98.25
1284	82.16	82.58	0.52	800	39.37	85.44	153.70	104.49
1322	85.16	86.12	1.12	900	48.00	87.16	163.86	110.53
1373	91.23	90.89	-0.37	1000	56.79	88.73	173.13	116.33
1448	99.04	97.98	-1.08	1100	65.74	90.22	181.66	121.89
1490	100.67	101.98	1.29	1200	74.84	91.64	189.57	127.20
1533	105.21	106.10	0.84	1300	84.07	93.02	196.96	132.29
1595	110.83	112.09	1.12	1400	93.44	94.36	203.90	137.16
1632	116.43	115.68	-0.64	1500	102.94	95.68	210.45	141.83
1678	120.93	120.18	-0.63	1600	112.57	96.99	216.67	146.31
1721	122.18	124.40	1.79	1700	122.34	98.28	222.59	150.63
1749	128.00	127.17	-0.65	1800	132.23	99.56	228.24	154.78
1803	134.35	132.53	-1.37					

ΔH_M : enthalpy increment – measured value; ΔH_F : enthalpy increment – fit value.

Table 4
Thermodynamic functions of $U_{0.45}Pu_{0.55}O_2$

T (K)	$H_T - H_{298}$ (kJ mol ⁻¹)		$100 \times (\Delta H_F - \Delta H_M) / \Delta H_F$ (%)	T (K)	$H_T - H_{298}$ (kJ mol ⁻¹)	C_p (J K ⁻¹ mol ⁻¹)	S_T (J K ⁻¹ mol ⁻¹)	$-(G_T - H_{298})/T$ (J K ⁻¹ mol ⁻¹)
	(ΔH_M) measured	(ΔH_F) fit						
960	53.48	53.35	-0.25	298	0	65.09	75.64	75.64
1021	59.81	58.77	-1.76	300	0.12	65.31	76.04	75.64
1069	64.45	63.08	-2.17	400	7.12	73.63	96.11	78.32
1113	67.30	67.06	-0.36	500	14.73	78.19	113.07	83.62
1163	72.22	71.62	-0.84	600	22.71	81.26	127.61	89.77
1210	74.46	75.94	1.94	700	30.96	83.63	140.32	96.10
1296	84.44	83.93	-0.61	800	39.42	85.63	151.62	102.35
1337	86.63	87.77	1.30	900	48.07	87.41	161.81	108.40
1368	90.24	90.70	0.50	1000	56.90	89.05	171.11	114.21
1419	96.68	95.54	-1.20	1100	65.88	90.61	179.67	119.78
1490	101.16	102.33	1.15	1200	75.02	92.11	187.62	125.11
1578	109.92	110.86	0.84	1300	84.30	93.56	195.05	130.20
1626	114.59	115.55	0.83	1400	93.73	94.99	202.04	135.09
1707	122.92	123.55	0.51	1500	103.30	96.39	208.64	139.77
1782	133.37	131.03	-1.79	1600	113.01	97.78	214.90	144.27
				1700	122.85	99.15	220.87	148.60
				1800	132.83	100.51	226.58	152.78

ΔH_M : enthalpy increment – measured value; ΔH_F : enthalpy increment – fit value.

Table 5
Thermodynamic functions of $U_{0.35}Pu_{0.65}O_2$

T (K)	$H_T - H_{298}$ (kJ mol ⁻¹)		$100 \times (\Delta H_F - \Delta H_M) / \Delta H_F$ (%)	T (K)	$H_T - H_{298}$ (kJ mol ⁻¹)	C_p (J K ⁻¹ mol ⁻¹)	S_T (J K ⁻¹ mol ⁻¹)	$-(G_T - H_{298})/T$ (J K ⁻¹ mol ⁻¹)
	(ΔH_M) measured	(ΔH_F) fit						
956	53.62	53.76	0.262	298	0	65.34	75.30	75.30
1019	59.65	59.44	-0.357	300	0.12	65.59	75.70	75.30
1068	63.93	63.89	-0.061	400	7.19	74.59	95.96	78.00
1115	68.18	68.20	0.023	500	14.90	79.40	113.17	83.36
1205	76.38	76.53	0.205	600	23.01	82.57	127.94	89.59
1274	82.48	83.00	0.623	700	31.39	84.96	140.86	96.01
1322	87.72	87.54	-0.212	800	39.99	86.94	152.33	102.35
1413	95.73	96.22	0.508	900	48.77	88.67	162.68	108.48
1467	102.06	101.43	-0.627	1000	57.72	90.26	172.10	114.38
1506	105.54	105.21	-0.313	1100	66.82	91.75	180.77	120.03
1572	111.81	111.66	-0.137	1200	76.07	93.17	188.82	125.43
1613	115.98	115.69	-0.245	1300	85.45	94.54	196.33	130.60
1694	123.15	123.73	0.470	1400	94.97	95.88	203.39	135.55
1746	129.10	128.93	-0.135	1500	104.63	97.20	210.05	140.29
1797	133.91	134.06	0.113	1600	114.41	98.50	216.36	144.85
				1700	124.33	99.78	222.37	149.24
				1800	134.37	101.05	228.11	153.46

ΔH_M : enthalpy increment – measured value; ΔH_F : enthalpy increment – fit value.

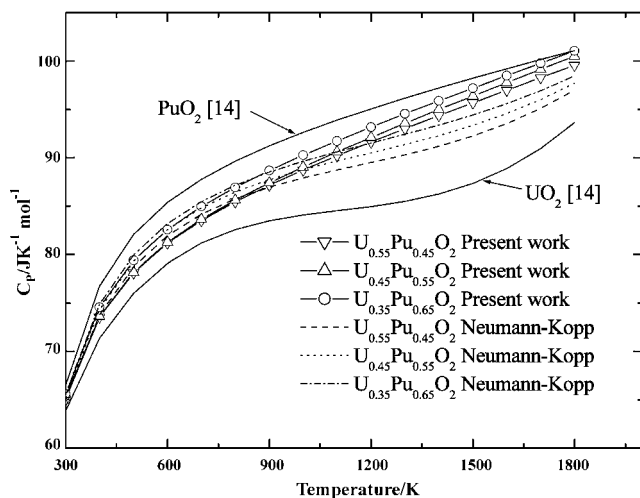


Fig. 2. Comparison of heat capacity data of $(\text{U,Pu})\text{O}_2$ solid solutions calculated from present enthalpy increment measurements with those calculated by Neumann–Kopp's rule.

experimental uncertainties. From Fig. 2, it can be seen that the heat capacity values of the solid solutions are in agreement with the computed mole average values using the equations of Carbajo et al. [14] the maximum deviation being 4%. The results indicate that the heat capacities of these plutonium rich $\text{U}_{(1-y)}\text{Pu}_y\text{O}_2$ solid solutions, in the temperature range 298–1800 K, obey the Neumann–Kopp's molar additivity rule.

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