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Calorimetric studies on urania–thoria solid solutions

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Abstract

The enthalpy increments of $(U_yTh_{1-y})O_2$ solid solutions with $y=0.1$, 0.5 and 0.9 were measured by using a drop calorimeter of isoperibol type. The experimental data cover the temperature range 473–973 K relative to 298 K. Other thermodynamic functions such as heat capacity, entropy and free energy function of these solid solutions were derived from the measured enthalpy increment values. The results indicate that the enthalpies of $(U_yTh_{1-y})O_2$ solid solutions in the temperature range 473–973 K obey the Neumann–Kopp molar additivity rule. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Urania–thoria solid solutions; Enthalpy increments; Drop calorimetry

1. Introduction

Studies on the oxides and mixed oxides of actinide elements such as thorium, uranium and plutonium are of great interest in nuclear industry since some of the oxides are used as nuclear fuels and some as blanket materials in various types of reactors [1]. The thermodynamic properties such as enthalpy and heat capacity of these materials are needed for reactor physics and safety calculations. The thermal properties of urania, thoria, plutonia and urania–plutonia have been studied extensively in the past and a reasonable body of data exists [2,3]. However, there is paucity of data on thoria–urania and thoria–plutonia mixed oxides. For example, in the case of urania–thoria solid solutions, enthalpies and heat capacities are available in the literature only for thoria-rich (≤20 mole % of urania) solid solutions over a limited temperature range [4,5]. In addition, it has not been clearly established whether the molar additivity rule of Neumann–Kopp is obeyed by these solid solutions. Hence, in the present study, the enthalpy increments of $(U_yTh_{1-y})O_2$ solid solutions with $y=0.1$, 0.5 and 0.9 were measured in the temperature range 473–973 K by using a drop calorimeter developed in our laboratory, with a view to generate more data on the thermal properties of these solid solutions which in turn will help to understand the U–Th–O system completely.

2. Experimental

2.1. Preparation of the sample

Urania–thoria solid solutions were prepared as follows: Ammonium diuranate and thorium hydroxide were co-precipitated from a mixture of uranium and thorium nitrate solution by the addition of aqueous ammonia. The precipitate was dried and calcined at 1073 K in air for 5 h. The calcined powders were then compacted at 500 MPa into pellets of 10 mm diameter and 2–3 mm thickness by employing an electrically operated double action hydraulic press. No binder or lubricant was added for the preparation of the compacts. The compacts thus prepared were sintered at 1873 K for 6 h in a flowing argon–8 vol. % hydrogen gas mixture. The oxygen to metal ratio of the compact was fixed at 2.000 by equilibrating the compact with H_2–H_2O gas mixture having an oxygen potential of -510 kJ mol.$^{-1}$ at 1073 K till equilibrium was established between the gas phase and $(U,Th)O_2$ compact [6]. Before carrying out calorimetric studies, the samples were characterised for their chemical composition (by elemental analyses for uranium and thorium as well as lattice parameter measure-

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ments), phase composition (by X-ray diffraction studies) and impurity content (by inductively coupled plasma mass spectrometry and optical emission spectrometry). The total metallic impurity of the mixed oxide samples employed in this study was less than 100 ppm (by weight).

2.2. Calorimeter

The calorimeter employed in this study for enthalpy measurements was a drop calorimeter of the isoperibol type. The equipment and the validation of the measurement technique are described elsewhere [7]. Essentially, the calorimeter consists of a nichrome wire wound furnace, with provisions for heating and holding the sample at the experimental temperatures, and a calorimeter proper. The temperature of the furnace was controlled within ±1 K. The calorimeter proper is essentially a brass 'receiving crucible' maintained at 298 K. The detector is a novel thermopile whose design and construction are described elsewhere [7]. The temperature of the sample was measured using a Type K thermocouple. In order to prevent the oxidation of the oxide samples, argon–8 vol.% hydrogen gas mixture was continuously flown over the sample.

2.3. Method of measurement.

In a typical experiment, the sample or the reference material was placed in the furnace at the desired temperature for a period of about 30 min. to ensure the temperature of equilibration. The sample size was approximately 0.2–0.5 g. The reference material employed in this study was the calorimetric standard, synthetic sapphire (≅0.05–0.1 g, SRM-720, α-Al_2O_3), obtained from NIST, USA. During a drop experiment, one sample and two standards at the experimental temperature were dropped alternatively into the working crucible maintained at 298 K. The resultant output of the detector was amplified and monitored continuously by using a high-impedance multimeter and the data acquired using a computer. The output from the computer gives the trace of the temperature change of the working crucible as a function of time. By using the values of the areas of the curves measured in the case of standard and sample, and the known enthalpy increment data of the standard, the enthalpy increment, $H_T^O - H_{298}^O$, of the sample was calculated.

3. Results and discussion

The measured enthalpy increments of $(U_{0.1}Th_{0.9})O_2$, $(U_{0.5}Th_{0.5})O_2$, and $(U_{0.9}Th_{0.1})O_2$ solid solutions were fitted to polynomials in temperature of the following form by the least squares method:

$$H_T^O - H_{298}^O = A*T + B*T^2 + C*T^{-1} + D$$

Table 1
Heat capacity and entropy values of $(U,Th)O_2$ solid solutions employed in this study for computations

Sample	$Cp,_{298.15}$ (J mol^{-1} K^{-1})	$S^O_{298.15}$ (J mol^{-1} K^{-1})
$(U_{0.1}Th_{0.9})O_2$	61.93	66.38
$(U_{0.5}Th_{0.5})O_2$	62.67	71.10
$(U_{0.9}Th_{0.1})O_2$	63.41	75.82

The differentiated form of this equation is the heat capacity over the given temperature range

$$Cp = A + 2*B*T - C*T^{-2}$$

The two boundary conditions used for the fitting were:

(i) $H^O T - H_{298}^O = 0$
at $T = 298.15$ and
(ii) Heat capacity of the solid solutions at 298.15 K ($Cp,_{298}$)

The heat capacity of $(U,Th)O_2$ solid solutions at 298.15 K are not available in the literature. Hence, they were obtained from the data on the heat capacity of pure urania and thoria [2] by applying the molar additivity rule. The calculated heat capacities of $(U_{0.1}Th_{0.9})O_2$, $(U_{0.5}Th_{0.5})O_2$, and $(U_{0.9}Th_{0.1})O_2$ solid solutions at 298 K are given in Table1. The values of the constants of the fit expressions obtained for the measured enthalpy values are given in Table 2.

The enthalpy values of $(U_{0.1}Th_{0.9})O_2$, $(U_{0.5}Th_{0.5})O_2$, and $(U_{0.9}Th_{0.1})O_2$ solid solutions computed from the fit expressions are given in Table 3 along with the measured values. The enthalpy values computed based on the molar additivity rule of Neumann–Kopp are also shown in this table. The standard error between the experimental result and the smoothed enthalpy values from the fit equation was computed using the following expression:

$$(\text{Standard error})^2$$

$$= (\Sigma \text{ differences})^2/(\text{no. of observations} - \text{no. of coefficients})$$

The computed standard error values are also shown in Table 3. The estimated error involved in the measurements is ±2% taking into account the precision of the measurements as well as the error involved in the measurement of the temperature of the sample.

Table 2
Constants for the fit equations of the enthalpy increments $H_T^O - H_{298}^O = A*T + B*T^2 + C*T^{-1} + D$

Solid solution	A	$B*10^4$	$C*10^{-4}$	D
$(U_{0.1}Th_{0.9})O_2$	71.923	34.659	107.20	−25347
$(U_{0.5}Th_{0.5})O_2$	74.249	35.114	121.54	−26526
$(U_{0.9}Th_{0.1})O_2$	72.344	67.454	115.177	−26032

Table 3
Enthalpies of urania–thoria solid solutions

T (K)	$H_T^O - H_{298}^O$ (J mol^{-1}) for $(U_{0.1}Th_{0.9})O_2$			$H_T^O - H_{298}^O$ (J mol^{-1}) for $(U_{0.5}Th_{0.5})O_2$			$H_T^O - H_{298}^O$ (J mol^{-1}) for $(U_{0.9}Th_{0.1})O_2$		
	Measured	Calculated (from fit eqn.)	Calculated (molar additivity rule)	Measured	Calculated (from fit eqn.)	Calculated (molar additivity rule)	Measured	Calculated (from fit eqn.)	Calculated (molar additivity rule)
473	11 469±247	11 713.88	11 613	12 489±697	11 948.94	11 894	12 211±389	12 130.93	12 174
523	15 721±385	15 265.94	15 128	15 652±472	15 590.59	15 522	15 700±257	15 851.27	15 916
573	19 011±236	18 873.15	18 700	19 113±842	19 292.67	19 216	19 649±137	19 645.98	19 731
623	22 555±221	22 526.39	22 322	22 815±367	23 044.86	22 964	23 245±389	23 505.25	23 607
673	27 684±1510	26 219.28	25 988	26 713±757	26 839.9	26 761	27 599±500	27 422.22	27 534
698	27 892±1080	28 079.08	27 837	28 414±718	28 751.79	28 676	29 197±1085	29 400.74	29 515
723	29 059±346	29 947.17	29 695	30 829±897	30 672.54	30 601	31 628±947	31 391.92	31 507
748	31 684±745	31 823.14	31 562	32 721±558	32 601.71	32 536	33 542±571	33 395.35	33 510
773	33 544±500	33 706.64	33 437	34 184±805	34 538.90	34 479	35 509±857	35 410.66	35 521
798	35 012±678	35 597.39	35 322	36 312±716	36 483.77	36 432	37 208±827	37 437.51	37 543
823	37 221±789	37 495.10	37 215	39 288±812	38 436.02	38 394	39 402±1108	39 475.64	39 572
848	38 998±309	39 399.55	39 116	40 037±946	40 395.39	40 363	42 092±647	41 524.78	41 611
873	41 147±470	41 310.54	41 025	42 504±622	42 361.65	42 341	43 333±463	43 584.72	43 658
898	44 472±1481	43 227.87	42 942	44 067±1707	44 334.57	44 327	45 507±987	45 655.25	45 712
923	45 386±821	45 151.39	44 866	46 446±646	46 313.99	46 320	47 372±624	47 736.21	47 775
948	47 095±721	47 080.94	46 798	48 125±979	48 299.73	48 321	50 214±1348	49 827.42	49 844
973	48 736±1723	49 016.40	48 737	50 435±832	50 291.64	50 330	51 857±1087	51 928.77	51 922
Standard error:		1915			1250			956	

The enthalpy increment values obtained from the fit equations are shown in Fig. 1 along with the experimental values. The literature data on the enthalpy increments of urania and thoria are also shown in Fig. 1 for the purpose of comparison. Fischer et al. [4] have measured the enthalpy increments of $(U_{0.08}Th_{0.92})O_2$, $(U_{0.15}Th_{0.85})O_2$, and $(U_{0.3}Th_{0.7})O_2$ over the temperature range 2300–3400 K. A comparison between our results and those of Fischer et al. is not appropriate because of the large difference in the temperature of the two sets of measurements. Springer et al. [5] have measured the enthalpy increments of $(U_{0.1}Th_{0.9})O_2$, and $(U_{0.2}Th_{0.8})O_2$ over the temperature range 573–2173 K. However, the data reported by them for $(U_{0.1}Th_{0.9})O_2$ lie below those of both urania and thoria, where as, the enthalpy increment data obtained in this study lie above that of thoria.

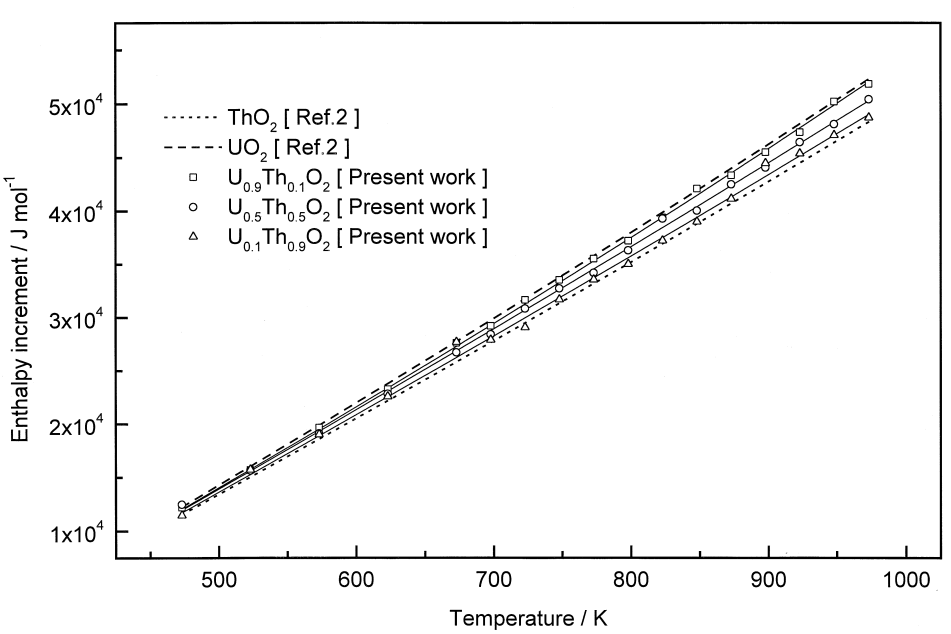

Fig. 1. Enthalpy increments of $(U,Th)O_2$ solid solutions.

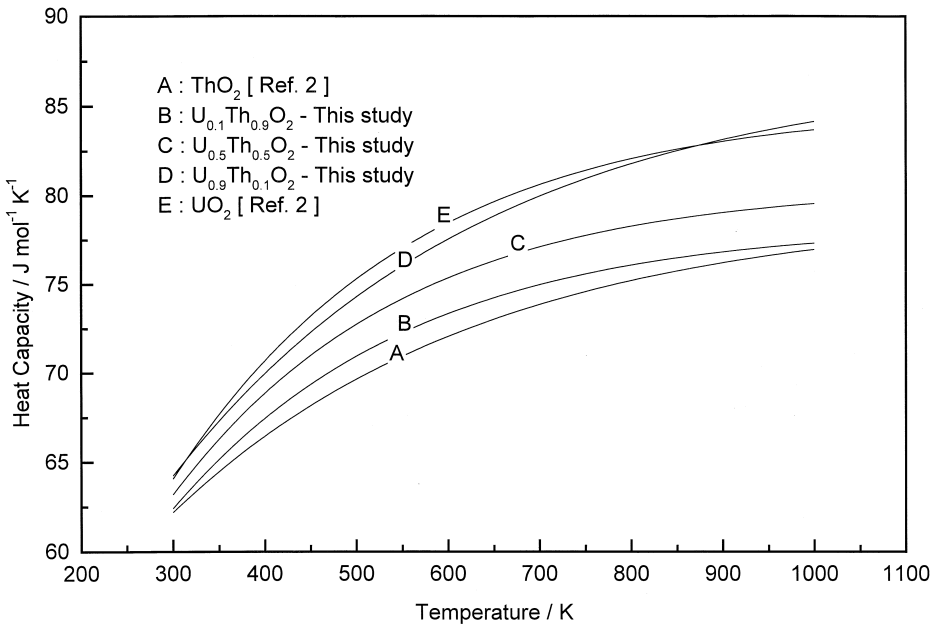

Fig. 2. Variation of heat capacities of $(U_{0.1}Th_{0.9})O_2$, $(U_{0.5}Th_{0.5})O_2$, and $(U_{0.9}Th_{0.1})O_2$ solid solutions with temperature.

The enthalpy increment data of this study were used to compute other thermodynamic functions such as heat capacity, entropy and free energy function of the solid solutions at various temperatures.* The results are shown in Table 4. The S^{O}_{298} values of the solid solutions required for the computation of free energy functions were again obtained from S_{298} of pure urania and thoria [2] by applying the molar additivity rule. The S_{298} values employed in this study for the computations are given in Table 1. Fig. 2 shows the variation of heat capacities of $(U_{0.1}Th_{0.9})O_2$ $(U_{0.5}Th_{0.5})O_2$ and $(U_{0.9}Th_{0.1})O_2$ solid solutions with temperature. The heat capacities of the solid solutions lie between the pure components of the solid solutions.

Figs. 3–5 compares the measured enthalpy increments with the values computed by applying the molar additivity

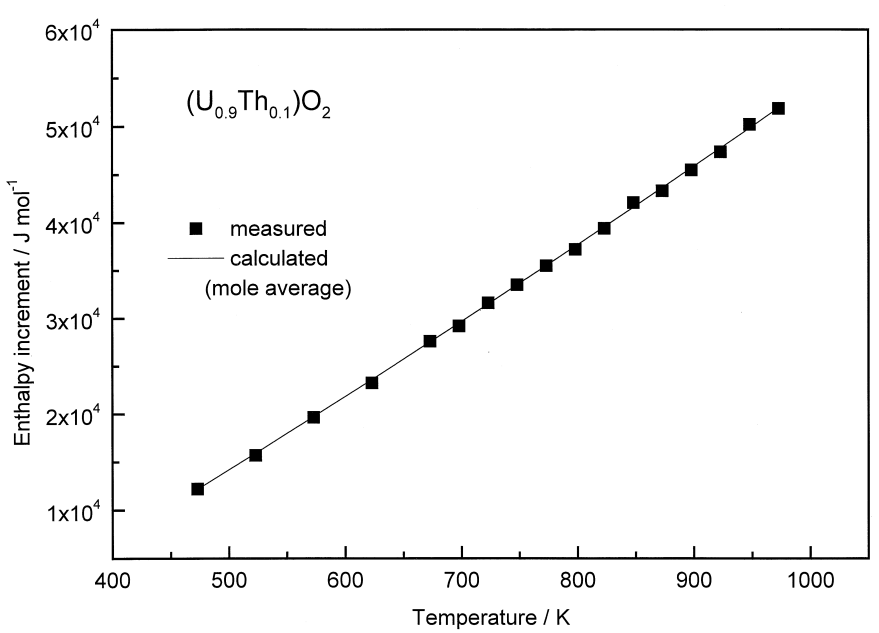

Fig. 3. Comparison of measured enthalpy increments of $(U_{0.1}Th_{0.9})O_2$ solid solution with the values computed by applying the molar additivity rule.

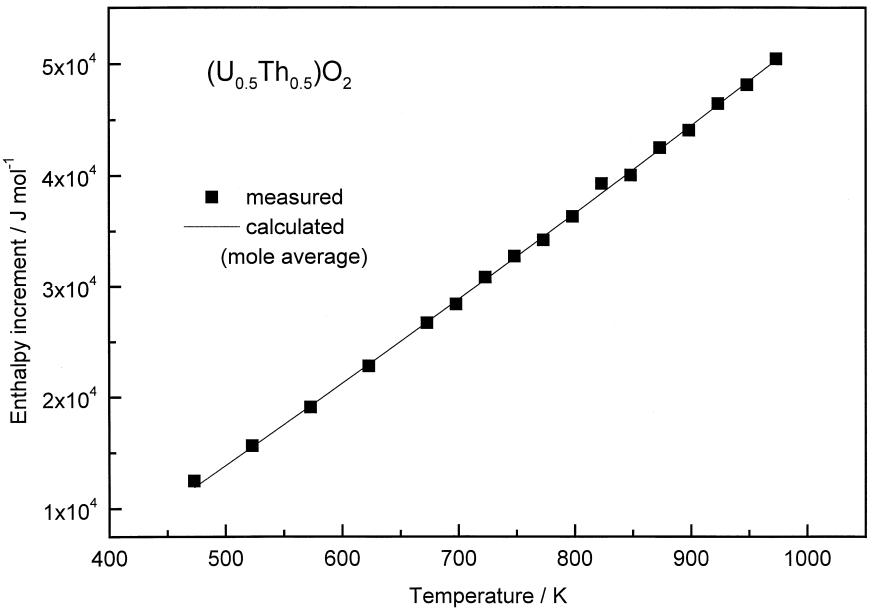

Fig. 4. Comparison of measured enthalpy increments of $(U_{0.5}Th_{0.5})O_2$ solid solution with the values computed by applying the molar additivity rule.

rule of Neumann–Kopp. The results indicate that the measured enthalpy increments of $(U_{0.1}Th_{0.9})O_2$, $(U_{0.5}Th_{0.5})O_2$, and $(U_{0.9}Th_{0.1})O_2$ over the temperature range 473–973 K obey the Neumann–Kopp molar additivity rule within the experimental uncertainty. The experimental results of Fischer et al. [4] for $(U_{0.15}Th_{0.85})O_2$, and $(U_{0.3}Th_{0.7})O_2$ over the temperature range 2300–3400 K and Springer et al. [5] for $(U_{0.2}Th_{0.8})O_2$ over the temperature range 573–2173 K were also found to obey the molar additivity rule. These results suggest that the stoichiometric urania–thoria solid solutions behave ideally. This is in agreement with the conclusion arrived at based on the oxygen potential measurements reported in the literature [8–14].

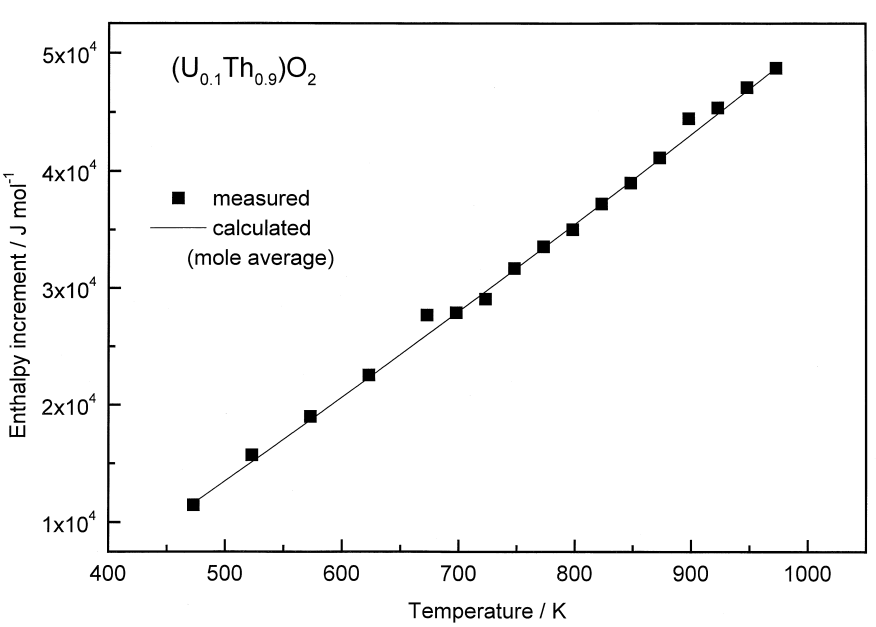

Fig. 5. Comparison of measured enthalpy increments of $(U_{0.9}Th_{0.1})O_2$ solid solution with the values computed by applying the molar additivity rule.

Table 4
Values for heat capacity, entropy and free energy functions of urania–thoria solid solutions (heat capacity, entropy and free energy functions are in J mol^{-1} K^{-1})

T (K)	$(U_{0.1}Th_{0.9})O_2$			$(U_{0.5}Th_{0.5})O_2$			$(U_{0.9}Th_{0.1})O_2$		
	Cp	S_T^O	FEF[a]	Cp	S_T^O	FEF	Cp	S_T^O	FEF
300	62.09	66.76	66.38	62.85	71.49	71.10	63.59	76.21	75.82
400	68.00	85.54	68.90	69.46	90.60	73.66	70.54	95.58	78.41
500	71.10	101.08	73.83	72.90	106.50	78.69	74.48	111.77	83.51
600	73.10	114.23	79.50	75.09	120.00	84.47	77.24	125.61	89.40
700	74.59	125.62	85.29	76.68	131.70	90.40	79.44	137.68	95.46
800	75.79	135.66	90.97	77.97	142.02	96.22	81.34	148.42	101.42
900	76.84	144.64	96.44	79.07	151.27	101.83	83.06	158.10	107.19
1000	77.78	152.79	101.68	80.06	159.65	107.20	84.68	166.93	112.73

[a] FEF = free energy function.

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