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Enthalpy increments and heat capacities of ThO_2 and $(Th_yU_{(1-y)})O_2$

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Abstract

Enthalpy increments of ThO_2, $(Th_{0.9804}U_{0.0196})O_2$, $(Th_{0.961}U_{0.039})O_2$, $(Th_{0.941}U_{0.059})O_2$, $(Th_{0.902}U_{0.098})O_2$ and simfuel of $(Th_{0.9804}U_{0.0196})O_2$ were measured using a high temperature Calvet drop calorimeter in the temperature range 375–991 K. The experimental values were used for calculating heat capacities of the compounds, which were compared with Neumann–Kopp's heat capacity values. On inter comparison of the heat capacity values of solid solution, $(Th_yU_{(1-y)})O_2$, with variation in the fraction of ThO_2, a trend was observed. In the temperature range of the present experiments, the compound $(Th_{0.961}U_{0.039})O_2$ showed minimum heat capacity values.

1. Introduction

With depleting uranium content in the earth soil, it is becoming important to explore other fissile elements, which can be used as a substitute of uranium in the nuclear fuel. Due to considerable abundance of thorium in some countries like India, thorium based mixed oxide fuels are being considered as future fuel for AHWR reactors. This fertile element can be converted into a fissile element ^{233}U in a nuclear reactor [1]. Though a considerable amount of fissile element inventory of ^{235}U or ^{239}Pu is required to start a reactor with thoria based fuel, the total amount of ^{235}U or ^{239}Pu required is much less because the reactor is able to sustain itself from converted fissile element, ^{233}U. In converter reactors, ^{233}U isotopes produced from ^{232}Th are not separated for feeding another reactor, but are burnt in the same reactor, thus reducing the problems related to handling, transportation and safeguard. Another important added advantage of thorium based fuels is that it reduces the transuranium wastes like plutonium, neptunium and americium, which cause main concerns during waste management as they are high level, long lived radioactive isotopes [2].

To understand in-pile behaviour of the fuel and to be able to predict its performance in accidental conditions, it is very important to understand thermophysical properties of the mixed oxide, $(Th,U)O_2$. Therefore, all the available literature data on enthalpy increment and heat capacity of the compounds, ThO_2, UO_2 and $(Th,U)O_2$ was critically analysed. A high temperature Calvet calorimeter was used for determining enthalpy increment values of ThO_2, various compositions of $(Th,U)O_2$ and simfuel of $(Th_{0.9804}U_{0.0196})O_2$. The values were optimized together with literature data. Estimated heat capacity values of the mixed oxide, $(Th,U)O_2$, using Neumann–Kopp's additivity rule were compared with the heat capacity values calculated from the polynomial fits obtained from experimental enthalpy increment data.

2. Experimental

The enthalpy increment measurements of ThO_2, $(Th_{0.9804}U_{0.0196})O_2$, $(Th_{0.961}U_{0.039})O_2$, $(Th_{0.941}U_{0.059})O_2$, $(Th_{0.902}U_{0.098})O_2$ compounds and simfuel of $(Th_{0.9804}$-

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$U_{0.0196})O_2$, were carried out using high temperature Calvet calorimeter in the temperature range 375–991 K. The thoria and urania samples were prepared by oxalate route. To obtain high density pellets at low sintering temperature, the oxides were mixed with approximately 500 ppm of MgO in the solution state, before precipitation. For making $(Th,U)O_2$ of different compositions, the ThO_2 (total impurity <1000 ppm) and UO_2 (total impurity <400 ppm) were mixed in required molar ratios and co-milled. Progressive milling technique was used for better homogeneity. The milled powders were compacted at 300 MPa, using a hydraulic press. The green pellets were sintered at 1923 K for 4 h in a molybdenum resistance furnace, in $N_2 + 8\%H_2$ atmosphere. For preparation of the simfuel, composition of the additives, Ba, Sr, Ce, Zr, Mo, Ru, Y, La and Nd, was calculated for 20 000 MWD/ton burn-up.

The details of the instrument used for determining enthalpy increment of the samples are given elsewhere [3]. For the sake of clarity, a brief description of the instrument is given here. The high temperature Calvet calorimeter used for the present experiments is an identical twin calorimeter with two identical alumina tubes. Two identical sets of Pt/Pt–Rh thermopiles are used for measuring heat flux from these alumina tubes during experiment. The whole set up is surrounded by massive block of alumina bricks to minimize thermal fluctuations. Through a vacuum tight assembly, a sample introducer is attached to the alumina tubes. The samples were loaded in sample introducer and maintained at ambient temperature. The heat change in the crucible when the sample was dropped from ambient temperature (298.15 K) to the experimental temperature was measured by heat flux principle. All the present enthalpy increment measurements were carried out in isothermal condition. To carry out the present measurements, 7 cm long quartz tubes were placed in the above mentioned alumina tubes. The whole set up was evacuated and flushed with argon two to three times while heating it to the experimental temperature. The experiments were carried out under steady argon atmosphere (purity 99.999%) at 1 atm pressure. When the experimental temperature was attained and calorimeter attained equilibrium, thermopile output became constant. At equilibrium experimental temperature, the calorimeter was calibrated using NBS standard synthetic sapphire (SRM 620). A weighed amount of the reference material was dropped from ambient temperature (298.15 K) into the calorimeter at experimental temperature. After four–five such drops, weighed amounts of the sample material were dropped at the same experimental temperature. These measurements were also repeated three to four times at the same temperature to confirm reproducibility of the measurements. Values showed good reproducibility with a standard deviation less than 1.0. For calibration, enthalpy increment values of synthetic sapphire was taken from literature [4]. Enthalpy increment values, $\Delta \mathbf{H}^{\mathrm{T}}_{298.15\,\mathrm{K}}$, of ThO_2, $(Th_{0.9804},U_{0.0196})O_2$, $(Th_{0.961},U_{0.039})O_2$, $(Th_{0.941},U_{0.059})O_2$ $(Th_{0.902},U_{0.098})O_2$, and simfuel of $(Th_{0.9804}U_{0.0196})O_2$ were determined at various temperatures.

3. Results

The experimentally determined enthalpy increment data acquired by above technique are listed in Tables 1–3. Enthalpy increment data of each selected compound was least square fitted into a polynomial equation, with a constraint, $\Delta \mathbf{H}^{\mathrm{T}}_{298.15\,\mathrm{K}} = 0$ at $T = 298.15$ K, using Origin software. The following set of polynomial equations were obtained:

$$\Delta H^{\mathrm{T}}_{298.15\,\mathrm{K}}\ (\mathrm{J/mol})\mathrm{ThO_2} = -25\,479.4 + 71.6726T + 4.1266 \times 10^{-3}T^2 + 1\,116\,094/T \qquad (298.15 - 940\ \mathrm{K}), \tag{1}$$

$$\Delta H^{\mathrm{T}}_{298.15\,\mathrm{K}}\ (\mathrm{J/mol})(\mathrm{Th_{0.9804}U_{0.0196}})\mathrm{O_2} = -29\,409.5 + 76.8601T + 1.7974 \times 10^{-3}T^2 + 1\,888\,448/T \qquad (298.15 - 981\ \mathrm{K}), \tag{2}$$

$$\Delta H^{\mathrm{T}}_{298.15\,\mathrm{K}}\ (\mathrm{J/mol})(\mathrm{Th_{0.961}U_{0.039}})\mathrm{O_2} = -22\,908.8 + 67.8243T + 4.399 \times 10^{-3}T^2 + 684\,523/T \qquad (298.15 - 914\ \mathrm{K}), \tag{3}$$

$$\Delta H^{\mathrm{T}}_{298.15\,\mathrm{K}}\ (\mathrm{J/mol})(\mathrm{Th_{0.941}U_{0.059}})\mathrm{O_2} = -29\,836.2 + 78.8135T - 3.042 \times 10^{-4}T^2 + 1\,897\,724/T \qquad (298.15 - 991\ \mathrm{K}), \tag{4}$$

$$\Delta H^{\mathrm{T}}_{298.15\,\mathrm{K}}\ (\mathrm{J/mol})(\mathrm{Th_{0.902}U_{0.098}})\mathrm{O_2} = -29\,336.0 + 78.3578T + 2.328 \times 10^{-4}T^2 + 1\,774\,856/T \qquad (298.15 - 991\ \mathrm{K}), \tag{5}$$

$$\Delta H^{\mathrm{T}}_{298.15\,\mathrm{K}}\ (\mathrm{J/mol})\ \text{simfuel of}\ (\mathrm{Th_{0.9804}U_{0.0196}})\mathrm{O_2} = -26\,902.2 + 73.2385T + 3.7114 \times 10^{-3}T^2 + 1\,412\,092/T \qquad (298.15 - 991\ \mathrm{K}). \tag{6}$$

Recently Bakker et al. [5] have evaluated thermal properties of ThO_2. After critical review of the enthalpy increment and heat capacity data available in literature, Bakker et al. [5] have derived an enthalpy increment equation based on the recommended data of Southard [6], Hoch and Johnston [7] and Fischer et al. [8]. The authors have ignored the data of Victor and Douglas [9], Jaeger and Veenstra [10] and Springer et al. [11,12] as they found that their values were not reliable in low

Table 1
A comparison of experimental enthalpy increment values ($\Delta_1 H^{\mathrm{T}}_{298.15\,\mathrm{K}}$) of ThO_2 and $(Th_{0.9804}U_{0.0196})O_2$ with enthalpy increment values calculated ($\Delta_2 H^{\mathrm{T}}_{298.15\,\mathrm{K}}$) using Eqs. (1) and (2), respectively

ThO_2						$(Th_{0.9804}U_{0.0196})O_2$					
T (K)	$\Delta_1 H^{\mathrm{T}}_{298.15\,\mathrm{K}}$ (J/mol)	$\Delta_2 H^{\mathrm{T}}_{298.15\,\mathrm{K}}$ (J/mol)	100× $\frac{\Delta_1 H-\Delta_2 H}{\Delta_1 H}$	c_p (Eq. (10)) (J/mol K)	c_p (Eq. (16)) (J/mol K)	T (K)	$\Delta_1 H^{\mathrm{T}}_{298.15\,\mathrm{K}}$ (J/mol)	$\Delta_2 H^{\mathrm{T}}_{298.15\,\mathrm{K}}$ (J/mol)	100× $\frac{\Delta_1 H-\Delta_2 H}{\Delta_1 H}$	c_p (Eq. (11)) (J/mol K)	c_p (Eq. (19)) (J/mol K)
376	4719	5021	−6.40	66.88	66.46	376	4780	4766	0.28	64.85	66.53
406	6839	7049	−3.07	68.25	67.84	406	6753	6743	0.14	66.86	67.92
406	7099	7049	0.71	68.25	67.84	427	8178	8160	0.22	68.04	68.79
437	9150	9184	−0.37	69.43	69.10	458	10 253	10 293	−0.39	69.50	69.95
458	10 642	10 649	−0.07	70.13	69.87	478	11 740	11 691	0.42	70.31	70.64
478	12 288	12 058	1.87	70.73	70.55	509	14 024	13 888	0.97	71.40	71.61
509	14 568	14 264	2.09	71.57	71.52	540	16 184	16 116	0.42	72.33	72.49
540	16 496	16 494	0.01	72.30	72.39	570	18 381	18 298	0.45	73.10	73.26
581	19 320	19 476	−0.81	73.16	73.43	601	20 540	20 575	−0.17	73.79	73.99
611	21 490	21 680	−0.88	73.73	74.11	632	22 689	22 872	−0.81	74.40	74.65
642	24 433	23 974	1.88	74.26	74.75	663	24 955	25 187	−0.93	74.95	75.26
673	25 948	26 284	−1.29	74.76	75.34	704	28 189	28 273	−0.30	75.58	75.97
714	30 160	29 362	2.65	75.38	76.03	734	30 289	30 547	−0.85	75.99	76.45
745	31 152	31 705	−1.78	75.81	76.50	765	32 886	32 909	−0.07	76.38	76.89
786	34 990	34 825	0.47	76.35	77.07	796	35 562	35 282	0.79	76.74	77.30
817	36 764	37 198	−1.18	76.74	77.45	817	37 120	36 896	0.60	76.97	77.55
847	38 937	39 505	−1.46	77.11	77.78	837	38 690	38 438	0.65	77.17	77.78
878	42 019	41 901	0.28	77.47	78.10	878	41 664	41 610	0.13	77.57	78.20
909	44 944	44 309	1.41	77.82	78.38	899	43 163	43 241	−0.18	77.76	78.39
940	46 534	46 726	−0.41	78.17	78.64	919	44 687	44 798	−0.25	77.93	78.57
						950	47 033	47 218	−0.39	78.18	78.82
						981	49 672	49 645	0.05	78.42	79.04

A comparison of heat capacity values calculated from Eqs. (10) and (11) with Bakker et al. and estimated heat capacity calculated from Eq. (19).

Table 2

A comparison of experimental enthalpy increment values ($\Delta_1 H^{T}_{298.15\,K}$) of $(Th_{0.961}U_{0.039})O_2$ and $(Th_{0.941}U_{0.059})O_2$ with enthalpy increment values calculated ($\Delta_2 H^{T}_{298.15\,K}$) from Eqs. (3) and (4), respectively

$(Th_{0.961}U_{0.039})O_2$						$(Th_{0.941}U_{0.059})O_2$					
T (K)	$\Delta_1 H^{T}_{298.15\,K}$ (J/mol)	$\Delta_2 H^{T}_{298.15\,K}$ (J/mol)	$100 \times \frac{\Delta_1 H - \Delta_2 H}{\Delta_1 H}$	c_p (Eq. (12)) (J/mol K)	c_p (Eq. (19)) (J/mol K)	T (K)	$\Delta_1 H^{T}_{298.15\,K}$ (J/mol)	$\Delta_2 H^{T}_{298.15\,K}$ (J/mol)	$100 \times \frac{\Delta_1 H - \Delta_2 H}{\Delta_1 H}$	c_p (Eq. (13)) (J/mol K)	c_p (Eq. (19)) (J/mol K)
376	4952	5036	−1.69	66.29	66.60	376	4806	4802	0.09	65.16	66.60
427	8314	8457	−1.72	67.83	68.87	401	6467	6452	0.24	66.77	68.87
453	10 140	10 229	−0.88	68.47	69.86	427	8203	8206	−0.04	68.15	69.86
478	12 000	11 948	0.43	69.03	70.73	427	8304	8206	1.18	68.15	70.73
504	13 734	13 750	−0.12	69.56	71.56	453	9947	9993	−0.46	69.29	71.56
529	15 618	15 495	0.79	70.03	72.29	478	11 739	11 737	0.01	70.22	72.29
581	19 202	19 160	0.22	70.91	73.63	504	13 531	13 574	−0.32	71.04	73.63
632	23 000	22 796	0.89	71.67	74.76	529	15 391	15 358	0.21	71.71	74.76
683	26 605	26 470	0.51	72.37	75.72	555	17 230	17 231	−0.01	72.31	75.72
734	30 273	30 177	0.32	73.01	76.55	555	17 190	17 231	−0.24	72.31	76.55
760	31 824	32 079	−0.80	73.33	76.93	581	19 064	19 118	−0.28	72.84	76.93
786	33 764	33 990	−0.67	73.63	77.27	581	19 054	19 118	−0.34	72.84	77.27
811	35 360	35 834	−1.34	73.92	77.58	581	19 078	19 118	−0.21	72.84	77.58
837	38 276	37 760	1.35	74.21	77.88	606	20 966	20 945	0.10	73.28	77.88
863	39 833	39 693	0.35	74.50	78.15	632	22 912	22 855	0.25	73.68	78.15
888	41 326	41 559	−0.56	74.77	78.39	683	26 686	26 630	0.21	74.33	78.39
914	43 668	43 506	0.37	75.05	78.63	734	30 413	30 434	−0.07	74.84	78.63
						786	34 409	34 338	0.21	75.26	77.39
						837	38 259	38 185	0.19	75.60	77.99
						888	42 046	42 047	0.00	75.87	78.50
						914	43 903	44 021	−0.27	75.99	78.73
						940	45 955	45 999	−0.09	76.09	78.95
						965	47 958	47 902	0.12	76.19	79.13
						991	49 870	49 884	−0.03	76.28	79.31

A comparison of heat capacity values calculated from Eqs. (12) and (13) with estimated heat capacity values calculated from Eq. (19).

Table 3
A comparison of experimental enthalpy increment values ($\Delta_1 H^{T}_{298.15\,K}$) of $(Th_{0.902}U_{0.098})O_2$ with enthalpy increment values calculated from Eq. (6) ($\Delta_2 H^{T}_{298.15\,K}$)

$(Th_{0.902}U_{0.098})O_2$									Simfuel of $(Th_{0.9804}U_{0.0196})O_2$				
T (K)	$\Delta_1 H^{T}_{298.15\,K}$ (J/mol)	$\Delta_2 H^{T}_{298.15\,K}$ (J/mol)	$100 \times \frac{\Delta_1 H - \Delta_2 H}{\Delta_1 H}$	c_p (Eq. (14)) (J/mol K)	c_p (Eq. (19)) (J/mol K)	c_p (Eq. (23)) (J/mol K)	c_p (Eq. (26)) (J/mol K)	c_p (Eq. (28)) (J/mol K)	T (K)	$\Delta_1 H^{T}_{298.15\,K}$ (J/mol)	$\Delta_2 H^{T}_{298.15\,K}$ (J/mol)	$100 \times \frac{\Delta_1 H - \Delta_2 H}{\Delta_1 H}$	c_p (Eq. (15)) (J/mol K)
376	4864	4880	−0.32	65.98	66.80	67.73	67.14	66.34	401	6620	6605	0.23	67.43
401	6498	6549	−0.78	67.51	68.00	68.51	68.12	67.91	427	8507	8350	1.85	68.66
427	8366	8322	0.53	68.82	69.11	69.21	68.98	69.24	453	10 084	10 123	−0.39	69.72
453	10 092	10 126	−0.34	69.92	70.12	69.82	69.73	70.32	478	12 090	11 921	1.40	70.61
478	11 930	11 885	0.37	70.81	71.00	70.34	70.36	71.18	504	13 773	13 742	0.23	71.42
504	13 651	13 737	−0.63	71.61	71.84	70.84	70.94	71.92	529	15 498	15 581	−0.54	72.12
529	15 650	15 536	0.73	72.26	72.58	71.27	71.44	72.52	555	17 327	17 439	−0.65	72.77
555	17 482	17 422	0.34	72.85	73.28	71.68	71.91	73.05	581	19 389	19 311	0.40	73.37
581	19 289	19 323	−0.18	73.37	73.94	72.07	72.34	73.49	606	21 182	21 199	−0.08	73.89
606	21 215	21 163	0.24	73.81	74.51	72.41	72.73	73.86	632	23 191	23 099	0.40	74.39
632	23 017	23 087	−0.31	74.21	75.07	72.75	73.10	74.19	658	25 253	25 012	0.95	74.86
683	26 979	26 890	0.33	74.87	76.04	73.37	73.76	74.71	683	27 143	26 936	0.76	75.28
734	29 866	30 722	−2.87	75.41	76.87	73.94	74.35	75.12	709	28 968	28 871	0.33	75.69
786	35 718	34 655	2.98	75.85	77.59	74.47	74.89	75.46	734	30 877	30 816	0.20	76.07
837	38 655	38 533	0.32	76.21	78.19	74.97	75.39	75.74	760	32 724	32 770	−0.14	76.44
888	42 430	42 428	0.00	76.52	78.70	75.45	75.86	75.98	786	34 589	34 734	−0.42	76.79
914	44 053	44 419	−0.83	76.66	78.93	75.69	76.08	76.1	811	36 939	36 706	0.63	77.11
940	46 000	46 414	−0.90	76.79	79.14	75.92	76.31	76.22	837	39 012	38 686	0.84	77.44
965	48 387	48 335	0.11	76.90	79.32	76.14	76.51	76.33	863	41 056	40 675	0.93	77.75
991	50 629	50 336	0.58	77.01	79.50	76.36	76.73	76.44	888	42 092	42 671	−1.38	78.04
									914	44 496	44 675	−0.40	78.33
									940	46 846	46 687	0.34	78.62
									965	49 012	48 705	0.63	78.89
									991	51 469	50 730	1.44	79.16

A comparison of heat capacity values calculated from Eq. (14) with estimated heat capacity values calculated from Eq. (19) and others.

temperature region. Fink [13] has recently published an excellent review on thermophysical properties of UO_2, where, the author has given equations for heat capacity and enthalpy increment of UO_2, obtained by a combined fit of some recommended enthalpy increment and heat capacity data [14–22], while ignoring some other publications [23–26] due to their disagreement with the recommended data. The equations for ThO_2 given by Bakker et al. and UO_2 given by Fink are as follows:

$$\begin{aligned}\Delta H^{T}_{298.15\,K}\ (\mathrm{J/mol})\mathrm{ThO_2} &= -20581.7 + 55.9620T + 25.62895 \times 10^{-3}T^{2} \\ &\quad - 12.2674 \times 10^{-6}T^{3} + 2.30613 \times 10^{-9}T^{4} \\ &\quad + 5.740310 \times 10^{5}/T, \end{aligned} \tag{7}$$

$$\begin{aligned}\Delta H^{T}_{298.15K}\ (\mathrm{J/mol})\mathrm{UO_2} &= -21176.2 + 52.1743T + 43.9735 \times 10^{-3}T^{2} \\ &\quad - 28.0804 \times 10^{-6}T^{3} + 7.88552 \times 10^{-9}T^{4} \\ &\quad - 0.52668 \times 10^{-12}T^{5} + 7.1391 \times 10^{5}/T. \end{aligned} \tag{8}$$

Fink has also given another expression for enthalpy increment of UO_2, a conventional form consisting of lattice, electronic contributions, etc. Normally this fits the enthalpy increment data better than the polynomial fit. Based on Browning et al. [27] comments that the constants determined by these fitting procedures need not necessarily have much relevance to the physical parameters that contribute to the heat capacity, Fink has recommended that the above polynomial and the following expression are equally good.

$$\begin{aligned}\Delta H^{T}_{298.15K}\ (\mathrm{J/mol})\mathrm{UO_2} &= 44779.42\left[\left(e^{548.68/T} - 1\right)^{-1} - \left(e^{548.68/298.15} - 1\right)^{-1}\right] \\ &\quad + 2.285 \times 10^{-3}\left[T^{2} - (298.15)^{2}\right] \\ &\quad + 2.360 \times 10^{7}e^{-185317/T}. \end{aligned} \tag{9}$$

In Fig. 1, the present experimentally determined enthalpy increment values of pure thorium oxide and $(Th,U)O_2$ mixed oxides are compared with polynomial fits of thorium oxide given by Bakker et al. [5] and uranium oxide given by Fink [13].

The following heat capacity equations of ThO_2 and mixed oxides were obtained by differentiating enthalpy increment expressions (1)–(5), with respect to temperature.

$$\begin{aligned}c_p\ (\mathrm{J/mol})\mathrm{ThO_2} &= 71.6726 + 8.2532 \times 10^{-3}T \\ &\quad - 1116094/T^{2}, \end{aligned} \tag{10}$$

$$\begin{aligned}c_p\ (\mathrm{J/mol})(\mathrm{Th_{0.9804}U_{0.0196}})\mathrm{O_2} &= 76.8601 + 3.598 \times 10^{-4}T - 1888448/T^{2}, \end{aligned} \tag{11}$$

$$\begin{aligned}c_p\ (\mathrm{J/mol})(\mathrm{Th_{0.961}U_{0.039}})\mathrm{O_2} &= 67.8243 + 8.798 \times 10^{-3}T - 684523/T^{2}, \end{aligned} \tag{12}$$

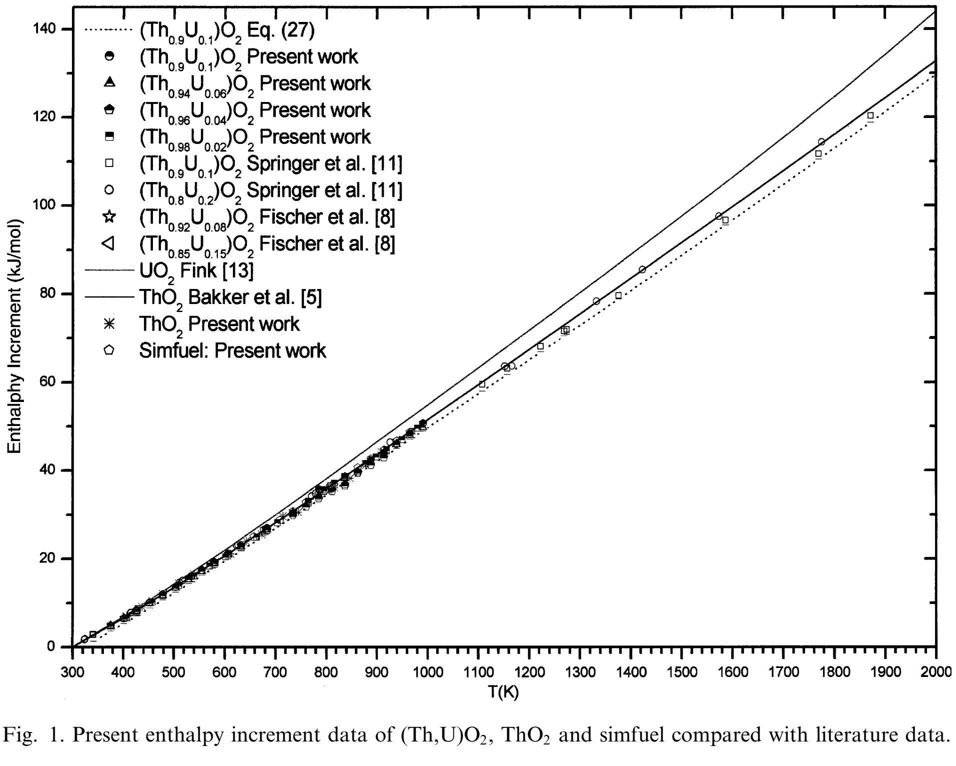

Fig. 1. Present enthalpy increment data of $(Th,U)O_2$, ThO_2 and simfuel compared with literature data.

$$c_p\ (\mathrm{J/mol})(\mathrm{Th}_{0.941}\mathrm{U}_{0.059})\mathrm{O}_2 = 78.8135 - 6.083\times10^{-3}T - 1\,897\,724/T^2, \quad (13)$$

$$c_p\ (\mathrm{J/mol})(\mathrm{Th}_{0.902}\mathrm{U}_{0.098})\mathrm{O}_2 = 78.3578 + 4.657\times10^{-4}T - 1\,774\,856/T^2, \quad (14)$$

$$c_p\ (\mathrm{J/mol})\ \text{simfuel of}\ (\mathrm{Th}_{0.9804}\mathrm{U}_{0.0196})\mathrm{O}_2 = 73.2385 + 7.4228\times10^{-3}T - 1\,412\,093/T^2. \quad (15)$$

On differentiating the enthalpy increment equation (7) for ThO_2, given by Bakker et al. [5] and Eqs. (8) and (9) for UO_2, given by Fink [13], the following expressions for heat capacity were obtained.

$$\begin{aligned} c_p\ (\mathrm{J/mol\,K})\mathrm{ThO}_2 &= 55.9620 + 0.05126T - 3.6802\times10^{-5}T^2 \\ &\quad + 9.2245\times10^{-9}T^3 - 5.7403\times10^5/T^2, \end{aligned} \quad (16)$$

$$\begin{aligned} c_p\ (\mathrm{J/mol\,K})\mathrm{UO}_2 &= 52.1743 + 0.08795T - 8.4241\times10^{-5}T^2 \\ &\quad + 3.1542\times10^{-8}T^3 - 2.6334\times10^{-12}T^4 \\ &\quad - 7.1391\times10^5/T^2, \end{aligned} \quad (17)$$

$$\begin{aligned} c_p\ (\mathrm{J/mol\,K})\mathrm{UO}_2 &= \frac{2.45696\times10^7 e^{(548.68/T)}}{T^2\left(e^{(548.68/T)}-1\right)^2} + 4.57\times10^{-3}T \\ &\quad + \frac{4.37348\times10^{11}e^{-18\,531.7/T}}{T^2}. \end{aligned} \quad (18)$$

Based on the heat capacity equations, (16) and (17) for pure ThO_2 and UO_2, respectively, the following equation was obtained for the heat capacity of mixed oxide $(\mathrm{Th}_y\mathrm{U}_{(1-y)})\mathrm{O}_2$, estimated using Neumann–Kopp's method.

$$\begin{aligned} c_p\ (\mathrm{J/mol\,K})(\mathrm{Th}_y\mathrm{U}_{(1-y)})\mathrm{O}_2 &= y(55.9620 + 0.05126T - 3.6802\times10^{-5}T^2 \\ &\quad + 9.2245\times10^{-9}T^3 - 5.740310\times10^5/T^2) \\ &\quad + (1-y)(52.1743 + 0.08795T - 8.4241\times10^{-5}T^2 \\ &\quad + 3.1542\times10^{-8}T^3 - 2.6334\times10^{-12}T^4 \\ &\quad - 7.1391\times10^5/T^2). \end{aligned} \quad (19)$$

4. Discussion

The mixed oxides, $(\mathrm{Th}_y\mathrm{U}_{(1-y)})\mathrm{O}_2$ taken for the present experimental work contained $\leqslant 10$ at.% UO_2. Whereas, Fischer et al. [28] have measured enthalpy increment of $(\mathrm{Th}_{0.70}\mathrm{U}_{0.30})\mathrm{O}_2$, $(\mathrm{Th}_{0.85}\mathrm{U}_{0.15})\mathrm{O}_2$ and $(\mathrm{Th}_{0.92}\mathrm{U}_{0.08})\mathrm{O}_2$ in the temperature range 2300–3400 K, using inverse drop calorimeter, where the samples were heated to required experimental temperature and dropped into an adiabatic calorimeter. The samples they investigated were prepared from enriched UO_2 with 93% ^{235}U isotope. They marked a discontinuity in the enthalpy increment data of these mixed oxides, though the transitions were less pronounced than in ThO_2. They have reported these transitions at 2900, 2950 and 2850 K for $(\mathrm{Th}_{0.70}\mathrm{U}_{0.30})\mathrm{O}_2$,$(\mathrm{Th}_{0.85}\mathrm{U}_{0.15})\mathrm{O}_2$ and $(\mathrm{Th}_{0.92}\mathrm{U}_{0.08})\mathrm{O}_2$, respectively. Whereas, in their previous work Fischer et al. [8] have reported a transition in ThO_2 at 2950 K. It is interesting to observe the change in the transition temperature with change in UO_2 content. When UO_2 is added in ThO_2, a sudden decrease in the transition temperature from 2950 K (for ThO_2) to 2850 K (for $(\mathrm{Th}_{0.92}\mathrm{U}_{0.08})\mathrm{O}_2$) is reported. On further addition of UO_2, the transition temperature increases back to 2950 K for $(\mathrm{Th}_{0.85}\mathrm{U}_{0.15})\mathrm{O}_2$ but then starts decreasing slowly with increase in UO_2 content. This trend is similar to the observation made for heat capacity variation of the mixed oxides with change in composition. The heat capacity of pure UO_2 is higher than that of ThO_2, but in mixed oxide it was observed that with increase in UO_2 content, the heat capacity decreases till U/(Th+U) fraction is approximately 0.04. After that the heat capacity values of the mixed oxide start increasing with further additions of UO_2. As seen from the Fig. 2, the heat capacity values of $(\mathrm{Th}_{0.8}\mathrm{U}_{0.2})\mathrm{O}_2$ calculated from enthalpy increment fit equation given by Springer et al. [11] are very similar to those of ThO_2. Springer et al. have reported enthalpy increment values of ThO_2, $(\mathrm{Th}_{0.902}\mathrm{U}_{0.098})\mathrm{O}_2$ and $(\mathrm{Th}_{0.804}\mathrm{U}_{0.196})\mathrm{O}_2$, in the temperature range 273–2270 K. They have also given least-square fit expression for the enthalpy increment data of the above mentioned compounds. As the data given by Springer et al. was for the enthalpy increments from 273 K to the experimental temperature, the values were corrected for enthalpy increments from 273 to 298 K by subtracting the $\Delta H_{273\,\mathrm{K}}^{298\,\mathrm{K}}$ values calculated from the polynomial enthalpy increment expressions given by them. These correction factors were 1474, 1425 and 1442 J/mol K for ThO_2, $(\mathrm{Th}_{0.902}\mathrm{U}_{0.098})\mathrm{O}_2$ and $(\mathrm{Th}_{0.804}\mathrm{U}_{0.196})\mathrm{O}_2$, respectively. For the sake of consistency, polynomial fits given by Springer et al. were also converted from cal/g K to J/mol K unit and are as follows:

$$\begin{aligned} \Delta H_{298.15\,\mathrm{K}}^{\mathrm{T}}\ (\mathrm{J/mol})\mathrm{ThO}_2 = -21\,856.8 &+ 66.6205T \\ &+ 5.043\times10^{-3}T^2 \\ &+ 460\,828/T, \end{aligned} \quad (20)$$

$$\begin{aligned} \Delta H_{298.15\,\mathrm{K}}^{\mathrm{T}}\ (\mathrm{J/mol})(\mathrm{Th}_{0.902}\mathrm{U}_{0.098})\mathrm{O}_2 &= -23\,526.1 + 70.0038T + 3.595\times10^{-3}T^2 \\ &\quad + 696\,160/T, \end{aligned} \quad (21)$$

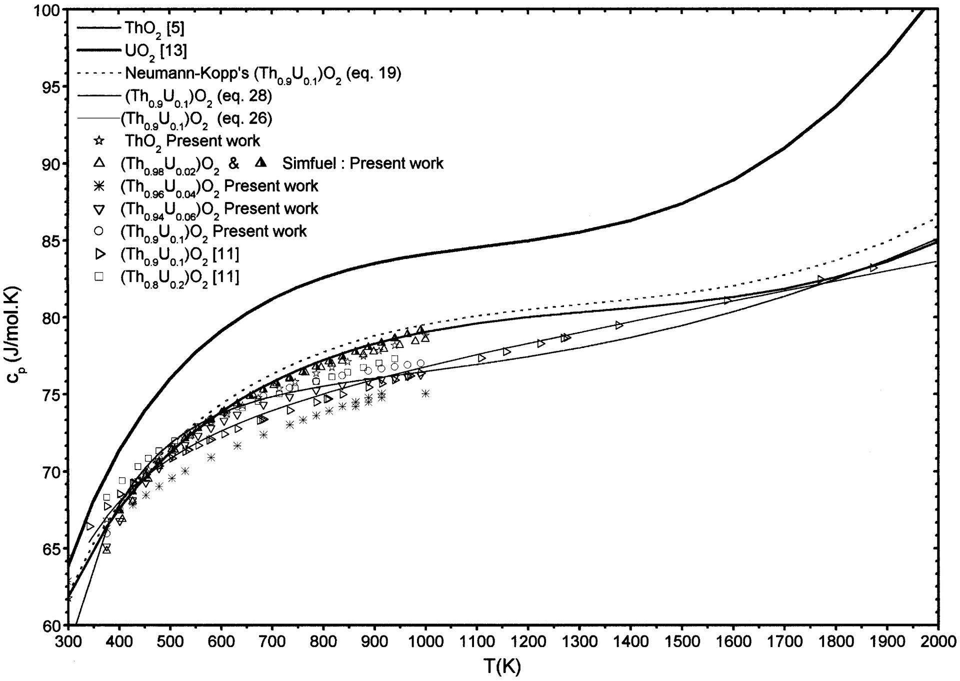

Fig. 2. A comparison of heat capacity data calculated from present enthalpy increment data with those calculated from enthalpy increment data reported in literature.

$$\Delta H^{\mathrm{T}}_{298.15\,\mathrm{K}}\ (\mathrm{J/mol})(\mathrm{Th}_{0.804}\mathrm{U}_{0.196})\mathrm{O}_2 = -24\,569.4 + 71.7804T + 3.479\times10^{-3}T^2 + 852\,371/T, \tag{22}$$

$$c_p\ (\mathrm{J/mol\,K})(\mathrm{Th}_{0.902}\mathrm{U}_{0.098})\mathrm{O}_2 = 70.0038 + 7.19\times10^{-3}T - 696\,160/T^2, \tag{23}$$

$$c_p\ (\mathrm{J/mol})(\mathrm{Th}_{0.804}\mathrm{U}_{0.196})\mathrm{O}_2 = 71.7804 + 6.958\times10^{-3}T - 852\,371/T^2. \tag{24}$$

Other than the enthalpy increment data of $(\mathrm{Th}_{0.902}\mathrm{U}_{0.098})\mathrm{O}_2$ by Springer et al. in the temperature range 273–2270 K and that of $(\mathrm{Th}_{0.92}\mathrm{U}_{0.08})\mathrm{O}_2$ by Fischer et al. [28] in the temperature range 2303–3302 K, all other mixed oxides investigated previously contained much higher U/(Th+U) compared to the present study. As the composition and temperature range of enthalpy increment data reported by Springer et al. [11] overlapped with the present work, the data was used along with the present enthalpy increment data for $(\mathrm{Th}_{0.902}\mathrm{U}_{0.098})\mathrm{O}_2$ to obtain a polynomial fit. The polynomial fit obtained from the combined enthalpy increment data of Springer et al. and the present work for $(\mathrm{Th}_{0.902}\mathrm{U}_{0.098})\mathrm{O}_2$ is given below along with heat capacity expression obtained by differentiating the enthalpy increment equation with temperature.

$$\Delta H^{\mathrm{T}}_{298.15\,\mathrm{K}}\ (\mathrm{J/mol})(\mathrm{Th}_{0.902}\mathrm{U}_{0.098})\mathrm{O}_2 = -24\,843.6 + 71.62T + 3.07\times10^{-3}T^2 + 959\,490/T, \tag{25}$$

$$c_p\ (\mathrm{J/mol\,K})(\mathrm{Th}_{0.902}\mathrm{U}_{0.098})\mathrm{O}_2 = 71.62 + 6.14\times10^{-3}T - 959\,490/T^2. \tag{26}$$

Another least-square polynomial fit was calculated using Origin software based on the enthalpy increment values of the present experiments and that reported by Springer for $(\mathrm{Th}_{0.902}\mathrm{U}_{0.098})\mathrm{O}_2$ along with the data of Fischer et al. [28] for $(\mathrm{Th}_{0.92}\mathrm{U}_{0.08})\mathrm{O}_2$ in the temperature range 2303–2800 K. Though Fischer et al. have reported enthalpy increment data of this composition in the temperature range 2303–3302 K, the values at temperatures $\geqslant$2850 K were not considered as Fischer et al. have reported a discontinuity in enthalpy increment for $(\mathrm{Th}_{0.92}\mathrm{U}_{0.08})\mathrm{O}_2$ at 2850 K. The best fitting polynomial expression (minimum chi-square value) obtained for this combined set of data is as follows:

$$\Delta H^{\mathrm{T}}_{298.15\,\mathrm{K}}\ (\mathrm{J/mol})(\mathrm{Th}_{0.9}\mathrm{U}_{0.1})\mathrm{O}_2 = -31\,835.8 + 85.1418T - 6.698\times10^{-3}T^2 + 2.274\times10^{-6}T^3 + 2\,082\,847/T, \tag{27}$$

$$c_p\ (\mathrm{J/mol\,K})(\mathrm{Th}_{0.9}\mathrm{U}_{0.1})\mathrm{O}_2 = 85.1418 - 1.3396\times10^{-2}T + 6.822\times10^{-6}T^2 - 2\,082\,847/T^2. \qquad (28)$$

The heat capacity values calculated from Eqs. (14), (19), (23), (26) and (28) are compared in the Table 3. It can be seen that the heat capacity values obtained from Neumann–Kopp's additivity rule are higher than the heat capacity values calculated from the present enthalpy increment data and this difference increases with increase in temperature and is maximum at the highest measurement temperature of the present studies, i.e., 991 K. Though Springer et al. [11] have measured enthalpy increment in the wide temperature range, 273–2270 K, but heat capacity calculated from their data also showed a maximum deviation from Neumann–Kopp's estimated heat capacity values in the same temperature zone. This can be explained from the observation that the heat capacity of thoria shows a flatter temperature dependence in the approximate temperature range 1000–1400 K. Whereas, heat capacity calculated from the present enthalpy increment data or the one calculated from the data of Springer et al. showed a change in slope at much lower temperature, ~650 K. Therefore, up to this temperature the heat capacity values calculated from the present enthalpy increment data are in very good agreement with those of Neumann–Kopp's. The heat capacity values calculated from the data of Springer et al. [11] showed only a slight decrease in slope at this temperature, whereas, the heat capacity of ThO_2 is almost independent of temperature in the above mentioned temperature range. The heat capacity values calculated from Eq. (28) follow the generic trend followed by heat capacities of ThO_2 and UO_2 compounds. Near room temperature, all the three show a steep heat capacity increase with increase in temperature, followed by a temperature region where the heat capacity variation with temperature is much flatter. After that heat capacity again increases steeply with increase in temperature. The heat capacity values calculated from Eq. (23), based on the enthalpy increment data given by Springer et al. and the heat capacity values calculated from Eq. (26), based on the present enthalpy increment data combined with that of Springer et al., are in good agreement with each other. They both show a steep increase in heat capacity with increase in temperature at lower temperatures but at temperatures greater than approximately 600 K, this effect decreases a little. They do not show a plateau region as observed in case of heat capacities of ThO_2 and UO_2. It was observed that in the temperature range of the present experiments, compared to the heat capacity values calculated from the enthalpy increment data of Springer et al., the heat capacity values obtained from the present enthalpy increment data were in better agreement with the ones calculated from Eq. (28). The present heat capacity equation (14) gives reasonably reliable heat capacity values when extrapolated by 200–300 K beyond experimental temperature range but after this the values are not reliable. Heat capacity values calculated from the enthalpy increment equation given by Fischer et al. for $(Th_{0.92}U_{0.08})O_2$ are very low compared to others. They have reported enthalpy increment measurements in temperature range 2303–2850 K, however, gave a temperature range 298.15–2850 K, for the polynomial equation obtained by fitting their enthalpy increment data. The disagreement between the heat capacity values obtained from other fits and those of Fischer et al. indicates that the temperature range of validity of their equation should be in proximity to the temperature range of their measurements i.e., 2303–2850 K. The heat capacity equation (28) for $(Th_{0.9}U_{0.1})O_2$, calculated from a combined fit of the enthalpy increment data in the temperature ranges 340–2271 K by Springer et al., 2303–2800 K by Fischer et al. [28] and 298.15–991 K of the present investigations, should be more reliable in the wide temperature range 298.15–2800 K. As seen in Fig. 2, the heat capacity values obtained from Eq. (28) are most reasonable over this wide temperature range as they do not deviate much from the heat capacity values of pure ThO_2 or heat capacity values of $(Th_{0.9}U_{0.1})O_2$ estimated using Neumann–Kopp's rule and show similar contours.

One important use of the heat capacity data is to calculate thermal conductivity of the material from the measured thermal diffusivity data. In the absence of any experimental heat capacity data, estimated heat capacity values, generally from Neumann–Kopp's method are used for the calculation of thermal conductivity. In the light of the present heat capacity values of the mixed oxide, it was considered important to understand the effect of this difference in estimated heat capacity values and the ones calculated from enthalpy increment data, on the thermal conductivity values. Sengupta et al. [29] have measured thermal diffusivity of $(Th_yU_{(1-y)})O_2$ for $y = 1.0$, 0.9804, 0.961, 0.941, 0.902 and 0.804 in the temperature range 973–1973 K. They have also reported thermal conductivity values calculated from their experimental data of thermal diffusivity and density and using Neumann–Kopp's heat capacity values, Eq. (16) for heat capacity of ThO_2 and Eq. (18) for heat capacity of UO_2. The temperature range of their thermal diffusivity measurements were such that the heat capacity values obtained from the present enthalpy increment data could not be used reliably over the whole temperature range. The thermal conductivity values of $(Th_{0.804}U_{0.196})O_2$ and $(Th_{0.902}U_{0.098})O_2$ were recalculated using the thermal diffusivity and density data given by them and the heat capacity values given by Springer et al. [11], i.e., Eq. (24) for $(Th_{0.804}U_{0.196})O_2$ and the heat capacity values obtained from the combined enthalpy

Table 4

A comparison of thermal conductivity values of $(Th_{0.92}U_{0.098})O_2$ and $(Th_{0.804}U_{0.196})O_2$, calculated using Neumann–Kopp's heat capacity values with the ones calculated using heat capacity Eqs. (28) and (24), respectively

T (K)	Thermal conductivity (W/m K) of $(Th_{0.902}U_{0.098})O_2$				T (K)	Thermal conductivity (W/m K) of $(Th_{0.804}U_{0.196})O_2$			
	Measured[a]	Corrected[a] (95% TD)	Measured[b]	Corrected[b] (95% TD)		Measured[a]	Corrected[a] (95% TD)	Measured[c]	Corrected[c] (95% TD)
873	5.3454	5.5917	5.167	5.4051	873	4.5826	5.02585	4.4469	4.877
973	4.8729	5.0974	4.6875	4.9035	973	4.4335	4.86224	4.3063	4.7228
1043	4.482	4.6885	4.3042	4.5026	1043	3.9893	4.37507	3.882	4.2574
1123	3.9742	4.1572	3.8152	3.9909	1123	3.5113	3.85085	3.4271	3.7585
1213	3.6537	3.822	3.5123	3.6741	1213	3.1928	3.50153	3.1289	3.4315
1313	3.3018	3.454	3.1844	3.3312	1313	2.9813	3.26959	2.9359	3.2199
1313	3.3018	3.454	3.1844	3.3312	1313	2.9815	3.26978	2.9361	3.2201
1413	3.0869	3.2291	2.9907	3.1284	1413	2.7688	3.03657	2.7392	3.0041
1513	2.6217	2.7425	2.5532	2.6708	1513	2.1678	2.3774	2.1523	2.3603
1613	2.2732	2.3779	2.225	2.3275	1613	2.0119	2.20636	2.0009	2.1943
1613	2.2087	2.3104	2.1618	2.2614	1613	2.0119	2.20636	2.0009	2.1943
1713	2.0541	2.1487	2.0191	2.1121	1713	1.9713	2.16194	1.9588	2.1482
1813	2.0464	2.1407	2.0171	2.11	1813	1.7085	1.8736	1.6904	1.8538
					1873	1.6943	1.85807	1.6689	1.8303

[a] Using estimated Newmann–Kopp's heat capacity values.

[b] Using heat capacity values calculated from Eq. (28).

[c] Using heat capacity values calculated from Eq. (24).

increment data, Eq. (28) for $(Th_{0.902}U_{0.098})O_2$, The thermal conductivity values of $(Th_{0.804}U_{0.196})O_2$, $(Th_{0.902}U_{0.098})O_2$ thus calculated were compared with the values obtained using Neumann–Kopp's estimated heat capacity. These values are given in Table 4 and compared in Fig. 3. For the compositions, $y = 0.9804$, 0.961 and 0.941, the thermal conductivity was recalculated using extrapolation of heat capacity equations obtained from the present enthalpy increment data to 1200 K. These values were also compared with thermal conductivity calculated using Neumann–Kopp's heat capacity data. All the thermal conductivity values were normalized to 95% TD before comparison. These values are given in Table 5 and plotted in Fig. 3. As seen from the table, the maximum difference between the values calculated using estimated and experimental heat capacity was not more than ±5%. As expected, maximum deviation between the two sets of thermal conductivity data was observed for $(Th_{0.961}U_{0.039})O_2$. This means that in the absence of experimental heat capacity values, Neumann–Kopp's estimated heat capacity values can also be used to get reasonably reliable thermal conductivity values for $(Th_yU_{(1-y)})O_2$. The thermal conductivity of $(Th_{0.9804}U_{0.0196})O_2$ in this temperature range is almost equal to that of pure ThO_2, therefore, the crossover of the curves seen in the figure is representative of scatter in the data. The effect of UO_2 addition on thermal conductivity in $(Th_yU_{(1-y)})O_2$ decreases with increase in temperature. A clear trend of decrease in thermal conductivity with increase in UO_2 content for $y \geqslant 0.9$ was observed for temperatures up to 1000 K [30,31]. However, as the temperature increases, thermal conductivity of the solid–solution decreases and so does the difference between the values of different U/M. Springer et al. [32] have reported that the thermal conductivity values were consistently lower for $(Th_yU_{(1-y)})O_2$ with $y = 0.9695$ and 0.925, particularly at low temperatures. Ferro et al. have also reported thermal diffusivity of $(Th_yU_{(1-y)})O_2$ for $y = 0.99$, 0.9, 0.96 [33] and $y = 1.0$, 0.94 [34]. In their earlier publication they have given density of the samples along with thermal diffusivity values, therefore, it was possible to calculate thermal conductivity using their data and heat capacity values calculated by Newmann–Kopp's estimation. But these values showed too big a scatter to understand any trend, therefore, they were not used for the present comparison. In the later publication, they have given only relative densities and not actual densities. Therefore, thermal conductivity values were calculated after back calculating the densities. These calculated values of thermal conductivity for $y = 0.94$ and 1.0 are shown in the Fig. 3. Pillai and Raj [35] have also reported thermal conductivity of ThO_2 and $(Th_{98}U_{0.02})O_2$. Instead of actual experimental values, they have given coefficients of the thermal conductivity fit, $1/(A + BT)$. For the purpose of comparison, thermal conductivity values of the two compounds were calculated using these coefficients, as shown in Fig. 3.

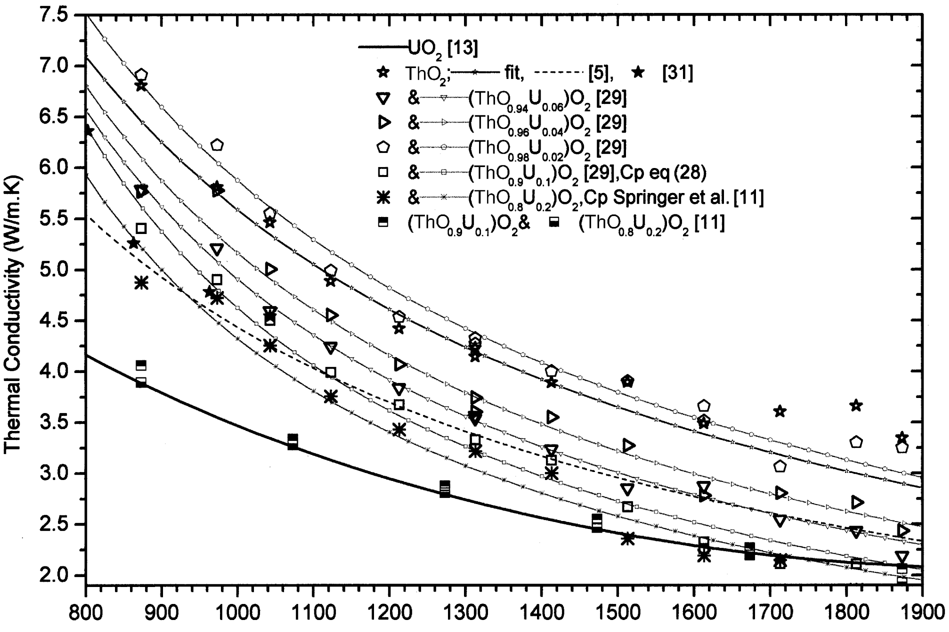

Fig. 3. Comparison of thermal conductivity values calculated from thermal diffusivity values given by Sen et al. with literature data.

Table 5
A comparison of thermal conductivity values of $(Th_{0.9804}U_{0.0196})O_2$, $(Th_{0.961}U_{0.039})O_2$ and $(Th_{0.941}U_{0.059})O_2$, calculated using Neumann–Kopp's heat capacity values with the ones calculated using heat capacity Eqs. (11)–(13), respectively

T (K)	Thermal Conductivity (W/mK) of $(Th_{0.9804}U_{0.0196})O_2$				Thermal conductivity (W/m K) of $(Th_{0.961}U_{0.039})O_2$				Thermal conductivity (W/m K) of $(Th_{0.941}U_{0.059})O_2$			
	Measured[a]	Corrected[a] (95% TD)	Measured[b]	Corrected[b] (95% TD)	Measured[a]	Corrected[a] (95% TD)	Measured[c]	Corrected[c] (95% TD)	Measured[a]	Corrected[a] (95% TD)	Measured[d]	Corrected[d] (95% TD)
873	7.0526	6.9699	6.9959	6.9139	6.0127	6.0451	5.7333	5.7642	5.8903	5.9807	5.6993	5.7867
973	6.3455	6.2711	6.2957	6.2218	6.0061	6.0385	5.7460	5.7770	5.3312	5.413	5.1318	5.2105
1043	5.6587	5.5923	5.6195	5.5535	5.1841	5.2121	4.9779	5.0048	4.7143	4.7868	4.5252	4.5947
1123	5.0763	5.0168	5.0498	4.9906	4.6912	4.7165	4.5283	4.5527	4.3672	4.4343	4.1811	4.2453
1213	4.6007	4.5468	4.5880	4.5342	4.1632	4.1857	4.0459	4.0678	3.9588	4.0196	3.7810	3.8391

[a] Using estimated Newmann–Kopp's heat capacity values.
[b] Using heat capacity values calculated from Eq. (11).
[c] Using heat capacity values calculated from Eq. (12).
[d] Using heat capacity values calculated from Eq. (13).

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