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Thermodynamic studies on $Cs_4U_5O_{17}$(s) and $Cs_2U_2O_7$(s) by emf and calorimetric measurements

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Abstract

The oxygen potentials over the phase field: $Cs_4U_5O_{17}(s) + Cs_2U_2O_7(s) + Cs_2U_4O_{12}(s)$ was determined by measuring the emf values between 1048 and 1206 K using a solid oxide electrolyte galvanic cell. The oxygen potential existing over the phase field for a given temperature can be represented by: $\Delta\mu(O_2)$ (kJ/mol) $(\pm 0.5) = -272.0 + 0.207T$ (K). The differential thermal analysis showed that $Cs_4U_5O_{17}$(s) is stable in air up to 1273 K. The molar Gibbs energy formation of $Cs_4U_5O_{17}$(s) was calculated from the above oxygen potentials and can be given by, $\Delta_f G^0$ (kJ/mol) $\pm 6 = -7729 + 1.681T$ (K). The enthalpy measurements on $Cs_4U_5O_{17}$(s) and $Cs_2U_2O_7$(s) were carried out from 368.3 to 905 K and 430 to 852 K respectively, using a high temperature Calvet calorimeter. The enthalpy increments, $(H_T^0 - H_{298}^0)$, in J/mol for $Cs_4U_5O_{17}$(s) and $Cs_2U_2O_7$(s) can be represented by, $H_T^0 - H_{298.15}^0$ $(Cs_4U_5O_{17})$ kJ/mol $\pm 0.9 = -188.221 + 0.518T$ (K) $+ 0.433 \times 10^{-3}T^2$ (K) $- 2.052 \times 10^{-5}T^3$ (K) (368 to 905 K) and $H_T^0 - H_{298.15}^0$ $(Cs_2U_2O_7)$ kJ/mol $\pm 0.5 = -164.210 + 0.390T$ (K) $+ 0.104 \times 10^{-4}T^2$ (K) $+ 0.140 \times 10^5(1/T$ (K)) (411 to 860 K). The thermal properties of $Cs_4U_5O_{17}$(s) and $Cs_2U_2O_7$(s) were derived from the experimental values. The enthalpy of formation of $(Cs_4U_5O_{17}$, s) at 298.15 K was calculated by the second law method and is: $\Delta_f H_{298.15}^0 = -7645.0 \pm 4.2$ kJ/mol. © 1997 Elsevier Science B.V.

1. Introduction

The fission of uranium and plutonium in a mixed oxide fuel results in an increase in the oxygen potential. Depending on the local oxygen potential and temperature, fission products like cesium and rubidium can react with fuel to form a variety of compounds. Cesium is found to migrate axially leading to the formation of voluminous cesium uranates at the interface of the mixed oxide fuel and the uranium oxide axial blanket [1–3]. Extensive studies have been made on the alkali metal uranates by Ippolitova et al. [4] indicating the existence of several polyuranates whose formation depends on the M/U ratio (M = alkali metal) and temperature. The phase behaviour of the Cs–U–O system has been extensively studied [5–9]. Fee and Johnson [1,10,11] identified the hexavalent uranates: $\langle Cs_2UO_4\rangle$, $\langle Cs_2U_2O_7\rangle$, $\langle Cs_4U_5O_{17}\rangle$, $\langle Cs_2U_4O_{13}\rangle$, $\langle Cs_2U_5O_{16}\rangle$, $\langle Cs_2U_5O_{22}\rangle$ and $\langle Cs_2U_{15}O_{26}\rangle$. Cesium uranate in the fifth valency state include $\langle Cs_2UO_{3.56}\rangle$, $\langle Cs_2U_4O_{12}\rangle$, $\langle Cs_2U_6O_{18}\rangle$ and $\langle Cs_2U_9O_{27}\rangle$. The phase diagram (Fig. 1) reported by Fee et al. [2] shows the coexistence of $Cs_2U_4O_{12}$(s), with $Cs_2U_4O_{13}$(s) and $Cs_2U_2O_7$(s) and $Cs_4U_5O_{17}$(s). Experimentally measured thermodynamic values on some of these cesium uranates are reported [12–15]. Venugopal et al. [16] have determined the thermal and thermodynamic properties of $A_2U_4O_{12}$(s) and $A_2U_4O_{13}$(s) (A = Cs, Rb) by emf and calorimetric measurements. O'Hare and Hoekstra [17] and Cordfunke and Hoekstra [12] have measured the enthalpy of formation for Cs_2UO_4(s) and $Cs_2U_2O_7$(s) at 298.15 K. Osborne et al. [18] obtained the standard entropy (S_{298}^0) of Cs_2UO_4(s). Lindemer et al. [19] estimated the thermodynamic values of $Cs_4U_5O_{17}$(s) and $Cs_2U_2O_7$(s). However there is no experimental thermodynamic values available for $Cs_4U_5O_{17}$(s) and $Cs_2U_2O_7$(s). In the present study the emfs were measured over the coexisting phase fields, $Cs_2U_2O_7(s) + Cs_2U_4O_{12}(s) + Cs_4U_5O_{17}(s)$, using a calcium oxide stabilized, zirconia electrolyte between 1048 and 1206 K. The thermodynamic properties of $Cs_4U_5O_{17}$(s) and $Cs_2U_2O_7$(s) were calculated from the enthalpy incre-

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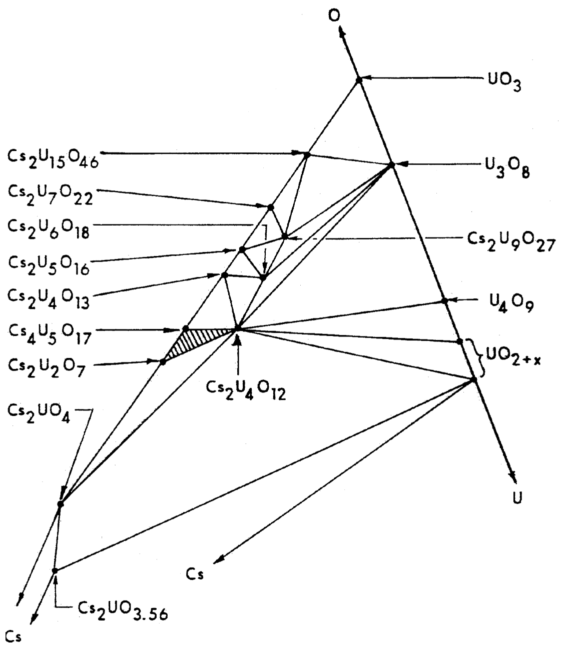

Fig. 1. A portion of Cs–U–O ternary phase diagram (Ref. [2]) around 1000 K.

ments measured using a high temperature Calvet calorimeter.

2. Experimental

2.1. Materials

$Cs_4U_5O_{17}(s)$, $Cs_2U_2O_7(s)$ and $Cs_2U_4O_{13}(s)$ were prepared by reacting stoichiometric ratios of $Cs_2CO_3(s)$ and $U_3O_8(s)$ at 1000 K in an alumina boat in air. $Cs_2U_4O_{12}(s)$ was prepared by the reduction of $Cs_2U_4O_{13}(s)$ under flowing purified argon gas, at 1200 K [16]. The reaction products obtained in the above experiments were identified exclusively as $Cs_4U_5O_{17}(s)$, $Cs_2U_2O_7(s)$ and $Cs_2U_4O_{12}(s)$ by X-ray diffraction analysis (XRD). The X-ray pattern was taken on a Cu Kα Diano X-ray diffractometer.

The compounds $Cs_2U_4O_{12}(s)$, $Cs_4U_5O_{17}(s)$ and $Cs_2U_2O_7(s)$ were mixed in 1:2:3 mole ratios and pelletized (4 mm diameter and 2 mm thickness). The pellets were annealed at 1273 K in quartz ampules sealed under vacuum for 50 to 60 h. These pellets were then used for the electromotive force (emf) measurement studies. The drop calorimetric experiments were carried out using pure $Cs_4U_5O_{17}(s)$ and $Cs_2U_2O_7(s)$ in the form of small pellets weighing between 25 and 50 mg.

2.2. Electromotive force (emf) measurements

The experimental details and cell assembly used for the experiments are reported in an earlier publication [20]. A double compartment cell assembly separating the gaseous environments by a calcia stabilized zirconia (CSZ) electrolyte in the form of a tube was used for the experiments. The cell was tested for its reliability by measuring emf between 1000 and 1200 K, developed on a cell of the type

$$\mathrm{Pt|Ni(s) + NiO(s)|CSZ|air|Pt} \quad \text{cell I,}$$

where Ni + NiO is a standard and air ($p(O_2) = 21.21$ kPa) is a reference electrode. The temperature of the cell was measured using a calibrated [21] chromel to alumel thermocouple. An argon cover gas was used for the experiment and the Ar was purified as described in earlier publication [16]. The oxygen concentration in the purified argon was 10^{-22} kPa. The cell used in the present studies can be represented by

$$\mathrm{Pt|Cs_2U_2O_7(s) + Cs_4U_5O_{17}(s) + Cs_2U_4O_{12}(5)}$$
$$\times\mathrm{|CSZ|air(}\,p(\mathrm{O_2}) = 21.21\ \mathrm{kPa})\mathrm{|Pt} \quad \text{cell II.}$$

The emf was measured under static argon atmosphere in the temperature range 1048 to 1206 K in the heating and cooling cycles. The X-ray diffraction pattern of the pellet was taken after the emf experiments.

2.3. Thermogravimetry (TG) and differential thermal analysis (DTA) studies

TG and DTA experiments were carried out on $Cs_4U_5O_{17}(s)$ using an Ulvac TGA 7000 simulataneous thermal analyzer. The temperature calibration was done using high purity Sn as standard. DTA experiments were calibrated using a high purity $K_2SO_4(s)$. Platinum cups were used as container material for the sample. The sample size used was 100 mg. The experiments were carried out in the heating and cooling mode. A heating rate of 10 K/min was used for the present studies. The reference material used for the experiments was preheated alumina. The temperatures were scanned up to 1233 K in 21.21 kPa oxygen partial pressure.

2.4. Enthalpy measurements

Enthalpy increment measurements were carried out in a high temperature Calvet calorimeter. The principle and the working of the calorimeter have already been described [22]. The Calvet calorimeter has identical twin compartments surrounded by thermopiles, kept inside a massive alumina block, whose temperature is monitored and controlled. The compartments exchange heat with the block. This exchange of heat gives an electrical signal from the thermopile which is amplified and fed into a computer for integration. The enthalpy increment measurements were carried out for $Cs_4U_5O_{17}(s)$ and $Cs_2U_2O_7(s)$ at isothermal temperatures in the temperature range 368 to 905 K and 430 to 852 K respectively at an interval of 20 to 30 K. Two independent measurements were carried out at each

Table 1
Emission spectroscopic analysis for impurities in ppm of U_3O_8(s) and Cs_2CO_3(s) used for the preparation of $Cs_4U_5O_{17}$(s), $Cs_2U_2O_7$(s), $Cs_2U_4O_{12}$(s) and $Cs_2U_4O_{13}$(s)

U_3O_8		Cs_2CO_3	
element	concentration (μg/g)	element	concentration (μg/g)
Al	12	Ca	50
B	< 0.01	Ba	100
Ca	14	Pb	20
Cd	< 0.01	Fe	20
Fe	< 10	Li	20
Mg	5	Mg	50
Mo	10	K	70
Na	3	Na	50
Si	590	Rb	500
W	68		
Zn	< 10		
	$\Sigma = 712$ μg/g		$\Sigma = 880$ μg/g

temperature. The calorimetric compartments were evacuated and flushed with purified argon before dropping the sample. The drop experiments were carried out under static argon pressure. The calibration factor (heat capacity equivalent) of the calorimeter was determined by electrical calibration method [22]. This was also checked at each isothermal temperature by dropping standard reference material, NBS alumina (SRM-720).

3. Results and discussion

The emission spectrometric analysis for the impurity content of the constituent compounds used for the preparation of the uranates are given in Table 1. It is assumed that there is no impurity picked up from the recrystallized alumina boat used for carrying out the reactions. From Table 1 it is seen that the total impurities in U_3O_8(s) and Cs_2CO_3(s) is less than 1000 ppm which accounts for a purity better than 99.9% for $Cs_4U_5O_{17}$(s), $Cs_2U_2O_7$(s) and $Cs_2U_4O_{12}$(s). The compounds were used as such without further purification. The emf values remained constant within 1 mV when measured with different pellets indicating that the above impurities do not affect the values.

3.1. X-ray analysis of $Cs_4U_5O_{17}$(s)

Potentiometric analysis of uranium in $Cs_4U_5O_{17}$(s) gave a value of 59.9 ± 0.3 wt% as against the theoretical value of 59.6 wt%. $Cs_4U_5O_{17}$(s) is obtained as a bright yellow crystalline phase. X-ray diffraction pattern of $Cs_4U_5O_{17}$(s) obtained from the present study is given in Fig. 2. The scanning was carried out for 2θ values ranging from 10° in steps of 2°. The *d*-spacing values (0.747, 0.367, 0.332 and 0.303 nm) were matching with the JCPDS data base reported by van Egmond [23]. $Cs_4U_5O_{17}$ is indexed [23] as orthorhombic crystal system with the cell parameters $a = 1.4985$, $b = 1.8776$ and $c = 0.7070$ nm.

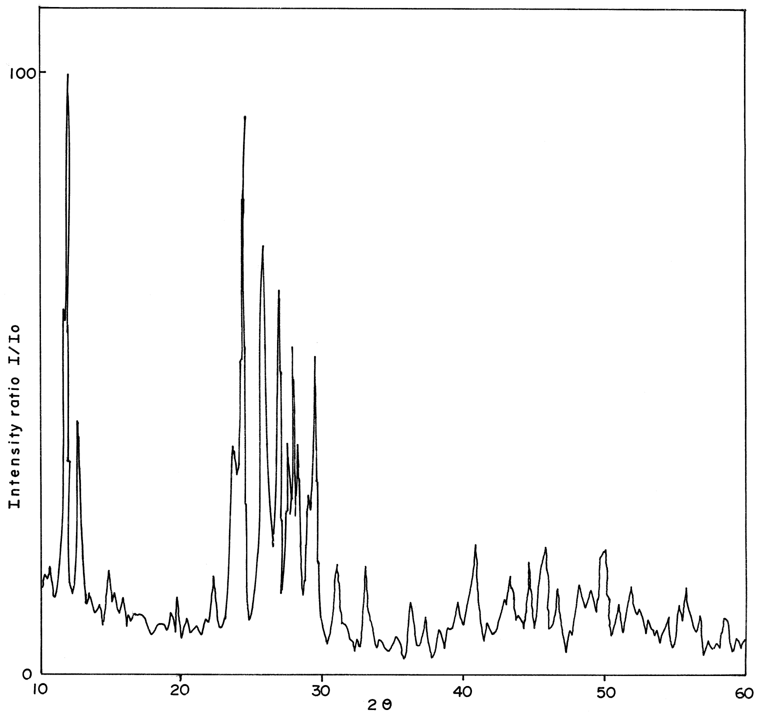

Fig. 2. X-ray diffraction pattern of $Cs_4U_5O_{17}$(s) at 298.15 K.

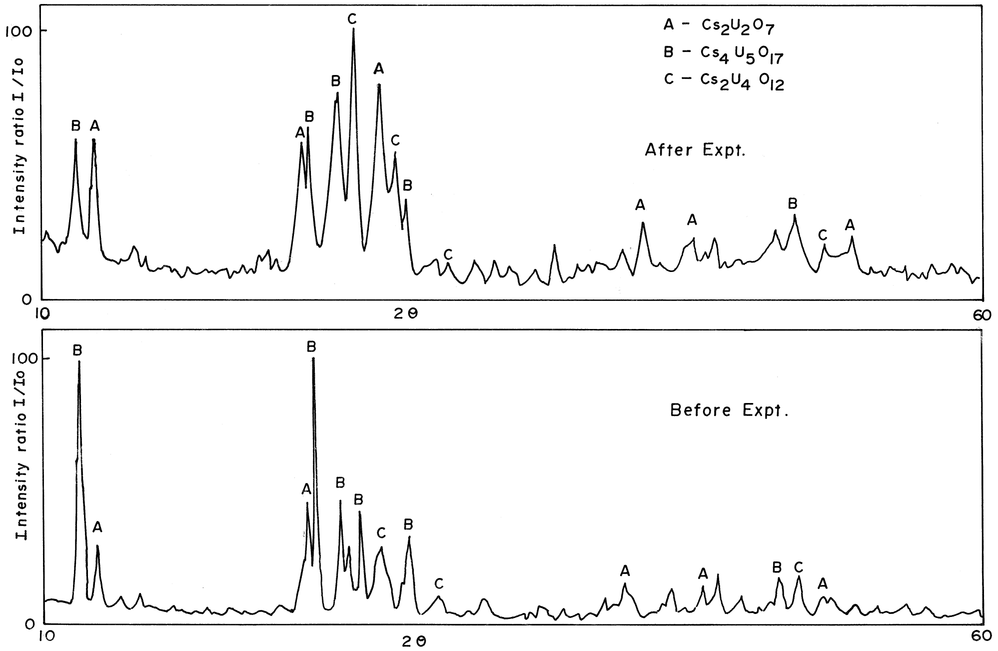

Fig. 3. X-ray (Cu Kα) diffraction pattern of the mixture: $Cs_4U_5O_{17}(s) + Cs_2U_2O_7(s) + Cs_2U_4O_{12}(s)$.

The X-ray pattern obtained for $Cs_2U_2O_7(s)$ matched with the α-$Cs_2U_2O_7(s)$ *d*-spacing values reported in JCPDS data base files [23]. The X-ray *d*-spacing values obtained for $Cs_2U_4O_{12}(s)$ matched well with the values reported in the literature [5,23]. The X-ray diffraction pattern of the mixture, $Cs_4U_5O_{17}(s) + Cs_2U_2O_7(s) + Cs_2U_4O_{12}(s)$ before and after the emf experiments is shown in Fig. 3. The pattern remained the same indicating the absence of any reaction between the constituent ternary oxides and with the CSZ. This confirms the coexistence of the phases, $Cs_4U_5O_{17}(s)$, $Cs_2U_2O_7(s)$ and $Cs_2U_4O_{12}(s)$ up to 1200 K.

DTA also did not show any peak ruling out the possibility of decomposition and solid state transition up to 1200 K. The thermogram taken for $Cs_4U_5O_{17}(s)$ did not show any weight change indicating the thermal stability of the compound up to 1273 K. TG and DTA experiments on $Cs_2U_2O_7(s)$ and $Cs_2U_4O_{12}(s)$ have been reported in the literature and hence these experiments were not performed in the present study. $Cs_2U_4O_{12}(s)$ is thermally stable up to 1250 K. However, $Cs_2U_2O_7(s)$ is thermally stable and reported to have a solid state transition at 873 K with a very low enthalpy of transition [5].

3.2. Galvanic cell measurements

The emf obtained for cell I in the temperature range 900 to 1200 K matched well with the reported value [24] and hence it is confirmed that using the present cell assembly, reliable emf can be measured.

The overall cell reaction of cell II is given by

$$Cs_2U_4O_{12}(s) + 3Cs_2U_2O_7(s) + \tfrac{1}{2}O_2(g) = 2Cs_4U_5O_{17}(s). \tag{1}$$

The emfs obtained at the experimental temperatures are given in Table 2. The emfs were least squares fitted with temperature and can be given by

$$E\ (\mathrm{mV}) \pm 1.1 = 705 - 0.536T\ (\mathrm{K}) \tag{2}$$

The dependence of emf on temperature for cell II is shown in Fig. 4. The Gibbs energy of Eq. (1) can be given by $\Delta_r G^0(\mathrm{II}) = -nFE$, where $n = 2$, electron change $F = 96\,486.4$ (C/mol) and $E =$ emf in V:

$$\Delta_r G^0(\mathrm{II}) \pm 0.2\ \mathrm{kJ} = -136.007 + 0.103T\ (\mathrm{K}). \tag{3}$$

The oxygen potential existing over the system

Table 2
Dependence of emf on temperature for the cell: Pt|$Cs_2U_2O_7(s) + Cs_4U_5O_{17}(s) + Cs_2U_2O_7(s)$|CSZ|air, $p(O_2) = 21.21$ kPa|Pt

T (K)	emf (mV)	*T* (K)	emf (mV)	*T* (K)	emf (mV)
1048	142.0	1124	104.5	1181	73.5
1062	136.2	1131	100.6	1189	68.8
1070	131.6	1141	93.2	1194	64.0
1081	127.4	1152	86.6	1205	59.3
1089	119.9	1169	78.6	1206	57.8
1098	116.9				

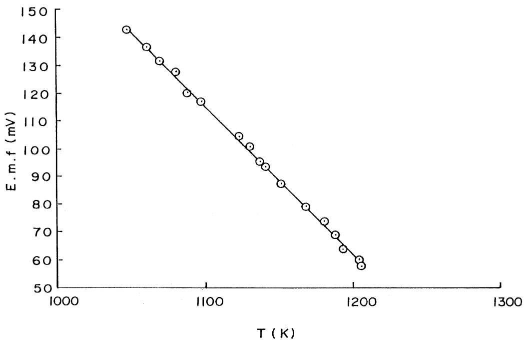

Fig. 4. Dependence of emf (mV) on temperature T (K) for the cell: Pt|$Cs_4U_5O_{17}$(s) + $Cs_2U_2O_7$(s) + $Cs_2U_4O_{12}$(s)|CSZ|air, Pt.

$Cs_2U_4O_{12}$(s) + $Cs_2U_2O_7$(s) + $Cs_4U_5O_{17}$(s) was also calculated using the relation

$$-4FE = RT \ln p(O_2)$$

$$\Delta\mu(O_2) \pm 0.5\ (\mathrm{kJ/mol}) = -272.0 + 0.207T\ (\mathrm{K}). \quad (4)$$

The molar Gibbs energy formation of $Cs_4U_5O_{17}$(s) was evaluated using the molar Gibbs energy formation values of $Cs_2U_4O_{12}$(s) [24] Eq. (5) and $Cs_2U_2O_7$(s) [19] Eq. (6):

$$\Delta_f G^0\ Cs_2U_4O_{12}(s)\ \mathrm{kJ/mol} \pm 4.0$$

$$= -5726 + 1.255T\ (\mathrm{K}) \quad (900-1200\ \mathrm{K}), \quad (5)$$

$$\Delta_f G^0\ Cs_2U_2O_7(s)\ \mathrm{kJ/mol} \pm 4.1$$

$$= -3199 + 0.670T\ (\mathrm{K}). \quad (6)$$

The molar Gibbs energy formation values for $Cs_2U_2O_7$(s) given in Eq. (6) is calculated using the equation

$$\Delta G_f^0(T) = \Delta H_f^0(298.15) - T\Delta S_f^0(298.15).$$

This is an approximation without consideration of heat capacity values. The $\Delta H_f^0(298.15)$ of $Cs_2U_2O_7$(s) taken for the above calculation was taken from Lindemer et al. [19]. The S_f^0 at 298.15 K values were evaluated from the $S^0_{298.15}$ values of Cs(l) [25], U(s) [25], O_2(g) [26] and $Cs_2U_2O_7$(s) [27] from literature. The molar Gibbs energy of formation of $Cs_4U_5O_{17}$(s) was calculated from the equilibrium reaction (1) using Eqs. (3), (5) and (6) and can be given by

$$\Delta_f G^0 T(Cs_4U_5O_{17},s)\ \mathrm{kJ/mol} \pm 5.7$$

$$= -7729 + 1.681T\ (\mathrm{K}). \quad (7)$$

3.3. Enthalpy measurements

The enthalpy increment values obtained for NBS synthetic sapphire from the calibration constant agreed with the certified values with in ±0.5%. This shows that the enthalpy values obtained in the present study are accurate. Enthalpy increment values on $Cs_4U_5O_{17}$(s) and $Cs_2U_2O_7$(s) obtained in the present study are given in Tables 3 and 4. The dependence of enthalpy increment values with temperature was expressed in the form of an analytical expression

Table 3
Dependence of enthalpy increment of $Cs_4U_5O_{17}$(s) on temperature along with the fit values at the experimental temperature

T (K)	$H_T^0 - H_{298.15}^0$ (J/mol)	Fit value (J/mol)	T (K)	$H_T^0 - H_{298.15}^0$ (J/mol)	Fit value (J/mol)
368.3	50 841 ± 205	50 864	580.7	222 482 ± 1200	219 676
370.0	50 006 ± 260	52 197	660.3	283 915 ± 1400	284 094
390.7	67 019 ± 320	68 535	725.1	339 044 ± 1600	336 999
411.2	83 915 ± 440	84 599	755.1	364 707 ± 1923	361 633
448.1	109 291 ± 560	113 763	796.0	395 691 ± 2000	395 362
478.1	145 703 ± 726	137 572	816.4	412 491 ± 2050	412 247
500.1	151 959 ± 760	155 089	852.6	442 313 ± 2200	442 031
529.1	174 743 ± 875	178 253	880.2	463 481 ± 2300	464 284
550.2	193 226 ± 1000	195 160	905.5	485 310 ± 1400	484 186

Table 4
Dependence of enthalpy increment of $Cs_2U_2O_7$(s) on temperature along with the fit values at the experimental temperature

T (K)	$H_T^0 - H_{298.15}^0$ (J/mol)	Fit value (J/mol)	T (K)	$H_T^0 - H_{298.15}^0$ (J/mol)	Fit value (J/mol)
430	38 932 ± 200	38 159	714	141 987 ± 600	139 497
452	46 821 ± 250	45 400	722	143 644 ± 730	142 446
581	84 305 ± 410	90 203	752	154 401 ± 695	153 842
632	99 778 ± 430	108 847	791	168 386 ± 810	168 926
680	128 592 ± 540	126 713	816	182 316 ± 980	178 406
			852	196 740 ± 935	192 356

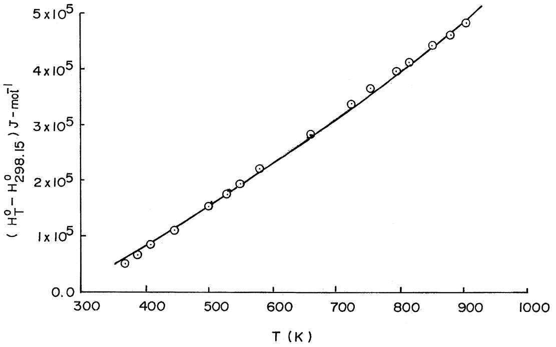

Fig. 5. Dependence of $H_T^0 - H_{298.15}^0$ (J/mol) on temperature T (K) for $Cs_4U_5O_{17}$(s).

Table 5
Thermal properties of $Cs_4U_5O_{17}$(s)

T (K)	$H_T^0 - H_{298.15}^0$ (J/mol)	C_p^0 (J/mol K)	S_T^0 (J/mol K)	$-(G_T^0 - H_{298.15}^0)$ /T(J/mol K)
298	00	550	777	777
350	37626	747	884	778
400	75488	767	973	783
450	114288	784	1052	798
500	153872	798	1121	813
550	194087	809	1181	828
600	234777	817	1234	843
650	275790	822	1281	856
700	316972	824	1321	868
750	358168	823	1355	878

with the constraint $H_T^0 - H_{298.15}^0 = 0$ at 298.15 K. The expressions are

$$H_T^0 - H_{298.15}^0(Cs_4U_5O_{17})\ \text{kJ/mol} \pm 0.9$$
$$= -188.221 + 0.518T\ (\text{K}) + 0.433 \times 10^{-3}T^2\ (\text{K}) - 2.052 \times 10^{-7}T^3\ (\text{K}), \quad (368-905\ \text{K}), \tag{8}$$

$$H_T^0 - H_{298.15}^0(Cs_2U_2O_7)\ \text{kJ/mol} \pm 0.5$$
$$= -164.210 + 0.390T\ (\text{K}) + 0.104 \times 10^{-4}T^2\ (\text{K}) + 0.140 \times 10^5(1/T\ (\text{K})) \quad (411-860\ \text{K}). \tag{9}$$

The enthalpy increment values obtained for $Cs_2U_4O_{12}$(s) and $Cs_2U_4O_{13}$(s) are reproduced from Ref. [16] and can be given by

$$H_T^0 - H_{298.15}^0(Cs_2U_4O_{12})\ \text{kJ/mol} \pm 1.1$$
$$= -92.10 + 0.325T + 0.100 \times 10^{-3}T^2 - 4.124 \times 10^3/T, \tag{10}$$

$$H_T^0 - H_{298.15}^0(Cs_2U_4O_{13})\ \text{kJ/mol} \pm 0.6$$
$$= -130.9 + 0.555T - 0.0902 \times 10^{-3}T^2 - 7.910 \times 10^3/T. \tag{11}$$

The dependence of enthalpy increment values on temperature is shown in Figs. 5 and 6. The molar specific heat is the first differential of $H_T^0 - H_{298.15}^0$ with respect to temperature and is given by

$$C_p^0(Cs_4U_5O_{17},s)\ (\text{J/mol K}) = 518 + 0.866T\ (\text{K}) - 0.062 \times 10^{-2}T^2, \tag{12}$$

$$C_p^0(Cs_2U_2O_7,s)(\text{J/mol K}) = 390 + 0.021T\ (\text{K}) - 0.140 \times 10^8(1/T^2). \tag{13}$$

From the enthalpy increment values the thermal properties of $Cs_4U_5O_{17}$(s) and $Cs_2U_2O_7$(s) were derived using the equations

$$S_T^0 = S_{298.15}^0 + \int_{298.15}^{T} C_p^0\,dT/T - \left(G_T^0 - H_{298.15}^0\right)/T$$
$$= S_T^0 - \left[\left(H_T^0 - H_{298.15}^0\right)/T\right].$$

$S_{298.15}^0$ values for $Cs_4U_5O_{17}$(s) [19] and $Cs_2U_2O_7$(s) [27] which are 777 and 332 J/mol K respectively were taken from literature for the calculation. The thermal properties of $Cs_4U_5O_{17}$(s) and $Cs_2U_2O_7$(s) are given in Tables 5 and 6. It is seen that the molar heat capacity of these com-

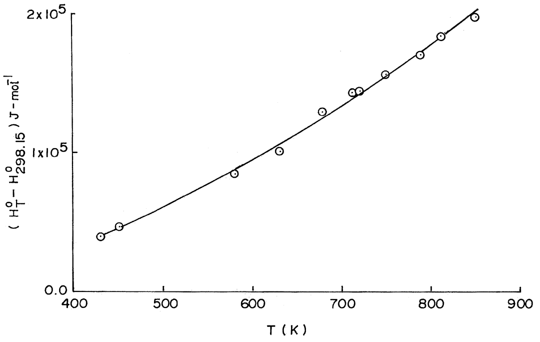

Fig. 6. Dependence of $H_T^0 - H_{298.15}^0$ (J/mol) on temperature T (K) for $Cs_2U_2O_7$(s).

Table 6
Thermal properties of $Cs_2U_2O_7$(s)

T (K)	$H_T^0 - H_{298.15}^0$ (J/mol)	C_p^0 (J/mol K)	S_T^0 (J/mol K)	$-(G_T^0 - H_{298.15}^0)$ / T (J/mol K)
298	00	239	332	332
350	13638	283	374	335
400	28548	311	413	342
450	44621	330	451	352
500	61523	344	487	364
550	79041	355	520	376
600	97035	363	551	390
650	115407	370	581	403
700	134086	376	609	417
750	153022	381	635	431
800	172177	385	660	444

Table 7
Standard molar Gibbs energy formation of uranates of cesium in the Cs–U–O system for $T > 950$ K: $-\Delta_f G^0_{m,s}$ (kJ/mol) = $A + BT$ (K)

Compound	A	B	T (K)			Ref.
			1000	1100	1200	[a]
$Cs_2UO_{3.5}$	−1739	0.340	−1399	−1364	−1331	
Cs_2UO_4	−1926	0.221	−1706	−1683	−1660	[a]
$Cs_2U_2O_7$	−3199	0.656	−2542	−2476	−2410	[a]
$Cs_2U_4O_{12}$	−5726	1.255	−4471	−4345	−4220	[15]
$Cs_2U_4O_{13}$	−5901	1.391	−4510	−4371	−4232	[16]
$Cs_4U_5O_{17}$	−7729	1.681	−6048	−5880	−5712	present study

[a] Calculated from $\Delta_f H^0_{298.15}$ and $\Delta_f S^0_{298.15}$.

pounds is increasing gradually with temperature as expected. No experimentally determined heat capacity values are available in literature for comparison. Using the presently obtained enthalpy increment values for $Cs_4U_5O_{17}$(s), $Cs_2U_2O_7$(s) and $Cs_2U_4O_{12}$(s) [16] and O_2(g) [26] the enthalpy of formation $\Delta_f H^0_{298.15}$ $Cs_4U_5O_{17}$(s) was calculated from the $\Delta_r G^0_T$ Eq. (3) by second law method and is -7645 ± 4.2 kJ/mol. This value is reasonably in good agreement with the reported value of −7667 kJ/mol [19]. The recent compilation of thermodynamic values of uranates by Grenthe et al. [27] did not give any thermodynamic values for $Cs_4U_5O_{17}$(s). Table 7 summarizes the thermodynamic values of different cesium uranates in the Cs–U–O system along with the available literature values.

4. Conclusion

The molar Gibbs energy formation of $Cs_4U_5O_{17}$(s) was determined by electromotive force measurement using a solid oxide electrolyte galvanic cell. The molar specific heats of $Cs_4U_5O_{17}$(s) and $Cs_2U_2O_7$(s) were calculated from the enthalpy increment values determined by drop calorimetric measurements in the temperature range 368 to 905 K and 430 to 852 K, respectively. The enthalpy of formation at 298.15 K of $Cs_4U_5O_{17}$(s) was interpolated using a second law method and can be given by $\Delta_f H^0$ kJ/mol $= -7645 \pm 4.2$.

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