

Thermodynamic Properties of $K_2U_4O_{12}(s)$ and $K_2U_4O_{13}(s)$ by EMF and Calorimetric Measurements

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The coexistence of $K_2U_4O_{12}(s)$ and $K_2U_4O_{13}(s)$ in the K–U–O system up to 1200 K was established. The EMF measurements over the above phase field were carried out using a calcia-stabilized zirconia solid electrolyte galvanic cell in the temperature range 1053 to 1222 K. The equilibrium oxygen partial pressure above the phase fields was calculated to be $\ln p(O_2) \text{ kPa} \pm 0.09 = -31452/T + 25.065$. The enthalpy increment values of $K_2U_4O_{12}(s)$ and $K_2U_4O_{13}(s)$ were measured using a high temperature Calvet calorimeter by drop method and the thermodynamic values were suggested for the compounds.

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INTRODUCTION

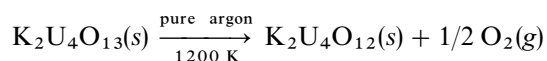
Sodium and sodium–potassium alloys are used as coolant in a liquid-metal cooled fast breeder reactor (LMFBR) with mixed oxide or carbide fuel (1). In the case of cladding breach, sodium and potassium would enter the fuel pin with the possibility of chemical interactions. The principal effect of these interactions are the local swelling of the fuel pin leading to blockage of coolant flow within the subassembly. This will result in overheating and failures in adjacent fuel pins. Basic thermodynamic data on the reaction product and fuel components are necessary to predict the conditions for their formation. The molar Gibbs energies of formation of the oxide species of the type $A_3MO_4(s)$ (where $A = Na/K$, $M = U, Pu$, $U_{1-x}Pu_x$ (2–4)) are important in determining the threshold oxygen potential of fuel. Literature on the Na–U–O system is fairly extensive (5), whereas there is a paucity of information on the K–U–O system. Van Egmond and Cordfunke (6) prepared and indexed the compounds $K_4UO_5(s)$, $K_2UO_4(s)$, $K_2U_2O_7(s)$, $K_2U_4O_{13}(s)$, $K_2U_7O_{22}(s)$, and pentavalent $KUO_3(s)$. The phase region $\langle K_2O \cdot nUO_3 \rangle$ ($3 \leq n \leq 6$) has not been studied well. The literature available on thermodynamic information on uranates of potassium are very scarce (7–9). Cordfunke and Ouweltjes (10) have determined the enthalpy of formation of $K_2UO_4(s)$ at 298.15 K by solution calorimeter. The com-

ound $K_2U_4O_{12}(s)$ is reported (11) as having an orthorhombic crystal structure. Figure 1 gives a section of the ternary system at $p(O_2) = 21.21 \text{ kPa}$ and $T = 1200 \text{ K}$. However, reliable thermodynamic data on $K_2U_4O_{13}(s)$ and $K_2U_4O_{12}(s)$ are not available in the literature. In the present study, the standard molar Gibbs energy formation of $K_2U_4O_{12}(s)$ was derived by EMF measurement. The enthalpy increment values of $K_2U_4O_{12}(s)$ and $K_2U_4O_{13}(s)$ were determined using a high-temperature Calvet calorimeter by the drop method.

EXPERIMENTAL

Materials

The compound $K_2U_4O_{13}(s)$ was prepared by heating the mixtures of $K_2CO_3(s)$ and nuclear grade $UO_3(s)$ with molar ratio 1:4 in a platinum boat at 900 K in air for several hours. The product was identified as $K_2U_4O_{13}(s)$ by X-ray diffraction (XRD) analysis. $K_2U_4O_{12}(s)$ was prepared by reducing $K_2U_4O_{13}(s)$ under high-purity argon according to the reaction (11)



The emission spectrometric analysis for the impurity content of the constituent compounds used for the preparation of the uranates are given in Table 1. From the table it is seen that the compounds used in the present study were better than 99% purity. The XRD pattern of $K_2U_4O_{12}(s)$ prepared in the present study matched with the pattern reported by Chawla *et al.* (11). $K_2U_4O_{12}(s)$ and $K_2U_4O_{13}(s)$ were intimately mixed in a 1:1 mole ratio and made in the form of pellets of 4 mm diameter and 2 mm thickness. These pellets were annealed at 1200 K in a high-purity argon atmosphere for 20 to 30 h and stored in a desiccator. XRD pattern of this mixture indicated absence of any extra lines other than $K_2U_4O_{12}(s)$ and $K_2U_4O_{13}(s)$ confirming their coexistence. These pellets were used for the EMF measurements.

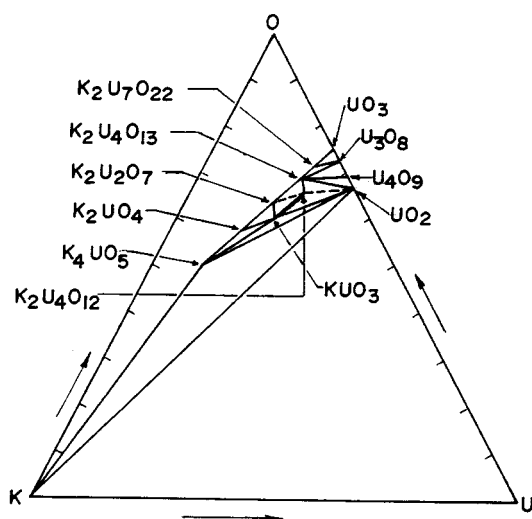


FIG. 1. A portion of K-U-O ternary phase diagram at $T \leq 1200$ K.

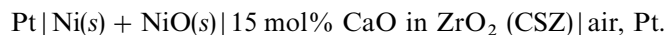
Thermogravimetry (TG) and Differential Thermal Analysis (DTA)

Simultaneous TG and DTA were carried out on a $K_2U_4O_{12}(s)$ sample using a thermal analyser (model Ulvac Sinku-Riko TA-7000) at a heating rate of 10 K/min. The temperature of the DTA measurements was calibrated using high-purity $K_2CrO_4(s)$ and Sn. Sintered alumina was used as a reference material for DTA measurements. The oxidation study of $K_2U_4O_{12}(s)$ was carried out in dry air. The sample size used was 50 mg. The container for the sample was a platinum cup.

Galvanic Cell Measurements

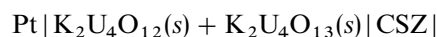
A 15 mol% calcia-stabilized zirconia (CSZ) tube with bottom end closed flat (Nippon Kakagu Togyo Co. Ltd.,

Japan) of 150 mm in length and 12.7 mm in outer diameter, with one end closed flat, was used for the determination of EMF. A two-compartment cell assembly as described in the earlier publication (12) was used for the measurement of EMF. The solid electrolyte tube separates the gaseous environment above the test electrode and the reference electrode. The inert gas blanket was provided by purified argon gas flowing at 10 ml/min. The purified argon gas is obtained by passing the gas through towers of molecular sieves, magnesium perchlorate, reduced form of BASF catalyst, and metallic calcium at 800 K. The temperature was measured by chromel to alumel thermocouple which was calibrated according to IPTS-68 for the melting points (13). The cell EMF was measured using a Keithley electrometer model 614, with input impedance $10^{16} \Omega$. The cell assembly was tested initially for the absence of asymmetric potentials. The oxygen pressure in the purified argon with reference to air was $\sim 10^{-21}$ kPa in the temperature range of the present work. The reliability of the galvanic cell was tested by measuring the EMF of the cell



Cell I

The EMF obtained was in good agreement with the reported values within ± 2 mV (12), indicating the smooth functioning of the cell. The galvanic cells used in the present study can be represented by



air, $p(\text{O}_2)$ 21.21 kPa, Pt.

Cell II

The EMFs were measured in the heating and cooling cycles in the temperature range 1053 to 1222 K. Two pellets of the same sample were used for the experiments. The XRD pattern before and after the experiments remained unchanged indicating the coexistence of the phase field in the temperature range of the present study.

Calorimetric Measurements

Enthalpy increment measurements were carried out in a high-temperature Calvet calorimeter. The principle and the working of the calorimeter have been already described (14). 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 causes an electrical signal from the thermopile which is amplified and fed into a computer for integration. The enthalpy increment measurements were carried out for $K_2U_4O_{12}(s)$ and $K_2U_4O_{13}(s)$ at isothermal temperatures in the temperature range 426 to 770 K and

TABLE 1

Emission Spectroscopic Analysis Result of Trace Metal Impurities in $K_2CO_3(s)$ and $U_3O_8(s)$ Used for the Preparation of $K_2U_4O_{13}(s)$

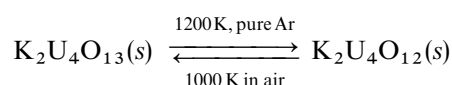
$U_3O_8(s)$		$K_2CO_3(s)$	
Element	ppm	Element	ppm
Al	25	Al	20
B	< 0.01	Fe	50
Ca	18	Mg	100
Fe	25	Si	250
Mg	10	Ca	20
Mo	10	Ba	50
Na	10		
Si	60		
W	68		

411.4 to 888 K, respectively, at an interval of 20 to 30 K. Two independent measurements were carried out at each temperature. The calorimetric compartments were evacuated and flushed with purified argon before dropping the sample. In the case of the $K_2U_4O_{12}(s)$ samples, special care was taken to avoid oxidation by incorporating *in situ*, getters. In the present case, tantalum foils were used as getters. The drop experiments were carried out under static argon pressure. The weight of the sample in the form of pellets used was 20 to 50 mg. The calibration factor of the calorimeter was determined by electrical calibration (14) and by dropping NBS alumina (SRM-720) at each isothermal temperature. The XRD pattern of $K_2U_4O_{12}(s)$ remained unchanged.

RESULTS AND DISCUSSION

TG and DTA Results

The weight gain in dry air shown in the thermogram accounts for 1/2 mole of oxygen. The reaction product was identified by X-ray as $K_2U_4O_{13}(s)$. The reaction is reversible and can be written as

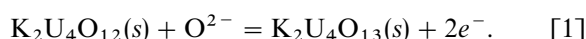


as in the case of the caesium analogue (5). It is seen that $K_2U_4O_{13}(s)$ remains stable up to 1250 K.

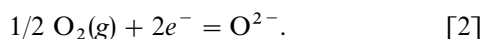
EMF Measurements

The cell reactions used in the study can be written as:

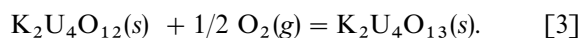
At the negative electrode (anode)



At the positive electrode (cathode)



The overall cell reaction can be given by



The EMFs obtained for the two pellets at the experimental temperatures are given in Table 2 and are compared with the fitted values in Fig. 2. It is seen from the figure that there is good agreement with the EMF values obtained for both the pellets. Hence the EMF values for both the pellets at the experimental temperatures were least squares fitted and can be given by

$$E(\text{mV}) \pm 2.1 = 677 - 0.440 T(\text{K}) \quad [4]$$

TABLE 2
Dependence of EMF on Temperature for the Cell
Pt | $K_2U_4O_{12}(s) + K_2U_4O_{13}(s)$ | CSZ | air, $p(O_2 = 21.21 \text{ kPa})$ | Pt

T(K)	EMF (mV)	T(K)	EMF (mV)
Pellet 1			
1053	214	1130	182
1060	210	1132	180
1076	202	1157	165
1085	198	1170	163
1100	195	1183	160
1116	186	1195	154
		1221	136
Pellet 2			
1054	214	1144	173
1068	206	1166	167
1112	190	1195	153
1117	187	1220	136
1121	185	1222	136
1129	182		

The molar Gibbs energy change for the above cell reaction (3) can be given by

$$\Delta_r G^\circ = -2FE,$$

where E is the EMF in volts and F is 96486.2 Coulombs/mol.

$$\Delta_r G^\circ(\text{kJ}) \pm 0.4 = -130.7 + 0.085 T(\text{K}) \quad [5]$$

The molar Gibbs energy of formation of $K_2U_4O_{13}(s)$ was calculated, assuming the heat capacity changes are negligible in the formation of the compound from the elements at 298.15, using the approximation

$$\Delta_f G_T^\circ = \Delta_f H_{298.15}^\circ - T\Delta_f S_{298.15}^\circ,$$

and can be given by

$$\Delta_f G_T^\circ(K_2U_4O_{13}, s) (\text{kJ/mol}) = -5690 + 1.176 T(\text{K}) \quad [6]$$

In the above calculation, the enthalpy of formation at 298.15 K for $K_2U_4O_{13}(s)$ was taken from Lindemer *et al.* (5). The $\Delta_f S^\circ$ at 298.15 K was calculated from the $S_{298.15}^\circ$ values (16, 17) of $K(s)$, $U(s)$ and $O_2(g)$, and $K_2U_4O_{13}(s)$ (5) in the literature. Using Eq. [6] and the oxygen potential values obtained in the present experiment, the molar Gibbs energy formation of $K_2U_4O_{12}(s)$ was calculated and can be given by

$$\Delta_f G_T^\circ(K_2U_4O_{12}, s) \text{ kJ/mol} \pm 0.4 = -5559 + 1.105 T(\text{K}) \quad [7]$$

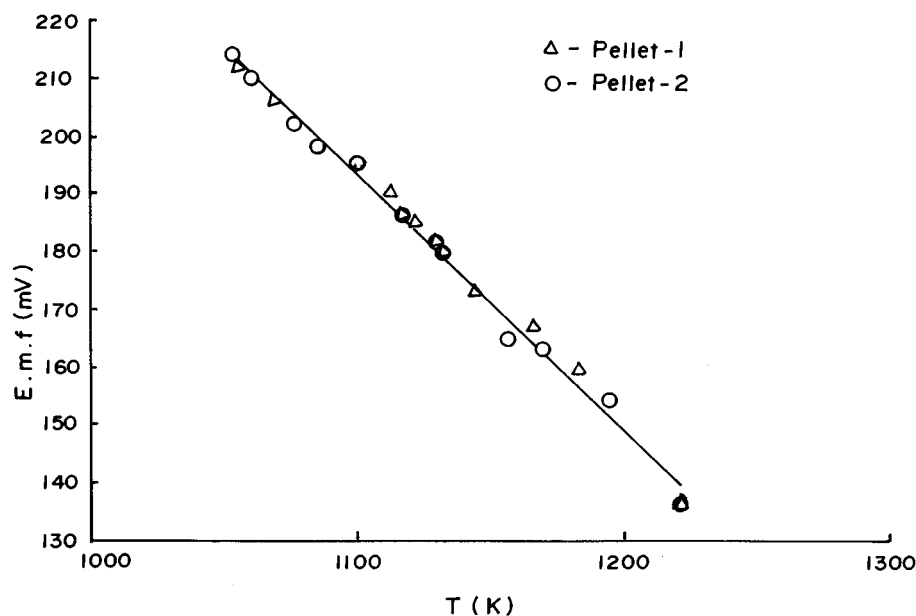


FIG. 2. Dependence of EMF (mV) on temperature T (K) for the cell $Pt | K_2U_4O_{12}(s) + K_2U_4O_{13}(s) | CSZ | air, p(O_2) 21.21 \text{ kPa}, Pt$.

The uncertainty reported in the above equation is attributed to the error in the EMF measurement.

The oxygen equilibrium pressure above the $K_2U_4O_{12}(s) + K_2U_4O_{13}(s)$ system is calculated from Eq. [5] and can be given by

$$\ln p(O_2) (\text{kPa}) \pm 0.09 = -31450/T(\text{K}) + 25.07. \quad [8]$$

It is calculated that the mixture $K_2U_4O_{12}(s) + K_2U_4O_{13}(s)$ would generate an oxygen pressure of 101.325 kPa at 1539 K.

Enthalpy Increment Measurements

The enthalpy increment values obtained for NBS synthetic sapphire from the calibration constant agreed with the certified values with in $\pm 0.5\%$. This shows that the enthalpy values obtained in the present study are reliable. Enthalpy increment values on $K_2U_4O_{12}(s)$ and $K_2U_4O_{13}(s)$ obtained in the present study are given in Table 3 and 4

TABLE 3
Dependence of Enthalpy Increment on Temperature
for $K_2U_4O_{12}(s)$

T (K)	$H_T^\circ - H_{298.15}^\circ$ J/mol	T (K)	$H_T^\circ - H_{298.15}^\circ$ J/mol
426.0	48022	654.5	152646
498.3	80061	683.4	166842
529.4	89369	703.6	183312
570.4	110175	770.4	214086
603.3	129673		

respectively. X-ray diffraction of the compounds before and after the experiments indicated that the compounds did not decompose during the experiment. The dependence of enthalpy increment values with temperature was expressed in the form of an analytical expression with the constraint $H_T^\circ - H_{298.15}^\circ = 0$ at 298.15 K. The expressions are

$$\begin{aligned} & (H_T^\circ - H_{298}^\circ)(K_2U_4O_{12}) \text{ kJ/mol} \pm 2.4 \\ & = -82.167 + 0.204 T(\text{K}) + 0.237 \times 10^{-3} T^2(\text{K}) \\ & (426-770 \text{ K}) \end{aligned} \quad [9]$$

$$\begin{aligned} & (H_T^\circ - H_{298}^\circ)(K_2U_4O_{13}) \text{ kJ/mol} \pm 1.4 \\ & = -128.7 + 0.431 T(\text{K}) + 0.305 \times 10^{-5} T^2(\text{K}) \\ & - 0.223 \times 10^{-8} T^3 \quad (411-888 \text{ K}). \end{aligned} \quad [10]$$

TABLE 4
Dependence of Enthalpy Increment on Temperature
for $K_2U_4O_{13}(s)$

T (K)	$H_T^\circ - H_{298.15}^\circ$ J/mol	T (K)	$H_T^\circ - H_{298.15}^\circ$ J/mol
411.3	49087	755.0	185479
478.4	77881	796.9	217174
581.0	122787	817.0	224826
683.0	164974	852.9	239296
714.1	182073	888.0	255042

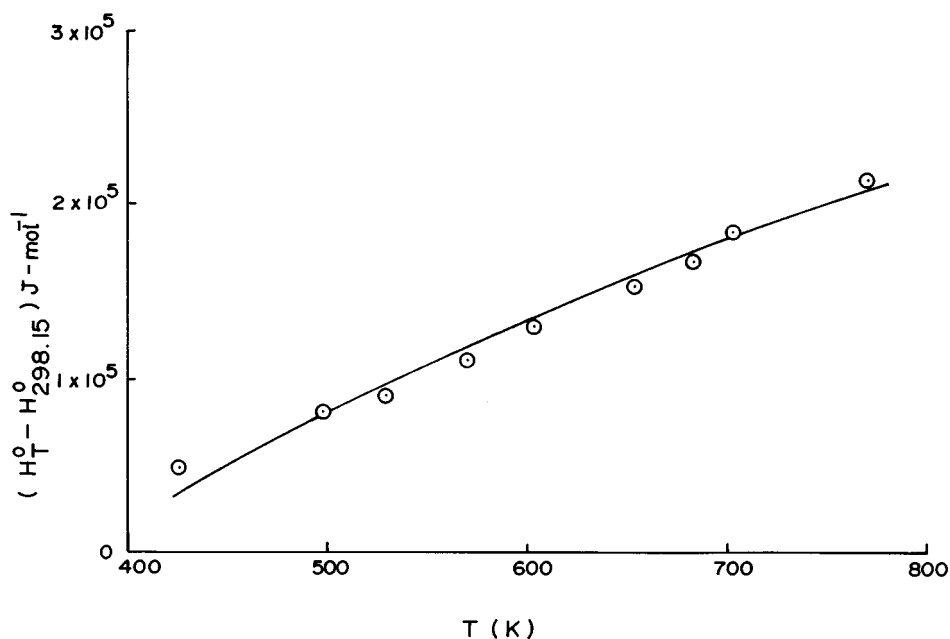


FIG. 3. Dependence of $H_T^0 - H_{298.15}^0$ (J/mol) on temperature T (K) for $K_2U_4O_{12}(s)$.

The enthalpy increment values for $K_2U_4O_{12}(s)$ and $K_2U_4O_{13}(s)$ are compared with the fit values at the experimental temperatures in Figs. 3 and 4, respectively. The molar specific heat is the first differential of $H_T^0 - H_{298.15}^0$ with respect to temperature. From the enthalpy increment values the free energy functions of $K_2U_4O_{12}(s)$ and

$K_2U_4O_{13}(s)$ were derived using the equations

$$S_T^0 = S_{298.15}^0 + \int C_p^0 dT/T \quad [11]$$

$$-(G_T^0 - H_{298.15}^0)/T = S_T^0 - [(H_T^0 - H_{298.15}^0)/T]. \quad [12]$$

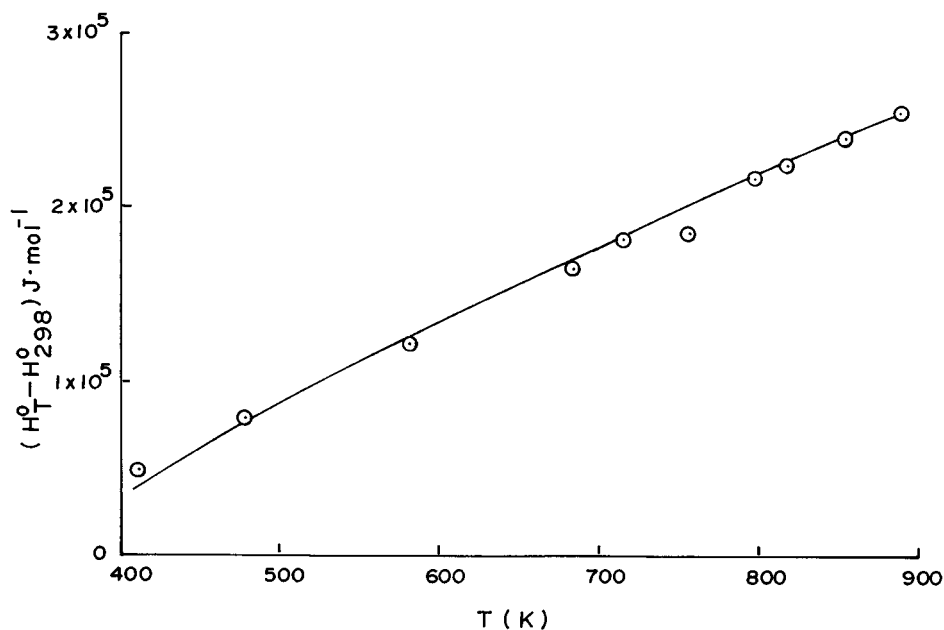


FIG. 4. Dependence of $H_T^0 - H_{298.15}^0$ (J/mol) on temperature T (K) for $K_2U_4O_{13}(s)$.

TABLE 5
Thermodynamic Values of $K_2U_4O_{12}(s)$ Obtained in This Study

T (K)	$H_T^\circ - H_{298.15}^\circ$ J/mol	C_p° J/mol.K	S_T° J/mol.K	$-[(G_T^\circ - H_{298.15}^\circ)/T(K)]$ J/mol.K
298.15	0	345	444	444
350	18403	370	501	448
400	37513	394	552	458
450	57810	418	600	471
500	79293	442	645	486
550	101961	465	688	503
600	125815	489	730	520
650	150856	513	770	538
700	177082	536	809	556
750	204494	560	846	574
800	233092	584	883	592

TABLE 6
Thermodynamic Values of $K_2U_4O_{13}(s)$ Obtained in This Study

T (K)	$H_T^\circ - H_{298.15}^\circ$ J/mol	C_p° J/mol.K	S_T° J/mol.K	$-[(G_T^\circ - H_{298.15}^\circ)/T(K)]$ J/mol.K
298.15	0	432	486	486
350	22504	433	556	492
400	44130	433	614	503
450	65759	433	664	518
500	87387	433	710	535
550	109018	433	751	553
600	130638	432	788	571
650	152257	432	823	588
700	173870	432	854	606
750	195474	432	884	623
800	217069	432	912	640

$S_{298.15}^\circ$ value for $K_2U_4O_{12}(s)$ is not available in the literature. The $S_{298.15}^\circ$ values (5) for $A_2U_4O_{13}(s)$ are 486.7, 509 and 536 J/mol.K, respectively, for $A = K, Rb,$ and Cs . Similarly for $A_2U_4O_{12}(s)$ ($A = Rb, Cs$) the values (5) are 500 and 562 J/mol.K, respectively. Since a systematic difference could be observed in the $S_{298.15}^\circ$ of the alkali uranate analogues an approximate value of 444 J/mol.K was used for the calculation of the heat values. The thermal properties of $K_2U_4O_{12}(s)$ and $K_2U_4O_{13}(s)$ are given in Tables 5 and 6. It is seen that the molar heat capacity of $K_2U_4O_{12}(s)$ gradually increases with temperature, whereas that of $K_2U_4O_{13}(s)$ remains more or less constant. The thermodynamic values of potassium uranates in the K–U–O system are compiled in Table 7 along with the available literature values.

CONCLUSION

It was found that $K_2U_4O_{12}(s)$ and $K_2U_4O_{13}(s)$ coexist up to 1200 K. The oxygen potential over the above phase fields derived from the experiments can be given by: $\Delta\mu(O_2)kJ/mol \pm 0.8 = -261.5 + 0.170 T(K)$. The stand-

ard molar Gibbs energy formation of $K_2U_4O_{12}(s)$ is suggested to be

$$\Delta_f G_T^\circ kJ/mol \pm 0.4 = -5559 + 1.104 T(K)$$

The variation of enthalpy increment with temperature and can be given by

$$\begin{aligned} (H_T^\circ - H_{298}^\circ)(K_2U_4O_{12}) kJ/mol \pm 2.4 \\ = -82.167 + 0.204 T(K) + 0.237 \times 10^{-3} T^2(K) \\ (426-770 K) \end{aligned}$$

$$\begin{aligned} (H_T^\circ - H_{298}^\circ)(K_2U_4O_{13}) kJ/mol \pm 1.4 \\ = -128.7 + 0.431 T(K) + 0.305 \times 10^{-5} T^2(K) \\ - 0.223 \times 10^{-8} T^3(K) \quad (411-888 K) \end{aligned}$$

The enthalpy of formation of $K_2U_4O_{12}(s)$ was calculated by second law method using the presently obtained enthalpy increment values and is $-5673 kJ/mol$.

TABLE 7
Thermodynamic Values of Potassium Uranates in the K–U–O System

Compound	$\Delta_f H_{298.15}^\circ$ kJ/mol	$S_{298.15}^\circ$ J/mol.K	A	B	$\Delta_f G_T^\circ = -A + BT(K)$ kJ/mol			Reference
					1000	1100	1200	
$K_2UO_4(s)$	-1889	180	-1889	0.819	-1070	-988	-906	(5)
$K_4UO_5(s)$	-2419	287	-2419	1.047	-1372	-1267	-1163	(5)
$K_2U_2O_7(s)$	-3200	291	-3200	0.656	-2544	-2478	-2413	(5)
$K_2U_4O_{12}(s)$	-5673	444	-5559	1.105	-4455	-4345	-4234	(present)
$K_2U_4O_{13}(s)$	-5690	486	-5690	1.176	-4514	-4396	-4279	(calculated)

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