



Molar Gibbs energy formation of $\text{KUO}_3(\text{s})$

K. Jayanthi, V.S. Iyer, G.A. Rama Rao, V. Venugopal *

Fuel Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085, India

Received 17 March 1998; accepted 17 August 1998

Abstract

The molar Gibbs energy formation of $\text{KUO}_3(\text{s})$ was determined by measuring the partial pressures of oxygen and potassium over the phase field, $\text{KUO}_3(\text{s}) + \text{K}_2\text{U}_2\text{O}_7(\text{s}) + \text{K}_2\text{UO}_4(\text{s})$ using electromotive force (emf) and Knudsen effusion mass loss method, respectively. The oxygen potential and the potassium potential existing over the phase field and their variation with temperature can be respectively given by: $\Delta\mu(\text{O}_2) \pm 0.6 \text{ (kJ mol}^{-1}\text{)} = -499.3 + 0.290 T \text{ (K)}$ (941–1150 K) and $\Delta\mu(\text{K}) \pm 0.17 \text{ kJ mol}^{-1} = -444.18 + 0.243 T \text{ (K)}$ (1265–1328 K). Enthalpy increment measurements on $\text{KUO}_3(\text{s})$ and $\text{K}_2\text{U}_2\text{O}_7(\text{s})$ were carried out from (369–714 K) to (391–683 K) respectively, using a high temperature Calvet calorimeter. The enthalpy increments, $(H_T^0 - H_{298.15}^0)$, in kJ mol^{-1} for $\text{KUO}_3(\text{s})$ and $\text{K}_2\text{U}_2\text{O}_7(\text{s})$ can be represented by $-39.15 + 0.129T + 0.101 \times 10^{-4}T^2 (\pm 0.7)$ and $-52.99 + 0.1361T + 0.146 \times 10^{-3}T^2 (\pm 0.7)$, respectively. From the standard molar Gibbs energy formation data, the equation $\log C_0 = 902.6/T(\text{K}) - 2.09$ was derived, where C_0 is the threshold oxygen level required for the formation of KUO_3 . © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Sodium and sodium–potassium alloy assume importance in their use as coolants in liquid metal cooled fast breeder reactor (LMFBR) using mixed oxide or carbide fuel [1]. In case of clad breach sodium/potassium would enter the fuel pin causing local swelling of the fuel pin. This will result in overheating and failures in adjacent fuel pins. Thermodynamic properties of their ternary oxides are a prerequisite for understanding their behaviour in an operating reactor. The molar Gibbs energy formation of the oxide species of the type A_3MO_4 (where $\text{A} = \text{Na/K}$, $\text{M} = \text{U, Pu}$, $\text{U}_{(1-x)}\text{Pu}_x$) [2–4] are important to evaluate the threshold oxygen potential necessary for their formation in the fuel. Literature on Na–U–O system is fairly extensive [5] whereas there is a paucity of information on the K–U–O system.

X-ray identification of pentavalent $\text{KUO}_3(\text{s})$ and other uranates $\text{K}_4\text{UO}_5(\text{s})$, $\text{K}_2\text{UO}_4(\text{s})$, $\text{K}_2\text{U}_2\text{O}_7(\text{s})$, $\text{K}_2\text{U}_4\text{O}_{13}(\text{s})$, $\text{K}_2\text{U}_7\text{O}_{22}(\text{s})$ are reported by van Egmond and Cordfunke [6]. Lindemer et al. [5] reported the

phase diagram of K–U–O system for $T < 950 \text{ K}$. The phase region $\langle \text{K}_2\text{O} \cdot n\text{UO}_3 \rangle$ ($3 \leq n \leq 6$) has not been studied well. The available literature on thermodynamic information on uranates of potassium is less [7–11]. Cordfunke and Ouweltjes [8] determined the enthalpy of formation of $\text{K}_2\text{UO}_4(\text{s})$ at 298.15 K by solution calorimetry. Recently the present authors have determined the thermodynamic properties of $\text{K}_2\text{U}_4\text{O}_{12}(\text{s})$ and $\text{K}_2\text{U}_4\text{O}_{13}(\text{s})$ by emf and calorimetric methods [12]. The present study is undertaken to determine the molar Gibbs energy formation of $\text{KUO}_3(\text{s})$ by measuring the oxygen and potassium potential above the coexisting phase field $\text{KUO}_3(\text{s}) + \text{K}_2\text{UO}_4(\text{s}) + \text{K}_2\text{U}_2\text{O}_7(\text{s})$ and the thermal properties of these compounds by calorimetry. The partial phase diagram obtained on the basis of theoretical calculation [5] showing the coexistence of the phase fields in the K–U–O system is shown in Fig. 1.

2. Experimental

2.1. Materials

$\text{K}_2\text{U}_2\text{O}_7(\text{s})$ and $\text{K}_2\text{UO}_4(\text{s})$ were prepared by reacting high purity $\text{K}_2\text{CO}_3(\text{s})$ with $\text{U}_3\text{O}_8(\text{s})$ in air in 3:2 and 3:1

* Corresponding author. E-mail: vvgopal@magnum.barc.ernet.in

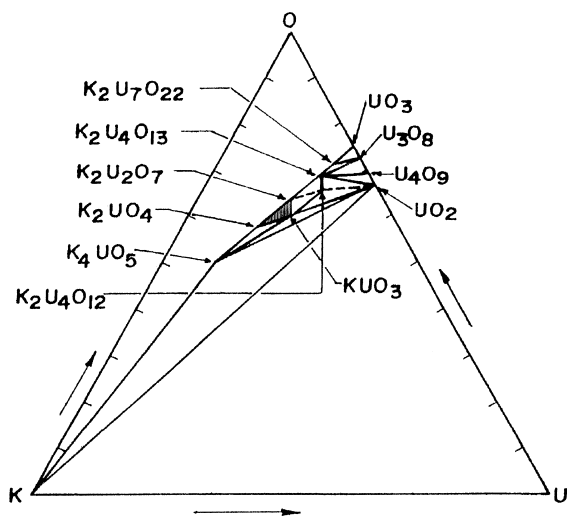


Fig. 1. Phase diagram of K–U–O system ($T < 1200$ K).

mole ratios, respectively, in alumina boats at 1000 K for 16 h. The products were exclusively identified as $K_2U_2O_7(s)$ and $K_2UO_4(s)$. $KUO_3(s)$ was prepared by reducing $K_2U_2O_7(s)$ in pure hydrogen at 1000 K in an alumina boat. The X-ray diffraction pattern matched with the one reported for $KUO_3(s)$ [13]. $KUO_3(s)$, $K_2U_2O_7(s)$ and $K_2UO_4(s)$ were mixed in 3:2:1 mole ratio and made in the form of pellets of 6 mm diameter and 3 mm thickness by pressing at 100 MPa pressure. These pellets were degassed under vacuum and used for all the measurements.

2.2. Enthalpy measurements

The enthalpy increment measurements on $KUO_3(s)$ and $K_2UO_4(s)$ were carried out using a high temperature Calvet calorimeter, model, Setaram HT-1000. The method of measurement is detailed in our earlier publication [14]. The Calvet calorimeter has identical twin compartments surrounded by thermopiles, kept inside a massive alumina block whose temperature is monitored and controlled by a platinum probe. The compartments exchange heat with the block. This exchange of heat gives rise to an electrical signal from the thermopile which is amplified and fed into a computer for integration. The calorimetric compartments were evacuated and flushed with purified argon before dropping the sample. The drop experiments were carried out under static argon pressure. In the case of $KUO_3(s)$, in situ tantalum getter was used during the calorimetric measurements to avoid oxidation of the sample. The enthalpy increment measurements were carried out for $KUO_3(s)$ and $K_2U_2O_7(s)$ at each isothermal temperatures in the temperature ranges 369–714 K and 391–683 K at an interval of 20–30 K, respectively. Two inde-

pendent measurements were carried out at each experimental temperature. The sample size used was 20 to 50 mg. The calibration factor (heat capacity equivalent) of the calorimeter was determined by electrical calibration [14]. This was also checked at each isothermal temperature by dropping standard reference material, NBS alumina (SRM-720). The X-ray diffraction pattern of $KUO_3(s)$ and $K_2U_2O_7(s)$ were taken after the experiments.

2.3. emf measurements

A two compartment cell assembly separating the gaseous environment by a 15 mol% calcium oxide stabilized zirconia electrolyte (CSZ) in the form of a tube was used for the measurement of emf. The cell was heated using a Kanthal wound resistance furnace having a constant temperature zone of 6 cm. The cell was tested by measuring the emf over the system $Ni(s) + NiO(s)$ using $Ni(s) + NiO(s)$ and air as a reference electrode.

High purity argon cover gas ($p(O_2) = 10^{-25}$ kPa) was passed over the sample during the experiments. The temperature was measured accurately to within ± 1 K using a calibrated chromel to alumel thermocouple. The thermocouples used for the measurement of temperature were calibrated by measuring the melting temperatures of ice, antimony and silver [15]. The details of the experimental assembly and the method of measurement have been reported in an earlier publication [16].

The emfs were measured using two different pellets, both in the heating and cooling cycles with a precision ± 2 mV in the temperature range 941–1150 K. The X-ray diffraction pattern of the pellet before and after the experiments remained the same indicating the coexistence of the phase field as shown in Fig. 2.

2.4. Knudsen effusion mass loss method

The potassium pressure was determined by Knudsen effusion method by measuring the mass loss of potassium in the equilibrium phases using a Cahn vacuum microbalance capable of detecting a mass change of 1 μ g. The details of the experiment and calibration of the Knudsen orifice are given in an earlier publication [17]. The performance of the microbalance was tested by measuring the tellurium vapor pressure over tellurium(s) in the temperature range 614–713 K. High purity tellurium was contained in a graphite Knudsen cell of 14 mm height and 8 mm width with a central orifice of 1 mm on the lid. The cell had a Clausing factor of 0.694 [17]. The cell was heated in an isothermal zone of a resistance furnace and the temperature was maintained within ± 1 K. A chromel to alumel thermocouple was positioned just near the Knudsen cell. In the present experiment boron nitride Knudsen cell with a small knife edged

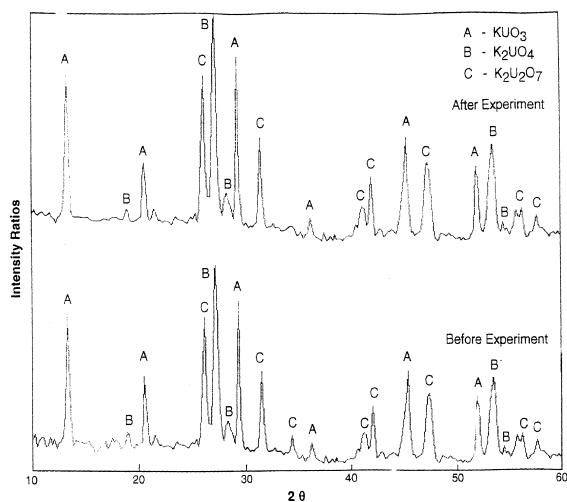


Fig. 2. XRD pattern of the sample pellet of the mixture: $\text{KUO}_3(\text{s}) + \text{K}_2\text{UO}_4(\text{s}) + \text{K}_2\text{U}_2\text{O}_7(\text{s})$ before and after the experiment. [(A) – KUO_3 peaks; (B) – K_2UO_4 peaks; (C) – $\text{K}_2\text{U}_2\text{O}_7$ peaks].

orifice was employed. Hence the Clausing factor of boron nitride cell was determined, using the partial pressure values of $\text{Te}_2(\text{g})$ obtained from the graphite cell and the mass loss of $\text{Te}_2(\text{g})$ from the boron nitride Knudsen cell. This Clausing factor was subsequently used for the evaluation of potassium pressures.

A mixture of $\text{KUO}_3(\text{s}) + \text{K}_2\text{U}_2\text{O}_7(\text{s}) + \text{K}_2\text{UO}_4(\text{s})$ along with $\text{Ni}(\text{s}) + \text{NiO}(\text{s})$ in the form of a small pellet was used in the experiments. The pellet approximately weighing 50 mg was loaded in the calibrated boron nitride Knudsen cell. The mass loss was monitored in a strip chart recorder with 1 mg at full scale in the temperature range 1265–1358 K. The XRD pattern was taken before and after the experiment.

3. Results and discussion

The XRD pattern taken for the samples before and after emf and KEML experiments indicated no additional lines confirming the coexistence of the compounds upto 1200 K (Fig. 2). The X-ray diffraction pattern of $\text{KUO}_3(\text{s})$ after the enthalpy increment experiment remained the same as the original sample indicating the absence of any oxidation. Table 1 gives the impurities of the compounds used for the preparation of uranates of potassium. The Table shows that the total impurities are less than 1000 ppm. It is assumed that there is no impurity pick up from the recrystallized alumina boat used for carrying out the reactions. This accounts for a purity better than 99.9% for $\text{K}_2\text{U}_2\text{O}_7(\text{s})$ and $\text{KUO}_3(\text{s})$. The compounds were used as such without further purification.

Table 1

Emission spectroscopic analysis result of trace metal impurities in K_2CO_3 and U_3O_8 used for the preparation of uranates of K

	Element	ppm
U_3O_8	Al	12
	B	<0.01
	Ca	14
	Fe	10
	Mg	10
	Mo	10
	Na	10
	Si	590
	W	68
	Mo	10
	Ba	19
K_2CO_3	Al	20
	Fe	50
	Mg	30
	Si	250
	Ca	20
	Ba	50

3.1. Enthalpy increment studies

Enthalpy increment values for $\text{KUO}_3(\text{s})$ and $\text{K}_2\text{U}_2\text{O}_7(\text{s})$ obtained at the experimental temperatures are given in Tables 2 and 3. The enthalpy increment values in kJ mol^{-1} obtained at experimental temperatures were expressed in the form of an analytical expression with the constraint $H_T^0 - H_{298.15}^0 = 0$ at 298.15 K. The expressions for $\text{KUO}_3(\text{s})$ and $\text{K}_2\text{U}_2\text{O}_7(\text{s})$ are given by Eqs. (1) and (2), respectively.

$$(H_T^0 - H_{298.15}^0) \text{kJ mol}^{-1} \pm 0.700 = -39.15 + 0.129T + 0.101 \times 10^{-4}T^2 \quad (369\text{--}714 \text{ K}), \quad (1)$$

$$(H_T^0 - H_{298.15}^0) \text{kJ mol}^{-1} \pm 0.700 = -52.99 + 0.1361T + 0.146 \times 10^{-3}T^2 \quad (391\text{--}683 \text{ K}). \quad (2)$$

Figs. 3 and 4 show the comparison of enthalpy increment values of $\text{KUO}_3(\text{s})$ and $\text{K}_2\text{U}_2\text{O}_7(\text{s})$, respectively,

Table 2

Dependence of enthalpy increment of $\text{KUO}_3(\text{s})$ on temperature along with the fit values at the experimental temperatures

T (K)	$H_T^0 - H_{298.15}^0$ (J mol^{-1})	Fit values (J mol^{-1})
369.6	10266 ± 177	9911
391.2	12219 ± 322	12863
411.4	16375 ± 370	15633
478.1	24341 ± 247	24836
525.9	32198 ± 355	31486
580.8	38838 ± 171	39181
631.0	46216 ± 27	46270
683.1	52857 ± 412	53681
714.1	58862 ± 378	58116

Table 3

Dependence of enthalpy increment of $K_2U_2O_7(s)$ on temperature along with the fit values at the experimental temperatures

T (K)	$H_T^0 - H_{298.15}^0$ J mol ⁻¹	Fit values J mol ⁻¹
391.2	23495 ± 117	22729
411.5	28795 ± 148	27884
478.2	45157 ± 268	45672
525.9	58488 ± 300	59194
580.0	75117 ± 298	75338
632.0	91775 ± 420	91664
683.0	108719 ± 510	108447

at the experimental temperatures with the fit values. The molar specific heats were obtained from the first differential of Eqs. (1) and (2) with temperature. $S_{298.15}^0$ values for $KUO_3(s)$ and $K_2U_2O_7(s)$ were taken from the literature [10] for the calculation of thermal properties. The thermal properties of $KUO_3(s)$ and $K_2U_2O_7(s)$ are given in Tables 4 and 5, respectively.

3.2. emf measurements

Oxygen potential over the system $KUO_3(s) + K_2UO_4(s) + K_2U_2O_7(s)$. The solid oxide electrolyte galvanic cell was tested for zero potential for $Ni(s) + NiO(s)$ with reference to $Ni(s) + NiO(s)$. The emf resulted for the cell: Pt | $Ni(s) + NiO(s)$ | CSZ | air | Pt ($p(O_2) = 21.21$ kPa.) is shown in Table 6 along with the literature values. The table shows that the emfs are in very good agreement with the literature values indicating that the present cell is reliable for thermodynamic measurements.

The same cell setup was used for the equilibrium emf measurement over the phase fields $KUO_3(s) + K_2U_2O_7(s) + K_2UO_4(s)$. The cell can be represented by

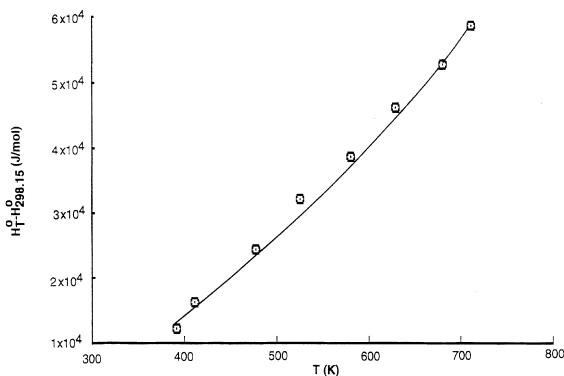


Fig. 3. Dependence of enthalpy increment on temperature of $KUO_3(s)$.

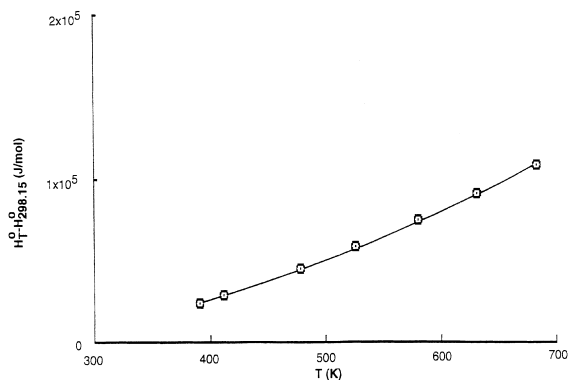


Fig. 4. Dependence of enthalpy increment on temperature of $K_2U_2O_7(s)$.

The cell reaction may be written as:

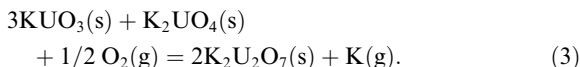


Table 7 gives the emf values at the experimental temperatures. The emf values were least squares fitted against temperatures and can be given by

$$E(\text{mV}) \pm 1.4 = 1293 - 0.749T(\text{K}) \quad (941-1150 \text{ K}). \quad (4)$$

The emf values at the experimental temperatures were compared with the fit values in Fig. 5.

The emf resulted in cell I at the experimental temperatures are under equilibrium conditions. The oxygen pressure above the system at a temperature is invariant and the potassium pressure does not alter the emf as the electrolyte senses only the oxygen at an isothermal temperature.

The oxygen potential existing over the system $KUO_3(s) + K_2U_2O_7(s) + K_2UO_4(s)$ can be given by: $\Delta\mu(O_2) = RT \ln p(O_2) = -4FE$, where $E = \text{emf}$ in volts and $F = 96486.4$ C/mol. The oxygen potential existing over the system $KUO_3(s) + K_2U_2O_7(s) + K_2UO_4(s)$ for cell I after correction of O_2 to 101.325 kPa can be represented by

$$\Delta\mu(O_2) \pm 0.6 \text{ kJ mol}^{-1} = -499.3 + 0.290T(\text{K}) \quad (941-1150 \text{ K}) \quad (5)$$

3.3. Knudsen effusion mass loss method

Tellurium pressure ($Te_{2,g}$) over $Te(s)$ obtained using the graphite Knudsen cell of known Clausing factor is in good agreement with the literature values indicating the reliability of the present experimental setup. Table 7 gives the mass loss obtained for $Te(s)$ using boron nitride Knudsen cell along with the calculated Clausing factor for the cell using the known Te_2 pressure [18] over the $Te(s)$. The Clausing factor of the boron nitride

Table 4
Thermal properties of $\text{K}_2\text{U}_2\text{O}_7(\text{s})$

T (K)	$H_T^0 - H_{298.15}^0$ (J mol ⁻¹)	C_p^0 (J mol ⁻¹ K ⁻¹)	$S_{(T)}^0$ (J mol ⁻¹ K ⁻¹)	$-(G_T^0 - H_{298.15}^0)/T$ (J mol ⁻¹ K ⁻¹)
350	7231	136	156	135
400	14057	137	174	139
450	20934	138	191	144
500	27862	139	205	149
550	34839	140	218	155
600	41867	141	231	161
650	48945	142	242	167
700	56074	143	253	172

Table 5
Thermal properties of $\text{K}_2\text{U}_2\text{O}_7(\text{s})$

T (K)	$H_T^0 - H_{298.15}^0$ (J mol ⁻¹)	C_p^0 (J mol ⁻¹ K ⁻¹)	$S_{(T)}^0$ (J mol ⁻¹ K ⁻¹)	$-(G_T^0 - H_{298.15}^0)/T$ (J mol ⁻¹ K ⁻¹)
350	14349	211	323	282
400	25494	234	353	289
450	37752	256	382	298
500	51124	278	410	307
550	65609	300	437	318
600	81208	323	464	329
650	97920	345	491	341
700	115746	367	518	352

Table 6
Dependence of emf on temperature for the cell Pt|Ni(s) + NiO(s)|CSZ|air, Pt

T (K)	emf (mV)	emf Ref. [17]
945	759.7	758.6
955	754.8	753.8
1030	717.8	717.7
1052	707.0	707.1
1065	700.0	700.8
1120	673.2	674.4

Knudsen cell was obtained from the mass loss and the p_{Te_2} from the literature [18] using the equation,

$$p(\text{kPa}) = (dw/dt)(101.325/44.33)(1/a)(1/k)(\sqrt{T/M}), \quad (6)$$

where p is the pressure in kPa of $\text{Te}_2(\text{g})$ from literature [18], dw/dt is the mass loss in kg s^{-1} , T is the temperature in K, M was taken as $0.2552 \text{ kg mol}^{-1}$, a is the area of cross section of the orifice which is assumed to be constant throughout the experiment, k is then Clausing factor of the cell. The calculated value of k is 0.945.

Table 8 gives the mass loss of potassium at each isothermal temperature over the coexisting phases and the corresponding pressures. The potassium pressure in reaction (3) was calculated using Eq. (6). The molar mass of K was taken as $0.039039 \text{ kg mol}^{-1}$. The potassium pressures were least-squares fitted with temperature and can be given by

$$\log p(\text{kPa}) \pm 0.02 = -23198/T(\text{K}) + 14.693 \quad (1265\text{--}1328 \text{ K}). \quad (7)$$

The pressure values at the experimental temperatures are compared with the fit values in Fig. 6.

The potassium (K) pressure over the phase field $\text{K}_2\text{U}_2\text{O}_7(\text{s}) + \text{K}_2\text{UO}_4(\text{s})$, can be defined as $\Delta\mu(\text{K}) = RT \ln p(\text{K})$. The dependence of potassium potential on temperature can be represented by:

$$\Delta\mu(\text{K}) \pm 0.17 (\text{kJ mol}^{-1}) = -444.18 + 0.243 T(\text{K}) \quad (1265\text{--}1328 \text{ K}). \quad (8)$$

The Gibbs energy changes for the cell reaction (1) can be given by:

$$\Delta_r G^0 = -2FE = -RT \ln K_e$$

where K_e is the equilibrium constant ($K_e = [p(\text{K})/p(\text{O}_2)]$) and R is the universal gas constant and the standard state of potassium is taken as K(g) at 101.325 kPa and the Gibbs energy is zero at all temperatures. The Gibbs energy change for the reaction (1) is given by:

$$\Delta_r G^0 (\text{kJ}) = -194.57 + 0.098 T(\text{K}). \quad (9)$$

3.4. Molar Gibbs energy formation of $\text{K}_2\text{U}_2\text{O}_7(\text{s})$

The molar Gibbs energy formation of $\text{K}_2\text{U}_2\text{O}_7(\text{s})$ is calculated using the relation,

$$\Delta_f G_T^0 = \Delta_f H_T^0 - T\Delta_f S_T^0. \quad (10)$$

Table 7

Dependence of emf (mV) on temperature T (K) for the cell I: Pt | $\text{K}_2\text{UO}_4(\text{s}) + \text{K}_2\text{UO}_7(\text{s})$ | CSZ | air ($p(\text{O}_2) = 21.21$ kPa), Pt

T (K)	emf (mV)	T (K)	emf (mV)	T (K)	emf (mV)
<i>Pellet I</i>					
941	588.5	991	551.0	1059	503.5
952	580.0	1001	544.0	1063	498.0
964	571.0	1023	526.5	1073	488.0
980	559.0	1029	522.0	1106	467.1
				1150	430.0
<i>Pellet II</i>					
948	583.0	1011	536.4	1093	477.1
964	571.0	1035	517.5	1115	458.0
974	561.0	1045	510.0	1132	442.5
		1088	479.5	1140	439.1

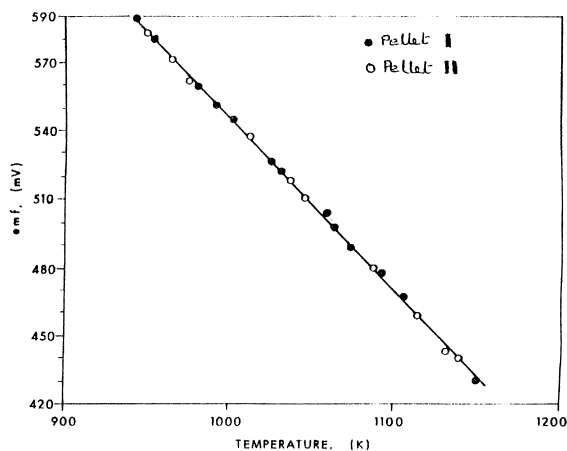


Fig. 5. Dependence of emf (mV) on temperature T (K) for the cell: Pt| $\text{K}_2\text{UO}_4(\text{s}) + \text{K}_2\text{UO}_7(\text{s})$ |CSZ|air($p(\text{O}_2) = 21.21$ kPa), Pt.

The enthalpy and entropy of formation at the average experimental temperature is calculated from the enthalpy and entropy of formation values at 298.15 K reported by Grenthe et al [10] and the molar heat capacity values derived from the presently obtained enthalpy increment values. The molar Gibbs energy formation of $\text{K}_2\text{UO}_7(\text{s})$ can be represented by,

$$\Delta_f G^0 (\text{kJ mol}^{-1}) = -3171 + 0.524 T (\text{K}) \quad (391-683 \text{ K}). \quad (11)$$

3.5. Molar Gibbs energy formation of $\text{K}_2\text{UO}_4(\text{s})$

In the absence of reliable C_p^0 values it is assumed that the enthalpy and entropy changes due to C_p^0 changes are negligible. Hence the molar Gibbs energy formation of $\text{K}_2\text{UO}_4(\text{s})$ was calculated using relation (14) taking the enthalpy and entropy of formation values from Grenthe et al [10] and can be given by:

$$\Delta_f G^0 \text{K}_2\text{UO}_4 (\text{kJ mol}^{-1}) = -1911 + 0.423 T (\text{K}) \quad (12)$$

3.6. Molar Gibbs energy formation of $\text{KUO}_3(\text{s})$

The molar Gibbs energy change for the reaction can be given by:

$$\begin{aligned} \Delta_r G^0 &= 2\Delta_f G^0 \text{K}_2\text{UO}_7(\text{s}) + RT \ln p_{(\text{K})}^0 \\ &\quad - 3\Delta_f G^0 (\text{KUO}_3(\text{s}) - \Delta_f G^0 (\text{K}_2\text{UO}_4(\text{s})) \\ &\quad - (RT/2) \ln p(\text{O}_2)_{\text{air}}. \end{aligned}$$

Using the above equation and the molar Gibbs energy formation of $\text{K}_2\text{UO}_4(\text{s})$ and $\text{K}_2\text{UO}_7(\text{s})$ and the molar Gibbs energy change for the reaction (1), the molar Gibbs energy formation of $\text{KUO}_3(\text{s})$ was calculated.

Table 8

Dependence of $p(\text{Te}_2)(\text{g})$ over $\text{Te}(\text{s})$ on temperature T (K) for Boron Nitride Knudsen cell

T (K)	$\text{d}w/\text{d}t^{-1} (\text{g s}^{-1}) 10^6$	$p(\text{Te}_2) \text{kPa } 10^3$	k (Clausing factor)
622	0.621	0.304	0.91
634	1.148	0.548	0.94
647	2.065	1.015	0.92
661	3.796	1.913	0.92
675	7.500	3.506	0.99
694	7.530	3.566	0.99

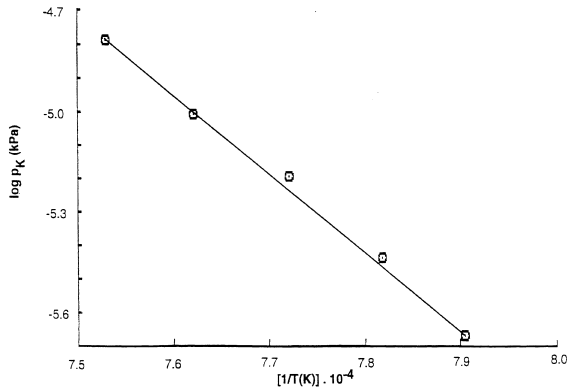


Fig. 6. Variation of $\log p(K)$ with $1/T$ for the reaction: $3\text{KUO}_3(\text{s}) + \text{K}_2\text{UO}_4(\text{s}) + 1/2\text{O}_2(\text{g}) = 2\text{K}_2\text{U}_2\text{O}_7(\text{s}) + \text{K}(\text{g})$.

The molar Gibbs energy formation of $\text{KUO}_3(\text{s})$ can be given by:

$$\Delta_f G^0(\text{KUO}_3) \pm 10(\text{kJ mol}^{-1}) = -1412 + 0.177 T(\text{K}) \quad (932\text{--}1165 \text{ K}) \quad (13)$$

An error of 10 kJ mol^{-1} shown in the molar Gibbs energy formation of $\text{KUO}_3(\text{s})$ is mainly attributed to the error approximation made in the molar Gibbs energy formation values of $\text{K}_2\text{UO}_4(\text{s})$ and $\text{K}_2\text{U}_2\text{O}_7(\text{s})$.

The oxygen potential, potassium potential and the molar Gibbs energy formation values of $\text{KUO}_3(\text{s})$ at 1000, 1100 and 1200 K are given in Table 9. Table 10 summaries the thermodynamic values of some of the ternary uranates of potassium determined presently along with the available literature values.

4. Discussion and conclusion

From Eq. (1) it is evident that the degree of freedom is two, but by fixing the temperature, the oxygen pressure and the potassium pressure are to be fixed. The emf measurements yield partial pressures of oxygen only over the coexisting phase field in the temperature range 941 to 1150 K. The KEML method yield total pressures of oxygen and potassium in the temperature range 1265 to 1328 K. As the oxygen pressure obtained from the emf values extrapolated to high temperatures are two to three times lower, the contribution of oxygen pressure to the total pressure is subtracted to obtain potassium

Table 9

Dependence of P_K (kPa) on temperature $T(\text{K})$ for reaction: $3\text{KUO}_3(\text{s}) + \text{K}_2\text{UO}_4(\text{s}) + 1/2\text{O}_2(\text{g}) = 2\text{K}_2\text{U}_2\text{O}_7(\text{s}) + \text{K}(\text{g})$

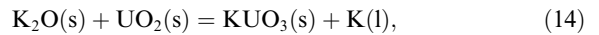
$T(\text{K})$	$d\text{w}dt^{-1} \text{ g s}^{-1} \times 10^8$	$p(\text{kPa}) 10^6$
1265	7.525	2.236
1279	11.88	3.551
1295	19.78	5.949
1312	33.54	10.15
1328	54.44	16.58

pressure. These pressure values are used for equilibrium constant calculations of Eq. (3).

In the present calculations, the potassium pressures were interpolated to obtain the molar Gibbs energy formation values in the temperature range reported. The experimentally determined molar Gibbs energy formation values for potassium uranates are reported for the first time in Table 11.

4.1. Threshold oxygen levels

For the reaction



the standard Gibbs energy change can be obtained by combining Eq. (13) and molar Gibbs energy formation value of $\text{UO}_2(\text{s})$ and $\text{K}_2\text{O}(\text{s})$ from literature [19].

$$\Delta G_T^0(\text{kJ}) = 25.334 - 0.116T(\text{K}). \quad (15)$$

In order to calculate the threshold oxygen level required for the formation of $\text{KUO}_3(\text{s})$ in a reactor operating on $\text{UO}_2(\text{s})$ and liquid potassium, the saturation solubility of oxygen in potassium is taken from the literature [20] which can be given by,

$$\log C_o^0(\text{wppm}) = 3.970 - 420.4/T(\text{K}). \quad (16)$$

The Gibbs energy change can also be given by:

$\Delta G_T^0 = -RT \ln K = RT \ln a_{[\text{O}]}$ where K is the equilibrium constant for reaction (15) and is equal to $a_{[\text{O}]}$, the activity of oxygen dissolved in $\text{K}(\text{l})$.

Incorporating Eq. (16) and using Eq. (15), the threshold oxygen solubility can be given by,

$\Delta G_T^0 = RT \ln(C/C_o^0)$ where C and C_o^0 are the threshold and saturation solubility of oxygen (in weight ppm) in potassium. The threshold oxygen level required for the formation of KUO_3 is calculated to be

Table 10

The oxygen potential $[-\mu(\text{O}_2)]$, potassium potential and molar Gibbs energy formation of KUO_3 at 1000, 1100 and 1200 K

$T(\text{K})$	$-\Delta\mu(\text{O}_2)$ (kJ mol ⁻¹)	$-\Delta\mu(\text{K})$ (kJ mol ⁻¹)	$-\Delta_f G^0$ (kJ mol ⁻¹)
1000	209.3	201.1	1227
1100	180.3	176.8	1194
1200	151.3	152.5	1160

Table 11
Thermodynamic values of potassium uranates in the K–U–O system

Compound	$-\Delta_f H_{298.15}^0$ (kJ mol ⁻¹)	$S_{298.15}^0$ (J mol ⁻¹ K ⁻¹)	$-\Delta_f G_T^0 = -A + BT(K)$ kJ mol ⁻¹				
			$-A$	B	1000 K	1100 K	1200 K
KUO ₃	1517 ^a	135	1412	0.177	1235	1217	1199(p)
K ₂ UO ₄	1889 ^a	180	1911	0.423	1488	1445	1403(c)
K ₄ UO ₅	2419 ^a	287	2419	1.047	1372	1267	1163(c)
K ₂ U ₂ O ₇	3200 ^a	291	3171	0.524	2647	2595	2542(c)
K ₂ U ₄ O ₁₂	–	–	5559	1.105	4455	4345	4234(p)
K ₂ U ₄ O ₁₃	5690 ^a	486	5690	1.176	4514	4396	4279(c)

^a [5], (p) present value (c) calculated value

$$\log C(\text{wppm}) = 902.6/T(\text{K}) - 2.09 \quad (17)$$

and at 873 K the value is 0.1 ppm by weight.

The molar specific heat of KUO₃(s) and K₂U₂O₇(s) were derived from the enthalpy increment measurements using a high temperature Calvet calorimeter for the first time. The thermal properties of these compounds were derived from the experimental values.

Acknowledgements

The authors are thankful to Mr. Rajendra Prasad, Head, Fuel Development Chemistry section and Dr. D.D. Sood, Director Radiochemistry and Isotope group for their constant encouragement during the course of the work.

References

- [1] M.A. Mignanelli, P.E. Potter, J. Nucl. Mater. 130 (1985) 289.
- [2] P.E. Blackburn, A.E. Martin, J.E. Battles, P.A.G. O'Hare, W.K. Hubbard (Eds.), in: Proc. Conf. Fast Reactor Fuel Element (R.F.) Technology, vol 3, American Nuclear Society, Hinsdale, IL, 1972, p. 479.
- [3] M.G. Adamson, E.A. Aitken, S.K. Evans, Behaviour and chemical state of irradiated ceramic fuels, Panel, in: Proceedings Series, IAEA, Vienna, 1974, p. 393.
- [4] M. Houssau, G. Deans, J.P. Marcon, J.F. Marin, Report CWA-N-1588, 1973.
- [5] T.B. Lindemer, M. Besmann, C.E. Johnson, J. Nucl. Mater. 100 (1981) 178.
- [6] A.B. van Egmond, E.H.P. Cordfunke, J. Inorg. Nucl. Chem. 38 (1976) 2245.
- [7] J.S. Anderson, Chimica 23 (1969) 438.
- [8] E.H.P. Cordfunke, W. Ouweltjes, J. Chem. Thermodyn. 13 (1981) 187.
- [9] E.H.P. Cordfunke, P.A.G. O'Hare, The Chemical Thermodynamics of Actinide Elements and Compounds, Part 3, Miscellaneous Actinide Compounds, IAEA, Vienna, 1978.
- [10] I. Grenthe, J. Fuger, J.M. Konings, R.J. Lemire, A.B. Muller, C.N.T. Cregu, H. Wanner, in: H. Wamer, I. Forest (Eds.), Chemical Thermodynamics of Uranium, OECD Nuclear Agency, Data Bank, France, 1992.
- [11] E.A. Ippolitova, D.G. Faustova, V.I. Splitsyn, in: V.I. Spitsyn (Ed.), Proc. Symp. on Invest. into the Field of Uranium Chemistry, Report ANL-TRANS-33, Moscow University, Argonne nat'l.Lab, 1964, p. 170.
- [12] V.S. Iyer, K. Jayanthi, V. Venugopal, J. Solid State Chemistry 132 (1997) 342.
- [13] A. van Egmond, thesis, University of Amsterdam, Amsterdam, Netherlands, private communication, 1976.
- [14] V.S. Iyer, R. Agarwal, K.N. Roy, S. Venkiteswran, V. Venugopal, D.D. Sood, J. Chem. Thermodyn. 22 (439) 1990.
- [15] Metrologia 27 (1990) 3; *ibid* 27 (1990) 107.
- [16] V. Venugopal, V.S. Iyer, K. Jayanthi, J. Nucl. Mater. 199 (1992) 29.
- [17] V.S. Iyer, K. Jayanthi, G.A. Rama Rao, V. Venugopal, D.D. Sood, J. Nucl. Mater. 183 (1991) 76.
- [18] R.A. Rapp, in: R.F. Bunshah (Ed.), Physicochemical Measurements in Metal Research, Technique of Metal Research, vol. 4, Part I, Wiley, New York, 1970.
- [19] O. Kubaschewski, C.B. Alcock, P.J. Spencer, Metallurgical Thermochemistry, 6th ed., Oxford Pergman, 1993, Xii, ISBN-0-08-041888-0, p. 366.
- [20] D. Krishnamoorthy, A. Thiruvengadasamy, N.P. Bhat, C.K. Mathews, J. Less Common Met. 135 (1987) 285.