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# Thermodynamic studies on $Ba_{2.875}UO_{5.875}(s)$

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ABSTRACT

The Gibbs energy of formation of $Ba_{2.875}UO_{5.875}(s)$ has been determined using manometric technique. The equilibrium $CO_2(g)$ pressures over the three phase mixture: $\{Ba_{2.875}UO_{5.875}(s) + Ba_3UO_6(s) + BaCO_3(s)\}$ have been measured using an absolute pressure transducer in the temperature range 1030–1220 K. The corresponding Gibbs energy expression as a function of temperature can be given as:

$$\Delta_f G^\circ_m(T)(Ba_{2.875}UO_{5.875},\ s,T)\ \ (\mathrm{kJ\ \ mol^{-1}}) \pm 5 = -3153.1 + 0.5573\ \ (T/\mathrm{K})$$

$\Delta_f H^\circ_m(298.15\,K)$ and $S^\circ_m(298.15\,K)$ data have been calculated from the above Gibbs energy expression using required values from the literature. The corresponding values are $-3143.4 \pm 2\,\mathrm{kJ\,mol^{-1}}$ and $270.8 \pm 4\,\mathrm{J\,K^{-1}\,mol^{-1}}$, respectively. The $\Delta_f H^\circ_m(298.15\,K)$ value has also been calculated from third law method as $-3137.7 \pm 4\,\mathrm{kJ\,mol^{-1}}$.

## 1. Introduction

Barium is an important fission product in an irradiated nuclear fuel. Thus, thermochemical stabilities of compounds in the Ba-U-O system are of importance. The stability of a compound can be calculated from its Gibbs energy of formation values. Hence, $\Delta_f G^\circ_m(T)$ of all barium uranates are required to compute the chemical form of barium in the reactor environment. Allpress [1] and Touzelin and Pialoux [2] investigated Ba-U-O system using X-ray diffraction technique. Thermodynamic functions of barium uranates are reported in the literature [3–14]. However, $\Delta_f G^\circ_m(T)$ data are limited [10,15,16]. Recently Banarjee et al. [15] have measured $\Delta_f G^\circ_m(T)$ of $BaU_2O_7(s)$ and $Ba_2U_3O_{11}(s)$ using e.m.f. technique. Yamawaki et al. [16] investigated the vaporization of $BaUO_3(s)$ by means of Knudsen effusion mass spectrometry in the temperature range of 1770–1920 K. Matsuda et al. [10] have calculated $\Delta_f G^\circ_m(BaUO_3,\ s,T)$ from their heat capacity measurements and literature data. The $\Delta_f G^\circ_m(T)$ values for other uranates are not reported. In this study, the $CO_2(g)$ pressure measurements have been carried out to determine $\Delta_f G^\circ_m(Ba_{2.875}UO_{5.875},\ s,T)$ values using a static manometric technique in the temperature range 1030–1220 K.

## 2. Experimental

### 2.1. Material preparation

$Ba_{2.875}UO_{5.875}(s)$ was prepared by the solid state reaction of $BaCO_3(s)$ (0.997 mass fraction, B.D.H, UK) with $U_3O_8(s)$ (0.9999 mass fraction purity, Nuclear Fuel Complex, Hyderabad, India) in the presence of air. $BaCO_3(s)$ and $U_3O_8(s)$ were mixed thoroughly in the ratio of 8.625:1 and calcined at 1273 K for 300 h in an alumina boat with intermediate grindings. $Ba_{2.875}UO_{5.875}(s)$ has been formed due to following reaction:

$$BaCO_3(s) + U_3O_8(s) + 1/2O_2(g) = 3Ba_{2.875}UO_{5.875}(s) + CO_2(g). \qquad (1)$$

The resulting reddish-orange coloured compound was characterized as $Ba_{2.875}UO_{5.875}(s)$ by X-ray diffraction (XRD). The XRD pattern was taken on a STOE X-ray diffractometer, Germany, using Ni filtered Cu K( radiation. The X-ray diffraction (XRD) pattern shown in Fig. 1 agreed well with that reported in the literature [17,18]. Griffiths and Kemmler [17] found this compound besides $Ba_3UO_6(s)$ in the BaO-$UO_3$ system.

A three phase mixture: $\{Ba_{2.875}UO_{5.875}(s) + Ba_3UO_6(s) + BaCO_3(s)\}$ was prepared under dry condition and made into pellets under a pressure of 100 MPa. The pellets were dried and stored in a desiccator for manometric measurements.

### 2.2. Equilibrium technique

An all-metal ultra-high vacuum system similar to that employed earlier [19] was used to measure $CO_2(g)$ pressures. The assem-

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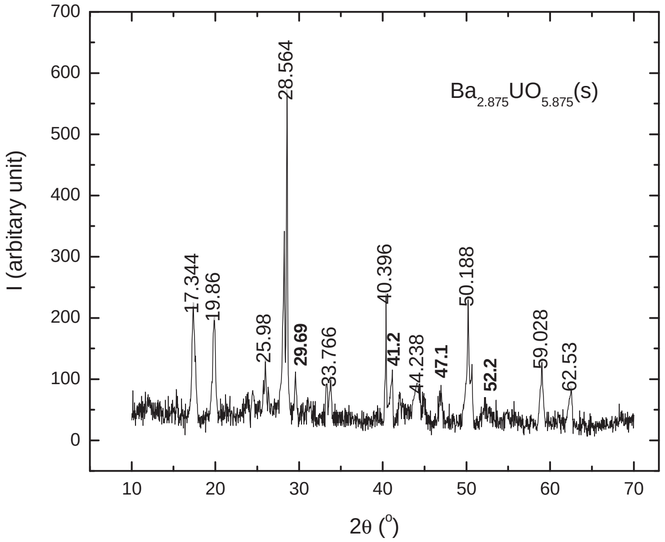

**Fig. 1.** X-ray diffraction pattern of $Ba_{2.875}UO_{5.875}$(s). The intensity, *I* (arbitrary unit) of peaks are plotted in y axis and the diffraction angle 2*θ* (°) in *x*-axis.

bly was evacuated and tested for leak tightness for 400 h before actual pressure measurements. The pellets of ternary mixture $\{Ba_{2.875}UO_{5.875}(s) + Ba_3UO_6(s) + BaCO_3(s)\}$ were placed in an alumina boat and loaded into the quartz reaction tube, which was attached to the vacuum system. The sample was heated by a Kanthal wire-wound furnace and the temperature of the sample was maintained within ±1 K and was measured using a pre-calibrated chromel-to-alumel thermocouple. Before measuring the $CO_2$(g) pressures, the pellets were annealed under vacuum at an oxygen partial pressure of $10^{-5}$ kPa at 500 K for 400 h.

The $CO_2$(g) pressures were measured by a absolute pressure transducer supplied by Edwards, USA. The accuracy of the transducer was ±0.25% of the reading. This transducer was calibrated by measuring oxygen pressure over two phase mixture: $\{Cu_2O(s) + CuO(s)\}$.

The attainment of equilibrium $p(CO_2)$ over $\{Ba_{2.875}UO_{5.875}(s) + Ba_3UO_6(s) + BaCO_3(s)\}$ was checked by evacuating some $CO_2$(g) and allowing the equilibrium to be attained again. An equilibrium time of 200–400 h was generally required for each experimental temperature. The X-ray diffraction pattern shown in Fig. 2 was taken after the experiment. It did not show any new peaks which is a proof of absence of any solid phases other than participating in reaction (2). This observation confirmed co-existence of the three phase mixture: $\{Ba_{2.875}UO_{5.875}(s) + Ba_3UO_6(s) + BaCO_3(s)\}$.

## 3. Results

The $CO_2$(g) pressures generated due to the reaction:

$$8Ba_{2.875}UO_{5.875}(s) + BaCO_3(s) = 8Ba_3UO_6(s) + CO_2(g) \qquad (2)$$

The variation of $p(CO_2,g)$ at various temperatures is given in Table 1 and shown in Fig. 3 and can be represented by the following least squares expression:

$$\{\ln p(CO_2, g)/\mathrm{kPa}\} \pm 0.05 = 12.278 – 12787 \quad (\mathrm{K}/T). \qquad (3)$$

The $\Delta_r G^\circ_m(T)$ for the reaction (2) can be given as:

$$\begin{aligned}\Delta_r G^\circ_m(T) = -RT \ln p(CO_2, g) &= 8\,\Delta_f G^\circ_m(Ba_3UO_6, s, T)\\ &+\Delta_f G^\circ_m(CO_2, g, T) - 8\,\Delta_f G^\circ_m(Ba_{2.875}UO_{5.875}, s, T)\\ &-\Delta_f G^\circ_m(BaCO_3, s, T)\end{aligned} \qquad (4)$$

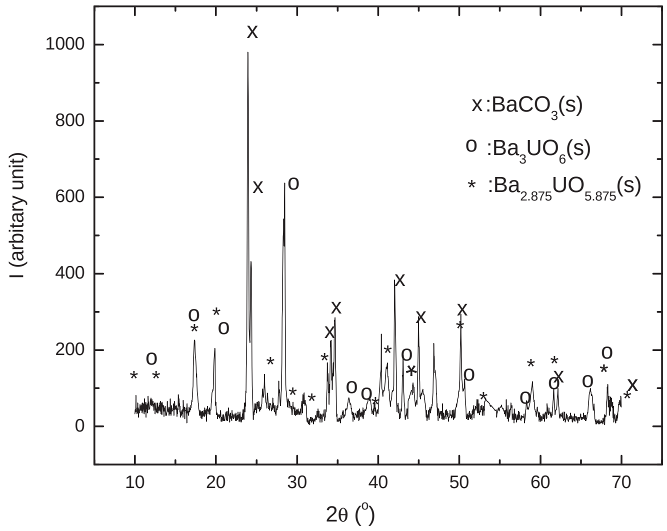

**Fig. 2.** X-ray diffraction pattern of the mixture: $\{BaCO_3(s) + Ba_3UO_6(s) + Ba_{2.875}UO_{5.875}(s)\}$ after the experiment). The XRD peaks of $BaCO_3$(s), $Ba_3UO_6$(s) and $Ba_{2.875}UO_{5.875}(s)\}$ are shown with different symbols.

**Table 1**
Equilibrium $CO_2$(g) pressures at different temperatures over the three phase mixture: $\{Ba_{2.875}UO_{5.875}(s)\ Ba_3UO_6(s) + BaCO_3(s)\}$.

| *T* (K) | $10 \cdot p(CO_2, g)$ (kPa) | *T*/K | $10 \cdot p(CO_2, g)$ (kPa) |
|---|---|---|---|
| 1030 | 8.65 ± 0.02 | 1110 | 22.8 ± 0.06 |
| 1040 | 9.32 ± 0.02 | 1120 | 24.2 ± 0.07 |
| 1060 | 12.0 ± 0.03 | 1140 | 28.71 ± 0.09 |
| 1070 | 14.4 ± 0.04 | 1157 | 35.16 ± 0.10 |
| 1071 | 13.3 ± 0.03 | 1168 | 37.48 ± 0.12 |
| 1080 | 15.8 ± 0.04 | 1178 | 39.91 ± 0.11 |
| 1090 | 17.0 ± 0.07 | 1191 | 48.85 ± 0.12 |
| 1100 | 19.8 ± 0.09 | 1220 | 55.96 ± 0.14 |

The $\Delta_r G^\circ_m(T)$ can be calculated from Eqs. (4) and (3) and are given as:

$$\{\Delta_r G^\circ_m(T)(\mathrm{kJ\ \ mol^{-1}})\} \pm 0.3 = 106.3 - 0.0637 \quad (T/\mathrm{K}) \times (1030 \le T/\mathrm{K} \le 1220) \qquad (5)$$

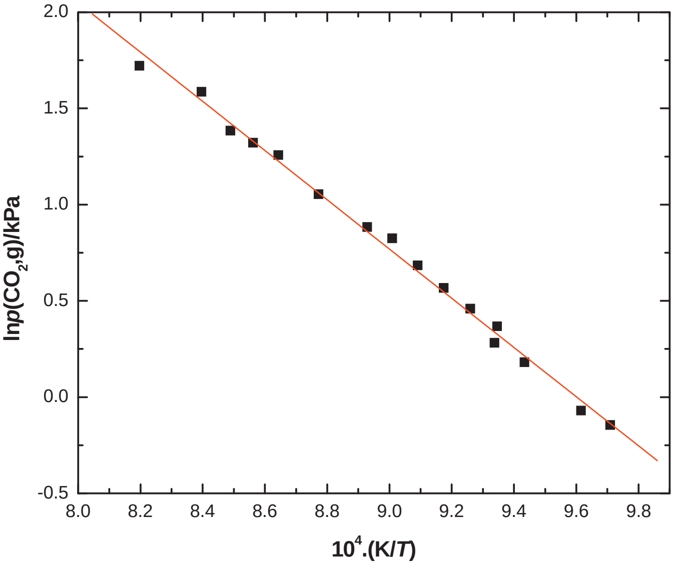

**Fig. 3.** Temperature dependence of equilibrium vapour pressure of $CO_2$(g) over phase mixture: $\{Ba_{2.875}UO_{5.875}(s) + Ba_3UO_6(s) + BaCO_3(s)\}$.

The $\Delta_f G^\circ_m(Ba_{2.875}UO_{5.875}, s, T)$ has been computed using Eq. (5) and $\Delta_f G^\circ_m(T)$ values for $BaCO_3(s)$ [20] and $CO_2(g)$ [21] from Eqs. (6) and (7)

$$\Delta_f G^\circ(BaCO_3, s, T)\ (kJ\ mol^{-1}) = -1194.7 + 0.2403\ (T/K), \tag{6}$$

$$\Delta_f G^\circ(CO_2, g, T)\ (kJ\ mol^{-1}) = -394.8 - 0.00108\ (T/K), \tag{7}$$

and that for $Ba_3UO_6(s)$ from Table 2. The corresponding $\Delta_f G^\circ_m(Ba_{2.875}UO_{5.875}, s, T)$ expression can be given as:

$$\Delta_f G^\circ_m(Ba_{2.875}UO_{5.875}, s, T)(\pm 5\ kJ\ mol^{-1}) = -3153.1 + 0.5573 \times (T/K)\ (1030 \leq T/K \leq 1220) \tag{8}$$

The intercept and slope of above Gibbs energy expression gives enthalpy of formation and entropy of $Ba_{2.875}UO_{5.875}(s)$ at 1125 K, experimental average temperature. Using heat capacity values from our studies [22], enthalpy and entropy of transitions of barium from JANAF tables [21] and uranium from CODATA [23], $\Delta_f H^\circ_m(298.15\ K)$ and $S^\circ_m(298.15\ K)$ have been calculated from second law method. The corresponding values are $-3143.4 \pm 2\ kJ\ mol^{-1}$ and $270.8 \pm 4\ J\ K^{-1}\ mol^{-1}$. The $\Delta_f H^\circ_m(298.15\ K)$ values were also calculated by the third law method for each experimental points using Gibbs energy functions: $\phi^\circ_m = \{(G^\circ_m(T) - H^\circ_m\ (298.15\ K))/T\}$ for $Ba_{2.875}UO_{5.875}(s)$ and $Ba_3UO_6(s)$ from our previous study [22] and that for $BaCO_3(s)$ and $CO_2(g)$ from the literature [20,21]. This value is $-3137.7 \pm 4\ kJ\ mol^{-1}$ which, is selected as $\Delta_f H^\circ_m(Ba_{2.875}UO_{5.875}, s, 298.15\ K)$.

## 4. Discussion

Experimental Gibbs energy data on $Ba_{2.875}UO_{5.875}(s)$ have not been reported in the literature. However, present authors [22] have calculated it from the heat capacity and literature data. This expression is included in Table 2 for comparisons. $\Delta_f G^\circ_m$ (1100 K) calculated from Ref. [22] ($-2545.6\ kJ\ mol^{-1}$) and this study ($-2540.1 \pm 5\ kJ\ mol^{-1}$) matches well. $\Delta_f G^\circ_m(T)$ values for $Ba_3UO_6(s)$ [22] and $BaUO_4(s)$ [11,20] have been fitted into expression and are included in Table 2. $\Delta_f G^\circ_m(T)$ values for $Ba_2U_3O_{11}(s)$ and $BaU_2O_7(s)$ reported in our previous study [15] have also been given in Table 2. Heat capacity expressions and $S^\circ_m(298.15\ K)$ data reported for Ba-U-O system [11,20,22,24] are also included in Table 2.

The $\Delta_f G^\circ_m(T)/g$ of $Ba_3UO_6(s)$, $Ba_{2.875}UO_{5.875}(s)$, $BaUO_4(s)$, $BaU_2O_7(s)$ and $Ba_2U_3O_{11}(s)$ have been plotted as a function of temperature in Fig. 4. It shows that, in the sixth oxidation state of uranium, $Ba_3UO_6(s)$ is the most stable and $BaU_2O_7(s)$ as least stable barium uranate. It leads to the conclusion that addition of $BaO(s)$ into $BaUO_4(s)$ increases its stability more than the addition of $UO_3(s)$ into $BaUO_4(s)$.

Fig. 5 gives the plot of enthalpy of formations of $Ba_xU_yO_{x+3y}(s)$ (hexa valent barium uranates, given in Table 2) as a function of atomic weight. It shows a regular decrease in $\Delta_f H^\circ_m(298.15\ K)$ with increase in atomic weight. The enthalpy of formation of $Ba_xU_yO_{x+3y}(s)$ can be calculated from the following expression:

$$\Delta_f H^\circ_m(Ba_xU_yO_{x+3y}, s, 298.15\ K)\{(\pm 1\%)\ \ kJ\ mol^{-1}\} = -684.43 \times -1252.518y + 62.9y/(x - 2y), \tag{9}$$

where $x$ and $y$ are the number of barium and uranium atoms in $Ba_xU_yO_{x+3y}(s)$. When $\Delta_f H^\circ_m(298.15\ K)/g$ values of hexa-valent barium uranates are plotted against Ba/U mole ratio, two different lines with opposite slope are obtained which are shown in Fig. 6. The $\Delta_f H^\circ_m(298.15\ K)/g$ of $Ba_2U_3O_{11}(s)$ [11] $BaU_2O_7(s)$ [24] and $BaUO_4(s)$ [25] fall in one series and $BaUO_4(s)$ [25], $Ba_{2.875}UO_{2.875}(s)$ and

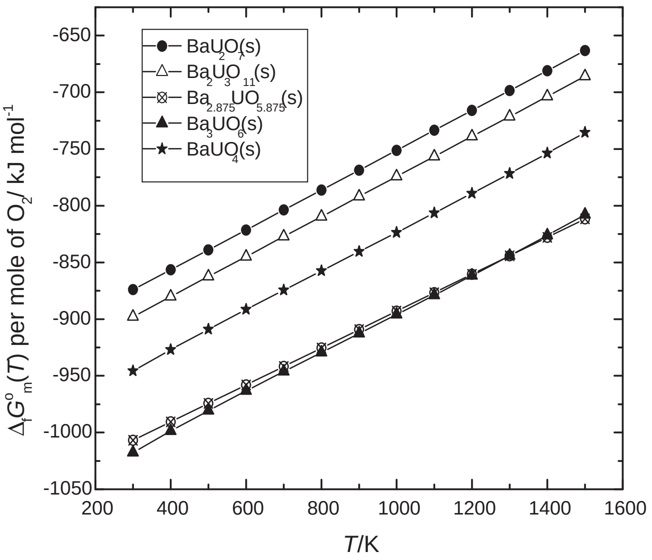

**Fig. 4.** The standard molar Gibbs energy of formatiom of barium uranates in BaO-$UO_3$ system.

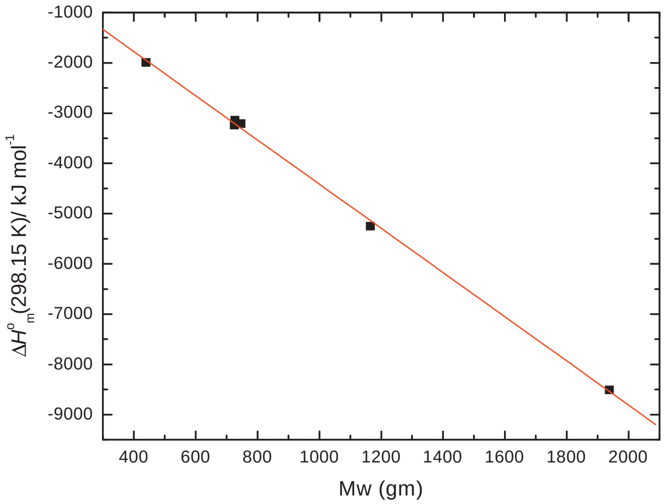

**Fig. 5.** The plot of $\Delta_f H^\circ_m(298.15\ K)$ versus temperature for barium uranates in BaO-$UO_3$ system.

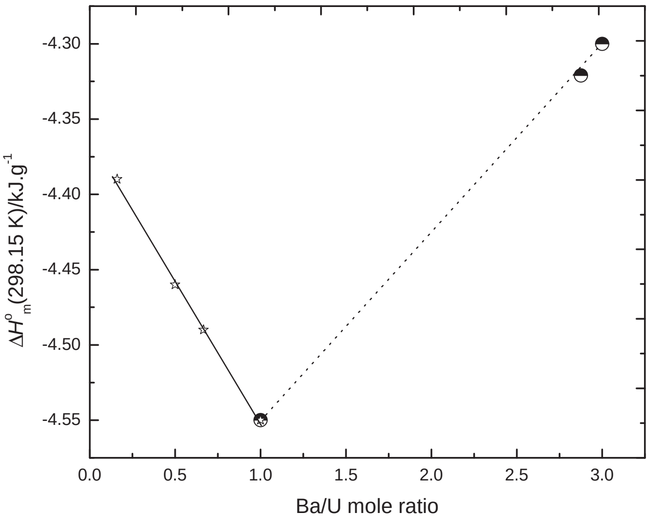

**Fig. 6.** The plot of $\Delta_f H^\circ_m(298.15\ K)/g$ versus Ba/U mole ratio for barium uranates in BaO-$UO_3$ system.

**Table 2**
Thermodynamic functions for compounds in Ba-U-O system. Gibbs energy is expressed as: $\Delta_f G^\circ_m(T)/\text{KJ mol}^{-1} = A + B\ (T/\text{K})$ and molar heat capacity is expressed as: $C^\circ_{p,m}(T)/\text{J K}^{-1}\ \text{mol}^{-1} = a + b(T/\text{K}) + c(\text{K}/T)^2$.

| Compounds | Method | Temperature range $T$/K | $\Delta_f G^\circ_m(T)$/KJ mol$^{-1}$ | | $\Delta_f H^\circ_m$(298.15 K)/kJ mol$^{-1}$ | $S^\circ_m$ (298.15 K)/J K$^{-1}$ mol$^{-1}$ | $C^\circ_{p,m}(T)/\text{J K}^{-1}\ \text{mol}^{-1} = a + b(T/\text{K}) + c(\text{K}/T)^2$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | $A$ | $B$ | | | $a$ | $b \times 10^3$ | $c \times 10^{-5}$ |
| $BaUO_3$(s) | KEMS [16] | 1770–1920 | – | – | −1742.5 ± 1.7 | – | – | – | – |
| [9,10,16,24] | E.m.f. [26] | 1060–1090 | – | – | – | – | – | – | – |
| | DSC [10] | 373–873 | −1722.7[a] | 0.2709 | – | 142 | 126.6 | 16.1 | −1.42 |
| | SC [9] | – | – | – | −1690 ± 10[24] | – | – | – | – |
| $Ba_2U_2O_7$(s) [7,24] | SC [7] | – | – | – | −3740.0 ± 6.3 [24] | 296 ± 15 [24] | – | – | – |
| $BaUO_4$(s) | SC [25] | – | – | – | −1993.8 ± 3.3 [24] | 154.0 ± 2.5 [24] | – | – | – |
| [11,19,24,25] | C [20] | – | −1994.8[b] | 0.3476 | – | – | 153.781[b] | 9.179 | −27.778 |
| | | | | | | | – | – | – |
| $BaU_2O_7$(s) | E.m.f. [15] | 1001–1206 | −3243.8 | 0.6148 | – | – | – | – | – |
| [7,15,22,24] | SC [7] | – | – | – | −3237.2 ± 5 [24] | 260 ± 15 [24] | – | – | – |
| | CV [22] | 299–1000 | −3239.2 | 0.6154 | – | 260.7 ± 4 | 214.51 | 61.254 | −37.665 |
| $Ba_2U_3O_{11}$(s) | E.m.f. [15] | 1009–1178.5 | −5229.3 | 0.9709 | −5237.2 | – | – | – | – |
| [11,15,22] | E [11] | – | – | – | −5250 ± 25 [11] | 405 ± 5 [11] | – | – | – |
| | CV [22] | 323–1000 | −5235.8 | 0.9755 | – | 411.2 ± 4 | 396.4 | 31.094 | 70.966 |
| $BaU_{6.42}O_{19.7}$(s) [32] | E [32] | – | – | – | −8509.6 | – | – | – | – |
| $Ba_3UO_6$(s) | SC [7] | – | – | – | −3210.4 ± 8 [24] | 298 ± 15 [24] | – | – | – |
| [7,11,22,24] | CV [22] | 302–1012 | −3239.8[c] | 0.5795 | – | 296.5 ± 4 | 307.12 | 7.4788 | −82.742 |
| $Ba_{2.875}UO_{5.875}$(s) | CV [22] | 306–1011 | – | – | – | 281.7 ± 4 | 287.64 | 9.498 | −67.054 |
| [22] | E | 900–1200 | −3137.0[c] | 0.5378 | – | – | – | – | – |
| Present study | M | 1030–1220 | −3153.1 | 0.5573 | 3137.3 ± 4 | 270.8 ± 4 | – | – | – |

KEMS = Knudsen effusion mass-spectrometry, E.m.f. = solid oxide galvanic cell method, DSC = Differential Scannining Calorimetry, SC = Solution Calorimetry, E = estimated, CV = Calvet Calorimetry, M = manometry, C = compilation.

[a] Calculated in this study from [10].

[b] Given in Ref. [11].

[c] Calculated in this study from [22].

$Ba_3UO_6$(s) [24] in a different series. In the former series, addition of $UO_3$(s) increases the $\Delta_f H^\circ_m$(298.15 K)/g value and in the latter series addition of BaO(s) decreases $\Delta_f H^\circ_m$(298.15 K)/g value. This observation also leads to a conclusion that BaO(s) stabilizes the barium uranates more than $UO_3$(s).

While plotting $\Delta_f H^\circ_m$(298.15 K) as a function of Ba/U, Cordfunke et al. [26] observed $\Delta_f H^\circ_m$(298.15 K) of $B_{1+y1}UO_{3+x1}$ and $Ba_3UO_6$(s) are on the same line as $BaUO_3$–$Ba_{1+y1}UO_{3+x1}$–$Ba_3UO_6$ belongs to perovskite series. In contrast, enthalpy of formation of $Ba_2U_2O_7$(s) does not fall on the line as crystal structure of $Ba_{1+y1}UO_{3+x}$ is different from $Ba_2U_2O_7$(s).

The stability of compounds in Ba-U-O system is poorly known [27]. The oxygen and barium potential diagrams for Ba-U-O system have been calculated using FactSage programme [28] and are shown in Figs. 7–9. Fig. 7 shows that $BaUO_3$(s) coexists with $UO_2$(s) as well as with BaO(s) whereas $Ba_3UO_6$(s) with BaO(s). $Ba_3U_2O_8$(s), $Ba_2U_2O_7$(s), $Ba_2U_3O_{11}$(s) and $BaUO_4$(s) coexist with $UO_2$(s) where as $BaU_2O_7$(s) with $U_3O_8$(s) and $BaU_{6.24}O_{19.7}$(s) with $UO_3$(s). Fig. 8 shows that $BaUO_3$(s) is stable above barium potential −225 kJ mol$^{-1}$ and $Ba_3UO_6$(s) in the range of −572 to −225 kJ mol$^{-1}$. $Ba_3U_2O_8$(s) is stable in a limited barium potential range that is −225 to −209 kJ mol$^{-1}$. $BaUO_4$(s) is stable in the barium potential range −600 to −510 kJ mol$^{-1}$. $BaU_2O_7$(s) and $Ba_2U_3O_{11}$(s) are stable below −600 kJ mol$^{-1}$ and $BaU_{6.24}O_{19.7}$(s) is stable at lowest barium potential of −823 kJ mol$^{-1}$. $UO_3$(s) is stable at very low barium activity. Adamson et al. [29] reported the oxygen potential for LWR fuel to be between −550 and −450 kJ mol$^{-1}$. Minato et al. [30] calculated the behavior of fission products in irradiated triso-coated $UO_2$(s) and given a plot for equilibrium vapor pressures of the species containing barium and strontium in the fuel. Cordfunke and IJdo [12] calculated Ba(g) over $UO_2$(s) at 1300 K to be around $10^{-13}$ kPa. In this study, the oxygen and barium potential of fuel are taken as −500 ± 50 and −200 ± 50 kJ mol$^{-1}$, respectively, to predict the form in which the barium compounds may be present in the fuel. Figs. 7 and 8 show that $BaUO_3$(s), $Ba_3U_2O_8$(s), $Ba_2U_2O_7$(s) or $Ba_3UO_6$(s) will be possible. From these figures it is evident that stability region of $Ba_3U_2O_8$(s) and $Ba_2U_2O_7$(s) are limited. Hence, either $BaUO_3$(s) or $Ba_3UO_6$(s) will be formed, depending on the oxygen and barium pressures in the fuel element. As the $BaUO_3$(s) coexists with $UO_2$(s) and $Ba_3UO_6$(s) with BaO(s), $BaUO_3$(s) may be formed in the $UO_2$(s) matrix. At 1600 K, BaO(g) pressure is more than $10^{-7}$ kPa [30], hence there is a possibility of precipitation of BaO(s) and formation of $Ba_3UO_6$(s) in the cooler zone of fuel. Using X-ray microanalysis of highly irradiated fuel, Kleykamp et al. [31] showed the presence of $BaUO_3$(s) in grey phase. Hence, $BaUO_3$(s) will be stable under the reactor conditions.

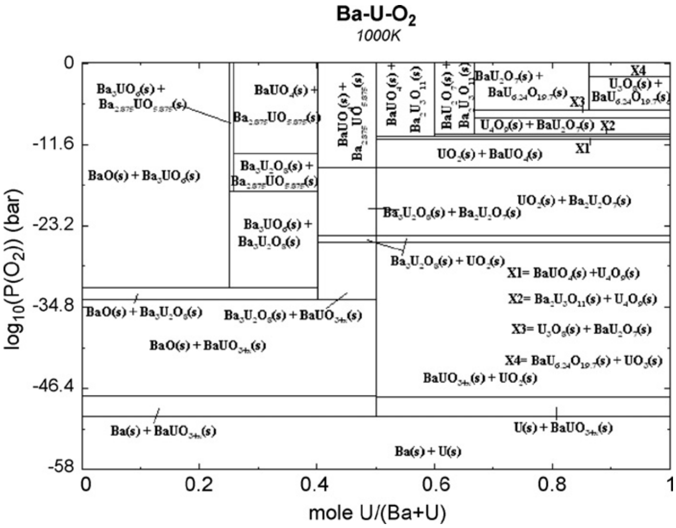

**Fig. 7.** Oxygen potential diagram for Ba-U-O system at 1000 K.

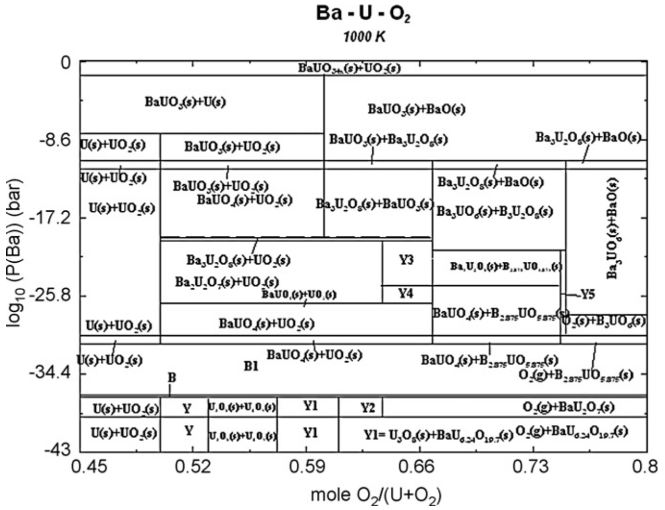

**Fig. 8.** Barium potential diagram for Ba-U-O system at 1000 K. $BaUO_{3+x}(s)$ is a non-Stoichiometric compound with distorted pervoskite structure. The equilibrium phase fields: Y = $UO_2(s) + U_4O_9(s)$, Y1 = $U_3O_8(s) + BaU_{6.24}O_{19.7}(s)$, Y2 = $BaU_2O_7(s) + BaU_{6.24}O_{19.7}(s)$ and Y3 = $Ba_2U_2O_7(s) + Ba_3U_2O_8(s)$, Y4 = $Ba_2U_2O_7(s) + BaUO_4(s)$, Y5 = $Ba_{2.875}UO_{5.875}(s) + BaUO_4(s)$ and Y6 = $Ba_{2.875}UO_{5.875}(s) + Ba_3UO_6(s)$.

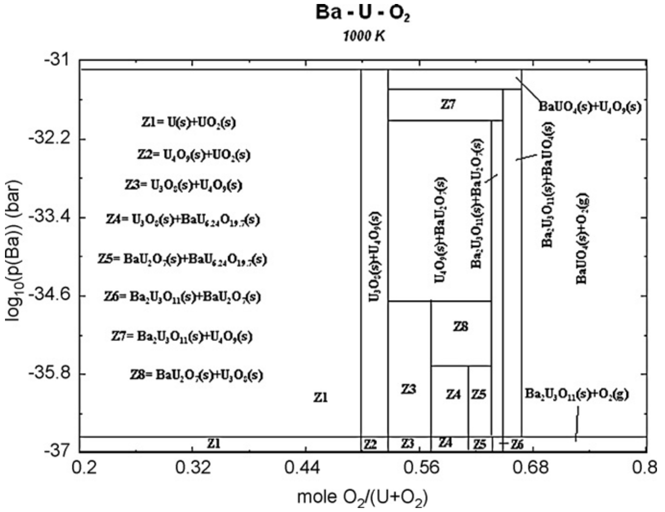

**Fig. 9.** The B and B1 portions of Fig. 8.

## 5. Conclusion

The standard molar Gibbs energy of formation of $Ba_{2.875}UO_{2.875}(s)$ has been measured for the first time. $\Delta_f H^\circ_m$ ($Ba_{2.875}UO_{2.875}$, s, 298.15 K) value calculated from third law is $-3137.7 \pm 4$ kJ mol$^{-1}$. $\Delta_f G^\circ_m(T)$ per mole of $O_2(g)$ data as a function of temperature have been plotted for various barium uranates in BaO-$UO_3$ system. It has been concluded from the plot that higher mole fraction of BaO(s) stabilizes the barium uranates. The oxygen and barium potential diagrams for Ba-U-O system have been calculated. The calculations show that $BaUO_3(s)$ will be formed in the $UO_2(s)$ matrix.

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