BRIEF COMMUNICATION

Molar Gibbs Energy of Formation of BaMo$_2$O$_7$(s) Using the Solid Oxide Galvanic Cell Method

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$\Delta_f G°$(BaMo$_2$O$_7$, s, T) has been determined using the emf technique. The cell used was: (−)Pt/(BaMo$_2$O$_7$(s)+BaMoO$_4$(s) +MoO$_2$(s))//CSZ//air (p(O$_2$(g) = 21.21 kPa)/Pt(+). The observed emfs in the temperature range 828–985 K could be represented by $E = 0.7663 − 4.953×10^{−4}T$ (±0.001) V. The standard molar Gibbs energy of formation of BaMo$_2$O$_7$(s) was evaluated from emf values and the $\Delta_f G°(T)$ of BaMoO$_4$(s) and MoO$_2$(s). The corresponding expression is given as $\Delta_f G°$(BaMo$_2$O$_7$, s, T) = −2269.7 + 0.6173T (±5.1) kJ mol$^{−1}$. Using the required literature values, the $\Delta_f H°$(BaMo$_2$O$_7$, s, 298.15 K) was calculated by the second-law method and the corresponding value is −2291.2 kJ mol$^{−1}$. The present study is the first experimental work for the determination of $\Delta_f G°$(BaMo$_2$O$_7$, s, T). © 1997 Academic Press

INTRODUCTION

The oxides of fission products barium, strontium, molybdenum, zirconium, and rare earths are found in irradiated fuel either as a solid solution of themselves or as separate phases (1, 2). The basic thermodynamic data on the Ba–Mo–O system are of relevance for understanding the fuel behavior during burnup and in accidental conditions. Depending upon temperature, oxygen potential, and burnup of the oxidic fuels, fission products barium and molybdenum may form different barium molybdates. No experimental thermodynamic data on BaMo$_2$O$_7$(s) are reported in the literature. In the present study, $\Delta_f G°(T)$ of BaMo$_2$O$_7$(s) has been determined using a solid oxide galvanic cell in the temperature range 828–985 K.

EXPERIMENTAL PROCEDURE

Materials

BaMo$_2$O$_7$(s) was prepared by heating equimolar quantities of high-purity BaMoO$_4$(s) and MoO$_3$(s) in an alumina

boat at 750 K for 300 h in dry air. The preparation of BaMoO$_4$(s) is given in our previous study (4). High-purity (99.99%) MoO$_3$(s) fine powder was supplied by Aldrich Chemical Co., Inc. (Milwaukee,WI). The X-ray pattern (XRD) of the reaction product indicated exclusively the presence of BaMo$_2$O$_7$(s) (3). MoO$_2$(s) was prepared by heating MoO$_3$(s) at 723 K in a molybdenum boat for 150 h under a flowing Ar + 8%H$_2$ gas mixture. XRD analysis of the deep violet product did not indicate any peaks corresponding to either unreacted MoO$_3$(s) or completely reduced Mo(s), but only peaks due to MoO$_2$(s). A three-phase mixture of BaMoO$_4$(s), BaMo$_2$O$_7$(s), and MoO$_2$(s) in the approximate mole ratio of 1 : 1 : 1 was made into pellets of 6-mm diameter and 3-mm thickness under a pressure of 100 MPa and annealed in an argon atmosphere at 700 K for 100 h. These pellets were used for emf measurements.

Emf Measurements

The emf cell was constructed using a 0.15 mole fraction calcia-stabilized zirconia (CSZ) electrolyte tube of 13-mm o.d. 9.0-mm i.d., and 380-mm length with one end closed flat (Nikatto Corp., Osaka, Japan). A two-compartment cell assembly with the solid electrolyte separating the gaseous environments of the two electrodes was used for the emf measurements. To obtain a low oxygen potential environment, a purified argon gas flow was maintained over the pellet throughout the experiment. The argon gas was purified by passing it through towers containing molecular sieves, magnesium perchlorate, the reduced form of BASF catalyst, and hot uranium metal at 550 K. The oxygen pressure in the purified argon was checked with reference to air and was determined to be about $10^{−17}$ Pa in the experimental temperature range. The cell temperature was measured with a chromel-to-alumel thermocouple. Details of the cell assembly are given elsewhere (5). Emf was measured with a Keithley 614 electrometer with an internal impedance greater than 10^{14} ohm. The internal consistency of the cell

was checked by measuring emf values during heating and cooling cycles. After the experiments, the XRD analysis of the pellet indicated no chemical reaction either with the electrolyte tube or with the platinum electrodes as shown in Fig. 1.

RESULTS AND DISCUSSION

The reliability of the experimental assembly was checked by measuring the emf of cell I: $(-)Pt/Ni(s) + NiO(s)//CSZ//$ air $(P(O_2) = 21.21 \text{ kPa})/Pt(+)$. According to the Nernst equation, the emf of the solid-state electrochemical cell I is related to the partial pressure of oxygen at the two electrodes by the following expression:

$$E = (RT/nF) \int_{P''(O_2)}^{P'(O_2)} t(O^{2-})d(\ln P(O_2)), \quad [1]$$

where E is the measured emf of the cell, R is the universal gas constant, n is the number of electrons participating in the electrode reaction, F is the Faraday constant ($96486.4 \text{ C mol}^{-1}$), T is the temperature, $t(O^{2-})$ is the transport number of O^{2-} ions in the CSZ solid electrolyte, and $P'(O_2)$ and $P''(O_2)$ are the equilibrium oxygen partial pressures at the reference and measuring electrodes, respectively. As the transport number of oxygen ion in CSZ is greater than 0.99 for the oxygen pressures and temperature range covered in this study, the emf of the cell is directly proportional to the logarithm of the ratio of the partial pressures of oxygen at the two electrodes.

The $\Delta_f G°(\text{NiO}, s, T)$ was obtained from emf values using the relation

$$\Delta_f G°(\text{NiO}, s, T) = -2FE + \tfrac{1}{2}RT \ln p(O_2)(\text{air})/p°(O_2), \quad [2]$$

where $p(O_2)(\text{air})$ is the partial pressure of oxygen in air and $p°(O_2)$ is 101.325 kPa. $\Delta_f G°(\text{NiO}, s, T)$ values calculated

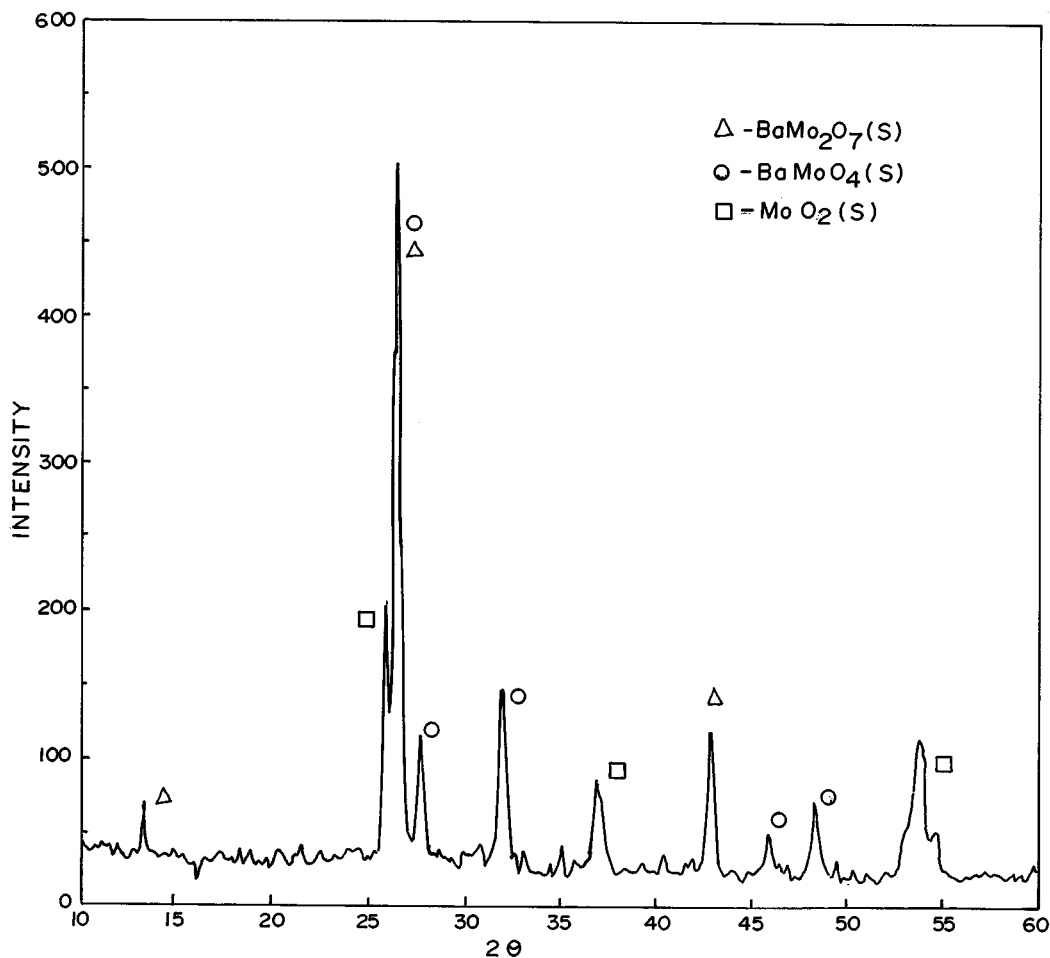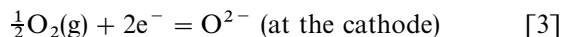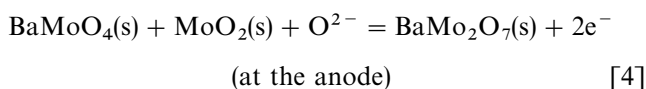**FIG. 1.** X-ray diffraction pattern of the three-phase mixture ($BaMo_2O_7(s) + BaMoO_4(s) + MoO_2(s)$). Intensity lines are indicated as: ($\triangle$) $BaMo_2O_7$, ($\bigcirc$) $BaMoO_4(s)$, and ($\square$) $MoO_2(s)$.

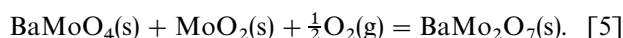from the present work agree very well with those in the literature (6–8).

The same experimental assembly was used for the measurement of the emf of cell II: $(-)\text{Pt}/(\text{BaMo}_2\text{O}_7(\text{s}) + \text{BaMoO}_4(\text{s}) + \text{MoO}_2(\text{s}))//\text{CSZ}//$ air $(p(\text{O}_2(\text{g}) = 21.21\text{ kPa}))/\text{Pt}(+)$. The cell reaction for cell II is given as follows:

$$\tfrac{1}{2}\text{O}_2(\text{g}) + 2\text{e}^- = \text{O}^{2-} \quad \text{(at the cathode)} \qquad [3]$$

and

$$\text{BaMoO}_4(\text{s}) + \text{MoO}_2(\text{s}) + \text{O}^{2-} = \text{BaMo}_2\text{O}_7(\text{s}) + 2\text{e}^-$$

$$\text{(at the anode)} \qquad [4]$$

The overall cell reaction is

$$\text{BaMoO}_4(\text{s}) + \text{MoO}_2(\text{s}) + \tfrac{1}{2}\text{O}_2(\text{g}) = \text{BaMo}_2\text{O}_7(\text{s}). \quad [5]$$

The measured emf values for cell II are given in Table 1 and the variation of emf as a function of temperature is shown in Fig. 2 and could be fitted to the least-squares expression

$$E = 0.7663 - 4.953 \times 10^{-4} T(\text{K}) \ (\pm 0.001)\text{ V.} \qquad [6]$$

The standard emf of cell II with respect to $\text{O}_2(\text{g})$ at 101.325 kPa can be calculated from the following

TABLE 1
Dependence of Emf on Temperature for the Cell: $(-)\text{Pt}/(\text{BaMo}_2\text{O}_7(\text{s}) + \text{BaMoO}_4(\text{s}) + \text{MoO}_2(\text{s}))//\text{CSZ}//\text{air}\,(p(\text{O}_2) = 21.21\text{ kPa})/\text{Pt}(+)$

T (K)	E (V)	T (K)	E (V)	T (K)	E (V)
828.0	0.3542	895.0	0.3224	956.0	0.2913
844.0	0.3469	910.0	0.3161	970.0	0.2864
859.0	0.3429	911.0	0.3155	985.0	0.2781
862.0	0.3413	925.0	0.3073		
894.0	0.3241	940.0	0.3013		

expression:

$$E^\circ = E - (RT/4F)\ln[p(\text{O}_2, p = 101.325\text{ kPa})/$$

$$p(\text{O}_2, p = 21.21\text{ kPa})]. \qquad [7]$$

Replacing the value of E in Eq. [7], E° is calculated as

$$E^\circ = 0.7663 - 4.616 \times 10^{-4} T(\text{K}) \ (\pm 0.001)\text{V.} \qquad [8]$$

The Gibbs energy change for reaction [5] is calculated from emf Eq. [8] as

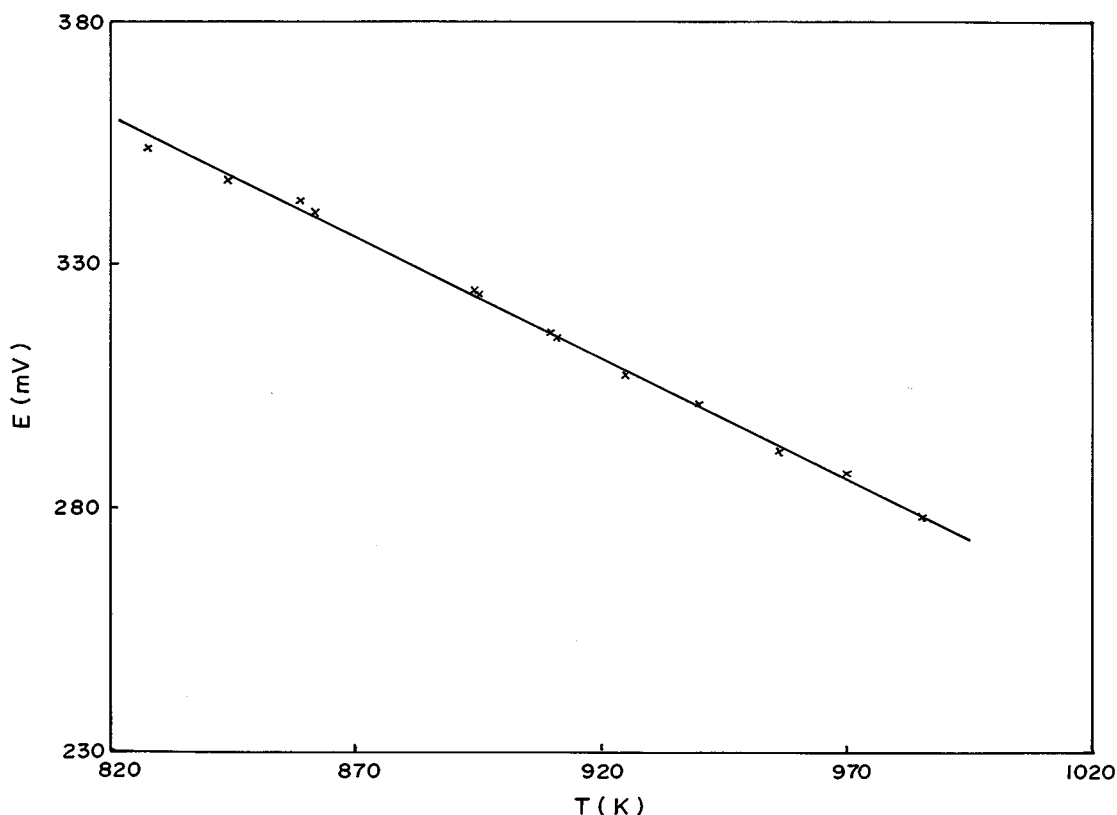$$\Delta_r G^\circ(T) = -147.9 + 0.08908\,T(\text{K}) \ (\pm 0.2)\text{ kJ mol}^{-1}. \quad [9]$$

**FIG. 2.** Temperature dependence of the emf of cell II.

The molar Gibbs energy of formation for $BaMo_2O_7$(s) was obtained using Eq. [9] and auxiliary data such as $\Delta_f G°(BaMoO_4, s, T)$ and $\Delta_f G°(MoO_2, s, T)$ from Singh *et al.* (4, 9) and can be represented as

$$\Delta_f G_m°(BaMo_2O_7, s, T) = -2269.7 + 0.6173 T(K)$$

$$(\pm 5.1)\, kJ\, mol^{-1} \qquad (828 \leqslant T(K) \leqslant 985). \qquad [10]$$

The slope and intercept of this least-squares line correspond respectively to the standard molar entropy and enthalpy of formation of $BaMo_2O_7$(s) at the experimental average temperature. $\Delta_f H°(BaMo_2O_7, s, 298.15\, K)$ from the second law was calculated from Eq. [11].

$$\Delta_f H°(BaMo_2O_7, s, 298.15\, K) = \Delta_f H°(BaMo_2O_7, s, T)$$

$$+ \int_T^{298.15\, K} \Delta C_p°(T)\, dT, \qquad [11]$$

where $\Delta C_p°(T)$ is the difference in molar heat capacities of the products and the reactants of reaction [12]:

$$Ba(s) + Mo(s) + O_2(g) = BaMo_2O_7(s). \qquad [12]$$
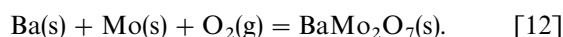
$C_p°(T)$ for $BaMo_2O_7$(s) is not available in the literature. The same has been estimated by the present authors using heat capacity values for $BaMoO_4$(s) from Saha *et al.* (10) and that for MoO_3(s) from JANAF tables (11) and can be given as

$$C_p°(BaMo_2O_7, s, T) = -204.580 + 66.268 \times 10^{-3} T(K)$$

$$- 23.452 \times 10^5/(T(K))^2\, J\, K^{-1} mol^{-1}. \qquad [13]$$

Using $C_p°(T)$ for Mo(s) and O_2(g) together with $C_p°(T)$ and transition enthalpies for Ba(s, l) from JANAF tables (10) and $C_p°(T)$ for $BaMo_2O_7$(s) from Eq. [13], the $\Delta_f H_m°(BaMo_2O_7, s, 298.15\, K)$ has been calculated as $-(2291.2 \pm 2.5)\, kJ\, mol^{-1}$. No experimental or estimated

Gibbs energy values for $BaMo_2O_7$(s) have been reported in the literature and thus the $\Delta_f G_m°(T)$ and $\Delta_f H°(BaMo_2O_7, s, 298.15\, K)$ values obtained in the present study could not be compared.

CONCLUSIONS

Thermodynamic studies on $BaMo_2O_7$(s) have been carried out for the first time. $\Delta_f G°(BaMo_2O_7, s, T)$ has been determined by the solid oxide galvanic cell method between 828 and 985 K. $BaMo_2O_7$(s) was found to melt at temperatures above 990 K. Heat capacity values of $BaMo_2O_7$(s) have been estimated and reported as a function of temperature.

ACKNOWLEDGMENTS

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