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Standard molar Gibbs energy of formation of $Ba_3Te_2O_9(s)$ by transpiration technique

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Abstract

The standard molar Gibbs energy of formation of barium tellurite, $Ba_3Te_2O_9(s)$, was determined by the transpiration technique using pure oxygen as the carrier gas in the temperature range from 1119 to 1280 K. The condensate was exclusively identified as $TeO_2(s)$ by chemical analysis. Chemical analysis of the residue left in the alumina boat after the transpiration experiments confirmed the coexistence of BaO(s) with $Ba_3Te_2O_9(s)$ during the vaporization reaction. The incongruent vaporization reaction could be established as: $Ba_3Te_2O_9(s)=3BaO(s)+2TeO_2(g)+O_2(g)$. From the quantitative chemical analysis of the condensed $TeO_2(s)$, the vapor pressure of $TeO_2(g)$ over pure $Ba_3Te_2O_9(s)$ was calculated. The equilibrium constant for the incongruent vaporization reaction at each temperature has been calculated from the vapor pressure data and is fitted to an expression: $\ln K (\pm 1.0) = 11.32-55518.6 \cdot (K/T)$. The Gibbs energy of formation of $Ba_3Te_2O_9(s)$ was computed from the above data and the values of $\Delta_f G^\circ_m$ for BaO(s) and $TeO_2(g)$ taken from the literature and are given by: $\{\Delta_f G^\circ_m (Ba_3Te_2O_9, s, T)\pm 3.0\}/(kJ mol^{-1}) = -2296.8 + 0.4302 \cdot (T/K)$. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Oxide materials; Gas-solid reaction; Enthalpy; Entropy; Calorimetry

1. Introduction

The thermochemistry of interoxide compounds in the M-Te-O system, where M is a fission product, is of considerable interest to understand the internal chemistry of the oxide fuel pins in an operating nuclear reactor. A knowledge of the thermodynamic stability of these tellurium bearing ternary oxides will help in predicting the performance of the fuel pins, the fuel reprocessing chemistry and the release of radioactive isotopes under normal and transient conditions. Thermodynamic data on the M-Te-O system (M=Ca, Sr) have been reported by several authors [1-5]. As there is paucity of information on the Ba-Te-O system, Chattopadhyaya and Juneja [6] have constructed a tentative phase diagram for the Ba-Te-O system on the basis of the binary Ba-Te, Ba-O and Te-O systems. The pseudo-binary boundary system BaO-TeO₂ is characterized by five intermediate line compounds: $Ba_3Te_2O_9$, $BaTeO_3$, $Ba_2Te_3O_8$, $BaTe_2O_5$ and $BaTe_4O_9$. Parida et al. [7] have studied the thermodynamic properties of BaTeO₃(s) by using transpiration technique and Calvet

micro-calorimeter. As a part of systematic thermodynamic studies on the Ba–Te–O system, measurements have been made on the ternary oxide $Ba_3Te_2O_9(s)$. The standard molar Gibbs energy of formation of $Ba_3Te_2O_9(s)$ has been determined by transpiration technique using pure oxygen as the carrier gas in the temperature range from 1119 to 1280 K.

2. Experimental methods

2.1. Materials

Preheated BaCO₃(s) (E. Merk, Germany, mass fraction purity = 0.99999) and TeO₂(s) (prepared from telluric acid, AR, BDH, UK, mass fraction purity = 0.99999) were carefully mixed in stoichiometric proportions in an agate mortar. The mixture was first heated at 900 K for 5 h and then at 1050 K for 24 h, in a platinum boat in pure oxygen atmosphere with intermediate grindings. The formation of the pale yellow colored compound $Ba_3Te_2O_9(s)$ was confirmed by an X-ray diffraction method. $Ba_3Te_2O_9(s)$ crystallizes in the hexagonal structure at room temperature. The values of the interplanar spacing *d* obtained in the

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present study using a DIANO X-ray diffractometer with Cu K α radiation, are in good agreement with those reported in JCPDS-file # 36-924. Gravimetric analyses of Ba and Te content in Ba₃Te₂O₉(s) were carried out to confirm the stoichiometry. The observed mass fraction content of Ba and Te for the compound were (0.508±0.002) and (0.314±0.002) compared with the calculated values of 0.508 and 0.315, respectively.

2.2. Transpiration technique

The apparatus and procedure used for the equilibrium vapor pressure measurement is described in our earlier publication [8]. It consisted of a 30 mm i.d. quartz reaction-tube with 'O'-ring-sealed end couplings. The end couplings had ports for carrier gas entry and evacuation and for insertion of a thermo-well and a condenser tube. The condenser was made of quartz with an 0.5-mm opening. A Kanthal wire-wound horizontal furnace with a flat temperature zone (within ± 0.5 K) of 75 mm at the center was used for heating. The temperature was measured by a calibrated chromel-to-alumel thermocouple. The thermocouple was calibrated against ITS-90. The sample (Ba₃Te₂O₉) was loaded in an alumina boat and placed inside the reaction tube. The system was repeatedly evacuated and flushed with pure oxygen gas up to T=300K and the temperature was rapidly raised at a rate of 15 K min⁻¹ to the desired value. Thermodynamic equilibrium was obtained by determining the flow rate plateau which was found to be between 1.5 and 2.4 dm³ per hour. Measurements were carried out in this flow rate region. The volume of carrier gas was measured by a wet-test meter. The mass of the condensate, TeO₂(s), was determined gravimetrically.

3. Results and discussion

Needle like crystals were observed in the condenser tube of the transpiration apparatus. An X-ray diffraction pattern of the condensate matched that of $TeO_2(s)$. The mass of $TeO_2(s)$ was determined gravimetrically. In theory, the residue material left in the alumina boat after the experiment should have contained both BaO(s) and $Ba_3Te_2O_9(s)$. However, the X-ray diffraction pattern of the residue did not show the presence of BaO(s). Hence, an alternative procedure was followed to detect the presence of BaO(s) in the residue material. The residue material left in the alumina boat following the transpiration experiment was put into distilled water, filtered using Whatman 542 filter paper and a few drops of dilute H₂SO₄ were added to the filtrate. A white precipitate was observed which confirmed the presence of BaO(s) in the residue material as $Ba_3Te_2O_0(s)$ is insoluble in water. The coexistence of BaO(s) with $Ba_3Te_2O_q(s)$ during the vaporization reaction was thus inferred from the above observation and the incongruent vaporization reaction could be established as:

$$Ba_{3}Te_{2}O_{9}(s) = 3BaO(s) + 2TeO_{2}(g) + O_{2}(g)$$
(1)

The mass of the condensate, $\text{TeO}_2(s)$, per dm³ of the carrier gas at each experimental temperature is given in Table 1. The apparent equilibrium vapor pressure of $\text{TeO}_2(g)$ at each experimental temperature is calculated from the equation:

$$p(\text{TeO}_2, g) = \{n(\text{TeO}_2, g) / [n(\text{TeO}_2, g) + n(\text{O}_2, g) + n(\text{carrier gas})]\} \cdot P$$
(2)

where, $n(\text{TeO}_2, \text{ g})$, $n(\text{O}_2, \text{ g})$ and n(carrier gas) are the respective number of moles. The values of $n(\text{O}_2, \text{ g})$ were calculated from those of $n(\text{TeO}_2, \text{ g})$ using the stoichiometry of reaction (1). The values of $p(\text{TeO}_2, \text{ g})$ thus obtained are given in Table 1.

The equilibrium constant for the incongruent vaporization reaction (1) at each temperature (Fig. 1) has been calculated from the vapor pressure data and are fitted to an expression:

$$\ln K (\pm 1.0) = 11.32 - 55518.6 \cdot (K/T)$$
(3)

The Gibbs energy of reaction (1) can be written as:

$$\Delta_{\rm r} G^{\circ} = -R \cdot T \cdot \ln K$$

= $\Delta_{\rm f} G^{\circ}_{\rm m} (\text{BaO}, \text{s}, T) + \Delta_{\rm f} G^{\circ}_{\rm m} (\text{TeO}_2, \text{g}, T)$
- $\Delta_{\rm f} G^{\circ}_{\rm m} (\text{Ba}_3 \text{Te}_2 \text{O}_9, \text{s}, T)$ (4)

The values of $\Delta_{f}G^{\circ}_{m}(Ba_{3}Te_{2}O_{9}, s, T)$ have been calculated by inserting the values of $\ln K$ obtained above in Eq. (4) and taking the values of $\Delta_{f}G^{\circ}_{m}(T)$ for $TeO_{2}(g)$ and BaO(s) from Refs. [9] and [10], respectively. The corresponding equation is given by:

$$\{\Delta_{\rm f} G^{\circ}_{\rm m} (\text{Ba}_{3}\text{Te}_{2}\text{O}_{9}, \text{s}, T) \pm 3.0\} / (\text{kJ mol}^{-1}) = -2296.8 + 0.4302 \cdot (T/\text{K})$$
(5)

The slope and intercept of Eq. (5) correspond to the standard molar enthalpy and entropy of formation of $Ba_3Te_2O_9(s)$ from the elements at an average experimental temperature, $T_{av} = 1198$ K.

Vapor pressure data p , mass of TeO ₂ (s) m and equilibrium constant K f	or
the incongruent reaction: $Ba_3Te_2O_9(s) = 3BaO(s) + 2TeO_2(g) + O_2(g)$	

Table 1

<i>T</i> (K)	$m\{\text{TeO}_2(s)\}$ (mg dm ⁻³)	$p(\text{TeO}_2, \text{ g})$ (kPa)	ln K
1119 1149 1174 1206 1239 1258	$\begin{array}{c} 2.225 \cdot 10^{-2} \\ 3.691 \cdot 10^{-2} \\ 5.345 \cdot 10^{-2} \\ 8.206 \cdot 10^{-2} \\ 9.024 \cdot 10^{-2} \\ 1.367 \cdot 10^{-2} \end{array}$	$3.444 \cdot 10^{-4} 5.694 \cdot 10^{-4} 8.274 \cdot 10^{-4} 1.292 \cdot 10^{-3} 1.812 \cdot 10^{-3} 2.124 \cdot 10^{-3}$	- 38.469 - 36.961 - 35.840 - 34.504 - 33.488 - 33.012
1280	$1.795 \cdot 10^{-1}$	$2.924 \cdot 10^{-3}$	- 32.053



Fig. 1. Variation of $\ln K$ as a function of reciprocal temperature for the reaction: $Ba_3Te_2O_9(s)=3BaO(s)+2TeO_2(g)+O_2(g)$.

An alternative value of $\Delta_{f}G^{\circ}_{m}(T)$ for Ba₃Te₂O₉(s) is not available in the literature for comparison. In the absence of thermodynamic parameters like enthalpy and heat capacity,

it is not possible to carry out second law and third law analysis for the calculation of $\Delta_r H^{\circ}_m$ of Ba₃Te₂O₉(s) at 298.15 K. It would be useful to determine the enthalpy and heat capacity for Ba₃Te₂O₉(s) in order to calculate other thermodynamic functions.

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