



Gibbs energy of formation of barium thorate (BaThO_3) by reactive carrier gas technique

S.R. Bharadwaj, R. Mishra, M. Ali(Basu), D. Das, A.S. Kerkar,
S.R. Dharwadkar *

Applied Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India

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Abstract

The Gibbs energy of formation of BaThO_3 was determined employing the heterogeneous reaction between the compound and water vapour involving the formation of gaseous barium hydroxide species according to the reaction $\text{BaThO}_3(\text{s}) + \text{H}_2\text{O}(\text{g}) = \text{ThO}_2(\text{s}) + \text{Ba}(\text{OH})_2(\text{g})$. The vapour pressure of barium bearing species over the univariant mixture containing barium thorate and thorium dioxide as the condensed phases in equilibrium with a controlled pressure of water vapour was measured in the temperature range 1548–1683 K employing the automatic recording transpiration apparatus. The vaporization of BaThO_3 was studied in the presence of flowing argon saturated with water vapour. The equilibrium constant of the above reaction could be expressed by the equation $\ln K_p (\pm 0.03) = -20306/T + 5.37$ ($1548 \leq T/\text{K} \leq 1683$). The Gibbs energy of formation for BaThO_3 derived from these data could be expressed as $\Delta_f G^\circ(\text{BaThO}_3) (\pm 38 \text{ kJ/mol}) = -1775.8 + 0.266T$ between 1548 and 1683 K. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Thorium is expected to play an important role in the third phase of the Indian Nuclear Power Generation program [1]. The fuel to be used in this phase will consist essentially of the solid solution of either uranium dioxide with thorium dioxide or plutonium dioxide with thorium dioxide. The thorium dioxide content in these fuels will be more than 90 mol%. As there is no operating experience with these types of fuels it is necessary to predict the fuel behavior during irradiation employing the computer codes developed for such purpose [2]. The computer codes developed at this centre have been used successfully for the prediction of PHWR fuel behavior during irradiation [3,4]. The use of computer codes, however, needs information on several thermophysical properties of the fuel and their changes during burn-up. The change in thermophysical properties of the fuel

obviously results from the changing chemistry of the fuel during irradiation.

In the type of fuels envisaged for use in the above mentioned reactors the oxygen potential is expected to increase much more rapidly during irradiation as compared to that in conventional types of BWR or PHWR. This is mainly because of the large inert thorium dioxide matrix which is not hyperstoichiometric. The rapidly increasing oxygen potential in the fuel during irradiation will dictate to a large extent the chemistry of the fuel pin during irradiation. The type and nature of the compounds formed in the fuel during burn-up will mainly be dependent on this oxygen potential. The mechanical integrity of the fuel pin, in turn, will also be dependent on the formation of these compounds. The program is therefore underway to study the thermodynamic stability of various compounds in the multicomponent systems involving the oxides of fission products and thorium dioxide.

The data obtained could be useful in the prediction of conditions for the formation of such compounds and the point of time at which such conditions could exist in the fuel pin during irradiation.

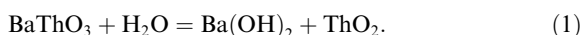
* Corresponding author: Tel.: +91-22 556 3060; fax: +91-22 556 0750; e-mail: htschem@magnum.barc.ernet.in

As a part of this program the Gibbs energy of formation of BaThO₃ was determined employing the vapour pressure measurement of the compound in presence of water vapour. The results obtained are presented in this paper.

2. Experimental

Barium thorate was prepared by the sol–gel method through the citrate–nitrate route by the Powder Metallurgy Division of BARC [5]. The purity and stoichiometry of the compound was confirmed from the results of chemical analysis and X-ray diffraction studies. A clear X-ray diffraction pattern of the compound could be obtained only when the powder prepared by the ignition of the gel at 950 K was heated above 1500 K for about 3 h in Ar atmosphere. The X-ray diffraction pattern of the compound was in close agreement with that reported for it in JPCD file 3-1102. On indexing the powder diffraction lines, the compound was found to be cubic with $a = (449.9 \pm 0.2)$ pm compared to $a = 449.5$ pm reported in the above JPCD file 3-1102. Thermogravimetric (TG) analysis of the compound carried out employing the SETARAM simultaneous TG/DTA unit (Model SETARAM-92-18.16) indicated that it was hygroscopic and had to be preserved in the desiccator before use. The TG curve further revealed that other than the initial moisture loss there was no measurable loss in the compound due to vaporization up to 1750 K.

The vapour pressure measurements were carried out employing the microthermogravimetric transpiration unit described earlier [6]. The temperature range of this unit was extended to 1770 K by introducing suitable changes in the temperature measuring thermocouple, reaction tube and the furnace. Since the compound had a negligible vapour pressure in dry flowing argon up to 1750 K advantage was taken of its reactivity with water vapour at high temperatures. Barium oxide, one of the components of this compound is known to vaporize as hydroxide at high temperatures in presence of water vapour [7–9]. Preliminary studies on the vaporization of this compound indicated that its vapour pressure increased measurably when heated in the stream of argon saturated with water vapour. Contrary to that in dry argon, the compound exhibited a significant loss due to vaporization at temperatures as low as 1525 K in the presence of moisture. The vaporization probably involved the formation of the gaseous barium hydroxide species Ba(OH)₂ according to the reaction expressed in Eq. (1) as reported in Refs. [7–9]:



The equilibrium constant K_p for the reaction in Eq. (1) could be expressed in terms of the partial pressure of barium bearing vapour species and water vapour as

Table 1

Vapour pressure of Ba bearing species over BaThO₃ as a function of $p(\text{H}_2\text{O})$ at 1643 K

Aqueous systems used to control $p(\text{H}_2\text{O})$ ^a	$p(\text{H}_2\text{O})$ (Pa at 300 ± 1 K)	Vapour pressure of Ba-bearing species (Pa at 1643 K)
Pure water	3333.0	3.09
BaCl ₂ ·2H ₂ O saturated	3033.03	2.79
SrCl ₂ ·2H ₂ O saturated	2333.14	2.49
CaCl ₂ ·H ₂ O saturated	1053.21	1.01
LiCl saturated	366.63	0.42

^a $p(\text{H}_2\text{O})$ data are taken from CRC Handbook of Chemistry and Physics, 78th edition, CRC Press, 1997–1998.

$$K_p = p(\text{Ba(OH)}_2)/p_{\text{H}_2\text{O}}. \quad (2)$$

The vaporization reaction of the compound was studied in the temperature range 1548–1683 K in the presence of flowing argon saturated with water vapour. The temperature of the sample during vaporization was measured with a Pt–Pt 13% Rh thermocouple calibrated at the melting points of tin, silver and gold by the drop method described in Ref. [10]. The partial pressure of water vapour in argon used as a carrier gas could be varied by bubbling the gas through different baths containing pure water and the saturated solutions of different hydrates maintained at a constant temperature of (300 ± 1) K. The vapour pressures of the saturated solutions of different hydrates are listed in Table 1.

The experiment for the equilibrium vapour pressure measurement consisted of two parts. In the first part, the condensed phase–vapour phase equilibrium was established by measuring the apparent vapour pressure of the sample at a fixed temperature as a function of the flow rate. The vapour pressure of the sample was calculated

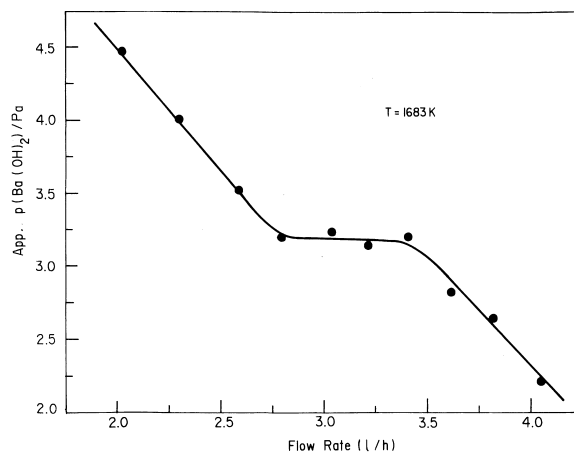


Fig. 1. Apparent pressure of barium bearing species as a function of the flow rate at 1683 K.

from the mass loss of the sample per liter of the carrier gas passed over it, assuming the vapour to be ideal. The mass loss of the sample was monitored with the help of the electronic microbalance coupled to the transpiration unit to an accuracy of $\pm 5 \mu\text{g}$. The mass loss of the sample per unit volume of the carrier gas (moisture saturated argon) swept over it was measured as a function of the flow rate at 1683 K. It was found to remain constant in the range of flow between 2.8 to 3.4 l/h, indicating thereby the saturation of the carrier gas by the vapor. The measurements at different temperatures were carried out employing the flow rate 3.26 l/h. The plot of the vapour pressure of the barium bearing species as a function of the flow rate of the carrier gas is given in Fig. 1.

3. Results

The vapour pressure of the barium bearing species in the reaction expressed in Eq. (1) could be calculated using the following relation assuming the vapour to behave ideally.

$$p_{\text{apparent}} = (W/V_c)(RT_c/M), \quad (3)$$

where W is the mass loss of the sample, V_c the volume of the carrier gas passed over the sample in liters, M the molecular weight of the vapour species, T_c the ambient temperature at which the volume of the carrier gas is measured and R is the gas constant.

The vapour pressure of barium bearing species at 1643 K measured as a function of partial pressure of water vapour in the argon stream swept over the sample are listed in Table 1. The plot of the logarithm of the vapor pressure of barium bearing species versus the logarithm of the partial pressure of water vapour in the carrier gas yielded a straight line with the slope $n = 0.93$ (Fig. 2) indicating that one mole of water reacted with one mole of BaThO_3 to give a gaseous barium hydroxide of the formula Ba(OH)_2 as expressed in Eq. (1).

X-ray diffraction analysis of the partially decomposed sample obtained at the end of the experiment showed the presence of BaThO_3 and ThO_2 crystals, indicating the coexistence of two solid phases during the vaporization reaction. The values of the partial pressure of barium hydroxide $\text{Ba(OH)}_2(\text{g})$ in the vapour phase and the corresponding equilibrium constants of the reaction represented by Eq. (1) are listed in Table 2. The equilibrium constant for the vaporization reaction as a function of temperature could be expressed by the relation

$$\ln K_p(\pm 0.03) = -20306/T + 5.37 \quad (1548 \leq T/\text{K} \leq 1683). \quad (4)$$

The plot of $\ln K_p$ versus $1/T$ is given in Fig. 3. The enthalpy change for the reaction obtained from the plot was found to be $168.8(\pm 4.1)$ kJ/mol.

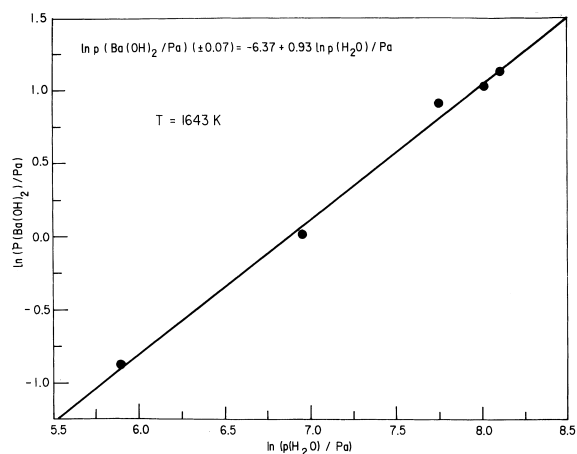


Fig. 2. $\ln p(\text{Ba(OH)}_2)$ of barium thorate versus partial pressure of water vapour at 1643 K.

3.1. Standard Gibbs energy of formation of BaThO_3

The standard Gibbs energy of formation of BaThO_3 could be expressed in terms of the equilibrium constant for reaction Eq. (1) and is given by

$$\Delta_r G^\circ(\text{BaThO}_3, \text{s}) = \Delta_r G^\circ(\text{ThO}_2, \text{s}) + \Delta_r G^\circ(\text{Ba(OH)}_2, \text{g}) - \Delta_r G^\circ(\text{H}_2\text{O}, \text{g}) + RT \ln K_p. \quad (5)$$

The key data for $\Delta_r G^\circ(\text{ThO}_2, \text{s})$, $\Delta_r G^\circ(\text{Ba(OH)}_2, \text{g})$, $\Delta_r G^\circ(\text{H}_2\text{O}, \text{g})$ needed for the calculation of Gibbs energy term were taken from Ref. [11]. Using the equilibrium constant values for reaction Eq. (1) evaluated from Eq. (4) and the above key data, the standard Gibbs energy of formation for the compound could be represented by the equation

$$\Delta_r G^\circ(\text{BaThO}_3, \text{s}) = -1775.8 + 0.266T (\pm 38.0 \text{ kJ/mol}) \quad (1548 \leq T/\text{K} \leq 1683). \quad (6)$$

Table 2 presents the $\Delta_r G^\circ(\text{BaThO}_3, \text{s})$ calculated from Eq. (6).

4. Discussion

The Gibbs energy of formation of BaThO_3 determined from the equilibrium constant for the heterogeneous reaction between $\text{BaThO}_3(\text{s})$ and water vapour could be expressed by Eq. (6). The corresponding Gibbs energy of formation obtained employing the incongruent vaporization reaction



Table 2
Standard Gibbs energy of formation of BaThO₃(s)

Sl. No.	Temperature (K)	Wt. loss (mg/l)	$p(\text{Pa})\text{Ba}(\text{OH})_2$	$K_p \times 10^6$	$\Delta_f G^0(\text{BaThO}_3)$ (kJ/mol)
1	1548	0.102	1.48	444.64	-1364.33
2	1558	0.106	1.54	460.87	-1362.3
3	1570	0.117	1.70	509.75	-1359.1
4	1578	0.133	1.94	580.92	-1356.12
5	1594	0.142	2.07	620.18	-1352.73
6	1612	0.169	2.47	739.89	-1347.48
7	1622	0.173	2.52	756.35	-1345.56
8	1627	0.188	2.74	821.48	-1343.65
9	1641	0.203	2.95	885.99	-1340.36
10	1646	0.208	3.03	908.51	-1339.18
11	1651	0.215	3.13	938.53	-1337.93
12	1660	0.244	3.55	1065.72	-1334.71
13	1669	0.263	3.84	1150.91	-1332.17
14	1673	0.273	4.02	1194.23	-1330.98
15	1683	0.286	4.16	1249.14	-1328.73

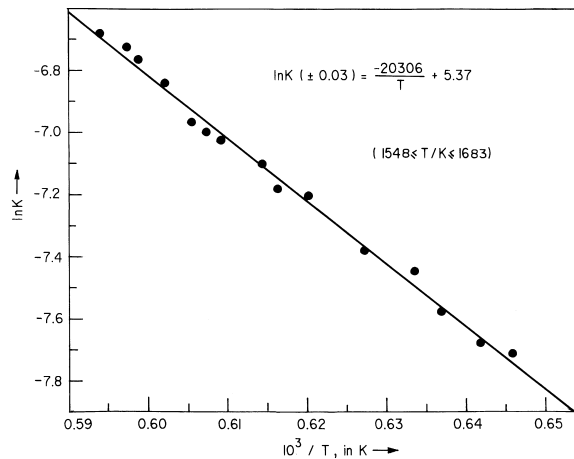


Fig. 3. $\ln K_p$ versus reciprocal temperature.

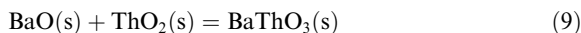
at high temperatures using the Knudsen effusion technique [12] could be expressed by the relation

$$\Delta_f G^0(\text{BaThO}_3, \text{s}) = -1801.8 + 0.276T (\pm 8.0 \text{ kJ/mol})$$

$$(1770 \leq T/\text{K} \leq 2136). \quad (8)$$

The consistent results obtained by two different methods establishes the accuracy of the data generated.

The standard Gibbs energy change for the formation of the compound from the component oxides in the reaction



was calculated employing the values of the Gibbs energy of formation of BaThO₃ obtained by the transpiration as well as Knudsen effusion techniques. The Gibbs energy change for the reaction could be expressed as a function of temperature by the equations

$$\Delta_f G^0 = -8.03 - 0.0101T (\pm 40.0 \text{ kJ/mol})$$

$$(1548 \leq T/\text{K} \leq 1683) \quad (10)$$

and

$$\Delta_f G^0 = -34.0 + 0.0004T (\pm 10.0 \text{ kJ/mol})$$

$$(1770 \leq T/\text{K} \leq 2136) \quad (11)$$

corresponding to the transpiration and Knudsen effusion techniques, respectively.

The Gibbs energy change for the reaction in Eq. (9) obtained from Eqs. (10) and (11) indicates that the compound BaThO₃ is likely to be formed within the fuel pin of thoria based reactors from the component oxides. Though both Eqs. (10) and (11) indicate the possibility of formation of barium thorate (BaThO₃) from the component oxides at temperatures of the fuel pin, Eq. (11) is given more weightage in view of lower

error involved in the Gibbs energy change for the reaction expressed in Eq. (9). The larger error in the Gibbs energy change for the reaction in Eq. (10) arises from the larger error involved in the value of the Gibbs energy of formation of $\text{Ba(OH)}_2(\text{g})$ used in Eq. (5) to derive the value of the Gibbs energy of formation of BaThO_3 .

It can be concluded from the present investigation that there is indeed a possibility of formation of BaThO_3 in thoria based fuels during irradiation. Attempts to prepare this compound in our laboratory directly by heating the mixture of the component oxides to temperatures as high as 1773 K did not succeed as the reaction was extremely sluggish because of the high kinetic barrier involved in the solid state reaction leading to the formation of the compound.

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