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Gibbs energy of formation of $Ba(OH)_2$ vapor species using the transpiration technique

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Abstract

The Gibbs energy of formation of $Ba(OH)_2$ was determined employing the heterogeneous reaction between solid BaO and water vapor and generating gaseous barium hydroxide species according to the reactions $BaO(s) + H_2O(g) = Ba(OH)_2(g)$. The equilibrium vapor pressure of $Ba(OH)_2$ species under a controlled pressure of water vapor was measured using an automatic recording transpiration apparatus. From the vapor pressure results, the equilibrium constant of the reaction obtained could be represented as $\ln K_p(\pm 0.04) = -16792.3/T + 4.94$, $K_p = p(Ba(OH)_2)/p(H_2O)$ $(1346 \leqslant T/K \leqslant 1451)$. The Gibbs energy of formation of $Ba(OH)_2$ derived from these data could be expressed as $\Delta_f G°(Ba(OH)_2, g)(\pm 2\ kJ\ mol^{-1}) = -667.29 + 0.118T$ $(1346 \leqslant T/K \leqslant 1451)$. From the study, the second-law and third-law values of $\Delta_f H°(Ba(OH)_2, g, 298.15\ K)$ were worked out to be $-(645.1 \pm 8.0)\ kJ\ mol^{-1}$ and $-(643.9 \pm 2.5)\ kJ\ mol^{-1}$, respectively. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Thermodynamic data of gaseous barium hydroxide species are useful in predicting the behavior of the radiologically hazardous fission product barium under the circumstances during and after a nuclear reactor accident. The thermochemistry of $Ba(OH)_2(g)$ has been studied by many authors [1–7]. The reported data on the standard enthalpy of its formation, $\Delta_f H°$ (298.15 K) are not consistent and lie in the range −644.2 to $-546\ kJ\ mol^{-1}$, the lowest and the highest values, respectively, being derived from flame spectral analysis [5] and transpiration studies [6]. As the result a large uncertainty has been assigned to the thermodynamic quantity, the value of which has been variously selected by different reviewers [8–10]. Recently, it was necessary to have reliable thermodynamic data of the hydroxide for evaluating the standard enthalpy of formation of barium thorate, $BaThO_3(s)$ predicted to be formed in thoria-based fuel [11]. $\Delta_f H°(BaThO_3, s)$ was evaluated by making use of the different selected values of $\Delta_f H°(Ba(OH)_2(g))$ together with the measured equilibrium pressures of $Ba(OH)_2(g)$ over the thorate in the presence of water vapor in a transpiration study [12]. However, it was found that in neither case of selections, the derived value of $\Delta_f H°(BaThO_3, s)$ was in agreement with the result of the Knudsen effusion study of the compound [11] where the evaporative path was $BaThO_3(s) = ThO_2(s) + BaO(g)$. From the consistent data of the second-law and third-law values of the sublimation enthalpy from the effusion study, the derived formation enthalpy of $BaThO_3(s)$ from its constituent oxides was $-(34 \pm 10)\ kJ\ mol^{-1}$ and the corresponding entropy change was negligibly small as expected for perovskite formation. On the other hand, the result of the transpiration yielded the enthalpy of formation from the constituent oxides of $BaThO_3(s)$ as $-(8 \pm 37)$ to $+(8 \pm 10)\ kJ\ mol^{-1}$ depending on the thermodynamic data selected for $Ba(OH)_2(g)$ [8,10]. The corresponding entropy change was seen to be unexpectedly high. Interestingly, reported correlations for the enthalpy of formation of $A(II)B(IV)O_3$ perovskites [13,14] considering ionic sizes of the metal ions corroborate to the effusion result of $BaThO_3$ and not to the result of the transpiration. The correlations predict values of −30 to $-40\ kJ\ mol^{-1}$ for the enthalpy of formation.

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The correctness of the enthalpy and entropy of formation of barium thorate derived from the transpiration result largely rests upon the accuracy of the reported thermodynamic data of $Ba(OH)_2(g)$. Thus, the reported thermodynamic data of $Ba(OH)_2(g)$ were considered to be inaccurate and the present study was planned. This study makes use of the carrier gas technique to monitor the transport of the hydroxide species from pure solid barium oxide under dynamic equilibrium at controlled pressure of water vapor. The automatic weight loss recording transpiration apparatus [15] employed in the study of barium thorate was used in this case also.

2. Experimental

BaO used for this study was obtained by complete decomposition of pure solid $BaCO_3$ (Aldrich, 99.99% purity) under a dynamic vacuum ($\approx 10^{-8}$ bar) at 1673 K, the purity was confirmed by X-ray diffraction studies. As BaO(s) is extremely moisture sensitive, the freshly prepared sample was kept overnight inside the transpiration apparatus at 1650 K, i.e., 200 K above the upper limit of working temperatures under flowing dry argon before starting the experiment. The step eliminated the moisture content of the sample.

The vaporization process from BaO(s) under the flow of argon containing moisture involves the formation of gaseous barium hydroxide species, $Ba(OH)_2$ [6,12] according to the reaction

$$BaO(s) + H_2O(g) = Ba(OH)_2(g). \tag{1}$$

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

$$K_p = p(Ba(OH)_2)/p(H_2O). \tag{2}$$

At a fixed value of $p(H_2O)$, the equilibrium value, $p(Ba(OH)_2)$ is governed by the temperature only. The vaporization reaction of BaO was studied in the temperature range 1350–1450 K in the presence of flowing argon containing a fixed partial pressure of moisture corresponding to the saturated vapor pressure of water at 300 K. For the control of $p(H_2O)$ the pure argon gas before entering into the system bubbled through a bath of distilled water with a large evaporating surface kept at a controlled temperature of 300 K. 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 [15]. The overall accuracy of the temperature measurement was ±1 K. The weight loss from the BaO(s) sample was monitored on-line in the transpiration set up by a microbalance described elsewhere [12]. The powder sample loaded in a stack of platinum containers made of fine meshed gauges and suspended from the balance arm was maintained at a defined temperature and flow rate of the gas mixture of argon and water vapor. The mass loss of the sample was monitored to an accuracy of ±5 μg.

The experiment for the equilibrium vapor pressure measurement consisted of two parts. In the first part, the proper flow regime of carrier gas for probing properties at dynamic equilibrium between the condensed and vapor phases was established by measuring the apparent vapor pressure of the sample as a function of the flow rate at a fixed temperature of 1450 K. The vapor pressure due to $Ba(OH)_2(g)$ was calculated from the mass loss of the sample per litre of the carrier gas which passed over it, assuming the vapor to be ideal. The rate of mass loss was found to remain constant in the range of flow between 3.3 and 3.8 $l\ h^{-1}$, indicating the flow regime for saturation of the carrier gas by the vapor. In the second part of the experiment, the weight loss due to $Ba(OH)_2(g)$ at defined temperatures in the range 1346–1451 K was continuously monitored and recorded over a typical period of 30 min at a fixed flow rate of 3.61 $l\ h^{-1}$. The weight loss versus time plotted on the X–Y recorder showed perfect linearity. The slope of the linear plot observed at a temperature gave the corresponding weight loss rate. Following the evaporation experiment, X-ray diffraction analysis of the residual sample was carried out to confirm the presence of the pure BaO(s) phase.

3. Results and discussion

The vapor pressure of barium hydroxide generated as expressed in Eq. (1) could be calculated using the following relation assuming the vapor to behave ideally:

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

In expression (3) W is the mass loss of the sample, V_c is the volume of the carrier gas passed over the sample in litres, M is the molecular weight of the vapor species, T_c the ambient temperature at which the volume of the carrier gas was measured and R is the gas constant. The confirmation of the existence of $Ba(OH)_2$ as the major barium bearing vapor species when moisture is passed over solid BaO is given elsewhere [6,12]. The apparent pressure p_{apparent} was equated to the equilibrium value, i.e., $p(Ba(OH)_2)$ of expression (2) when the weight loss of the sample was monitored at 3.61 $l\ h^{-1}$, the flow rate that falls within the measured region of weight loss independency at 1450 K. The plot of apparent vapor pressure of barium bearing species as a function of the flow rate of the carrier gas is shown in Fig. 1. The equilibrium vapor pressure of $Ba(OH)_2$ and the corresponding K_p values obtained at different temperatures

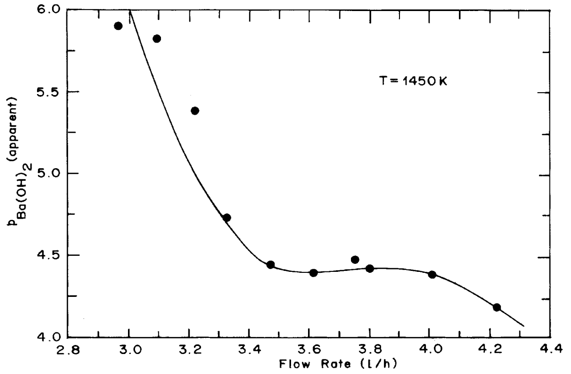

Fig. 1. Dependence of $Ba(OH)_2$ vapor transport on $Ar + H_2O$ carrier gas flow.

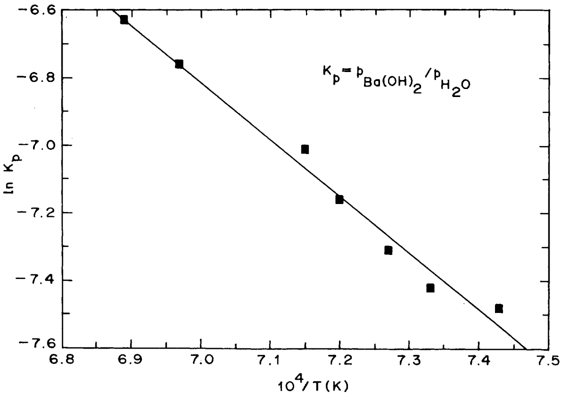

Fig. 2. Temperature dependence of $BaO(s) + H_2O(g) = Ba(OH)_2$ reaction equilibrium.

are given in Table 1. The plot of $\ln K_p$ against the reciprocal temperature is given in Fig. 2. The equilibrium constant for the vaporization reaction as a function of the temperature could be expressed by the relation

$$\ln K_p(\pm 0.04) = -16792.3/T + 4.94 \quad (1346 \leqslant T/\mathrm{K} \leqslant 1451). \tag{4}$$

The Gibbs energy change, $\Delta_r G^\circ$ for reaction (1) is, therefore, given by

$$\Delta_r G^\circ \equiv -RT \ln K_p = 139.6 - 0.0411T \ (\mathrm{kJ\ mol^{-1}}). \tag{5}$$

Using the reported thermal functions of BaO(s), H_2O(g), and $Ba(OH)_2$(g) [9], the second-law and third-law values of $\Delta_r H^\circ$ (298.15 K) were found to be (144.8 ± 8) and (157.3 ± 0.53) kJ mol^{-1}, respectively. The difference of 12.5 kJ mol^{-1} was interpreted to be due to the uncertainty in the reported values of the thermal function of $Ba(OH)_2$ (g). It is to be noted that the absolute value of the entropy of $Ba(OH)_2$ (g) used in evaluating the thermal functions [9] is about 7 J K^{-1} mol^{-1} higher than the value obtained from a similar transpiration study (Alexander et al., see Table 4 in [1]). The entropy value of 468.6 J K^{-1} mol^{-1} reported at 1800 K in this study compares well with that of 466.7 J K^{-1} mol^{-1} obtainable from Eq. (5) of this study at the same temperature. If one corrects the reported [9] Gibbs energy function of $Ba(OH)_2$(g) by making use of the average entropy value from the two transpiration works, the third-law value of $\Delta_r H^\circ$ (298.15 K) of this study works out to be 146.0 kJ mol^{-1} which compares well with the corresponding second-law enthalpy.

The thermodynamic data of reaction (1) lead to the evaluation of standard Gibbs energy of formation of $Ba(OH)_2$(g) as

$$\Delta_f G^\circ(Ba(OH)_2, g) = \Delta_f G^\circ(BaO, s) + \Delta_f G^\circ(H_2O, g) + \Delta_r G^\circ.$$

The above expression was evaluated considering relation (5) and also, the reported data for $\Delta_f G^\circ$(BaO,s) and $\Delta_f G^\circ(H_2O, g)$ [9]. The evaluated expression for the standard Gibbs energy of formation for $Ba(OH)_2$(g) is given by

$$\Delta_f G^\circ(Ba(OH)_2, g)(\pm 2.0\ \mathrm{kJ\ mol^{-1}}) = -667.29 + 0.118T \quad (1346 \leqslant T/\mathrm{K} \leqslant 1451). \tag{6}$$

Table 1 presents the Gibbs energy of formation values of barium hydroxide calculated from expression (6).

Expression (6) for $\Delta_f G^\circ(Ba(OH)_2, g)$ was used for the evaluation of $\Delta_f G^\circ(BaThO_3, s)$ considering the transpiration data on the Gibbs energy change, $\Delta_r G'^\circ$ of the following reported heterogeneous reaction [12]:

Table 1
Vapor pressure data and the Gibbs energy of formation of $Ba(OH)_2$(g)

Serial no.	Temperature (K)	Weight loss (mg/l)	$p(Ba(OH)_2)$ (Pa)	$K_p \times 10^6$	$\Delta_f G^\circ(Ba(OH)_2, g)$ (kJ/mol)
1	1346	0.116	1.885	566	−508
2	1364	0.123	1.996	599	−506
3	1376	0.137	2.220	666	−505
4	1389	0.159	2.586	776	−503
5	1399	0.185	3.004	901	−502
6	1435	0.237	3.855	1157	−498
7	1451	0.278	4.400	1320	−496

$$BaThO_3(s) + H_2O(g) = Ba(OH)_2(g) + ThO_2(s) \quad (1550 \leqslant T/K \leqslant 1680). \qquad (7)$$

Thus,

$$\begin{aligned}\Delta_f G^\circ(BaThO_3, s) &= -\Delta_r G'^\circ + \Delta_f G^\circ(Ba(OH)_2, g) \\ &\quad + \Delta_f G^\circ(ThO_2, s) - \Delta_f G^\circ(H_2O, g) \\ &= -1805.99 + 0.288T \\ &\quad (\pm 2.6\ kJ\ mol^{-1}). \qquad (8)\end{aligned}$$

With the help of thermodynamic key data for the constituent oxides, $BaO(s)$ and $ThO_2(s)$, the above expression leads to the following expression for the Gibbs energy change during formation of barium thorate from its constituent oxides:

$$\Delta_r G^\circ = -29.23 + 0.0032T \quad (\pm 3.6\ kJ\ mol^{-1}). \qquad (9)$$

From expression (9) it is seen that the average enthalpy and entropy changes during the synthesis are −29.23 kJ mol^{-1} and −3.2 J K^{-1} mol^{-1}, respectively. Considering the experimental uncertainties involved in the measurement techniques the above values of the respective thermodynamic quantities are in agreement with the result of the effusion study [11].

The agreement obtained above for the thermodynamic data of $BaThO_3(s)$ from the two independent studies suggests that the Gibbs energy of formation of $Ba(OH)_2(g)$ derived from the present study is more appropriate. Expression (6) obtained from this study led to the average value of the enthalpy of formation of the species as −667.29 kJ mol^{-1} within the temperature range ($1346 \leqslant T/K \leqslant 1451$). With the help of the reported thermal functions of $BaO(s)$, $H_2O(g)$ and $Ba(OH)_2(g)$ [9] the second-law value of $\Delta_f H^\circ$ ($Ba(OH)_2$,g, 298.15 K) was thus obtained as $-(645.1 \pm 8.0)$ kJ mol^{-1}. The corresponding third-law value was $-(643.9 \pm 2.5)$ kJ mol^{-1}. Among the reported data of the standard enthalpy of formation, the closer ones to the presently arrived value are from the flame spectral work of Cotton and Jenkins [5] on the hydroxide and the Knudsen effusion mass spectrometric study [2] of the heterogeneous reaction (1). Their values are $-(644.2 \pm 16)$ and $-(626.56 \pm 3)$ kJ mol^{-1}, respectively at 298 K [1]. The possible sources of errors in the reported mass spectroscopic studies [1,2,7] could arise from uncertainties in the ionization cross-section for the relevant vapor species and also from fragmentation of $Ba(OH)_2$ molecules during its electron impact ionization as indicated [1]. The reported transpiration data by Sasamoto et al. [6] on the heterogeneous reaction (1) suffer from a drift in their second-law plot and lead to a much higher value $-(582.4 \pm 18)$ kJ mol^{-1} for $\Delta_f H^\circ(Ba(OH)_2$,g, 298.15 K).

4. Conclusion

The Gibbs energy of formation and related thermodynamic properties of barium hydroxide vapor were derived from the experimental result of the reactive transpiration study presented. The generated information yielded consistent values of the thermodynamic stability of barium thorate. The standard enthalpy of formation of gaseous barium hydroxide species at 298.15 K derived from the present study is $-(643.9 \pm 2.5)$ kJ mol^{-1}.

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