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Letter to the Editors

Vaporization behavior and Gibbs energy of formation of Cs_2ThO_3

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Abstract

The thermodynamic stability of cesium thorate, prepared by the sol–gel method following the citrate–nitrate route, was determined by measuring the vapor pressure of Cs_2O by the Knudsen effusion collection technique. $Cs_2ThO_3(s)$ vaporized incongruently according to the reaction $Cs_2ThO_3(s) = ThO_2(s) + Cs_2O(g)$. The Gibbs energy of formation of Cs_2ThO_3 derived from the measured vapor pressure of Cs_2O and other auxiliary data could be given by the equation $\Delta_f G^\circ(Cs_2ThO_3, s)(\pm 20\ \text{kJ/mol}) = -1780.1 + 0.437T \quad (1100 \leqslant T/\text{K} \leqslant 1254)$. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The third phase of the nuclear energy generation program in India envisages the use of thoria based fuels. For smooth and safe operation of reactors using thoria based fuels, it is important to look into the chemical reactivity of the thoria matrix with various fission products. Cesium formed in significant amounts can react in presence of a higher oxygen partial pressure with the matrix forming the compound Cs_2ThO_3. The thermodynamic stability of this and the other cesium based compounds such as Cs_2ZrO_3 [1] and $Cs_2U_4O_{12}$ would govern the availability of cesium in fixing the volatile fission product iodine as cesium iodide, CsI [2–4]. At the oxygen potential of −400 kJ/mol and the temperature of 1000 K, it is reported [2–4] that the formation of Cs_2ZrO_3 on Zircaloy and $Cs_2U_4O_{12}$ in urania fuel results in sufficient dissociation of CsI releasing thereby elemental iodine at the critical concentration for stress corrosion cracking (SCC) of the clad. To obtain a similar knowledge for the feasibility of the reactive decomposition of cesium iodide due to formation of the compound, Cs_2ThO_3 in thoria based fuel, the thermodynamic data of cesium thorate are required.

In this paper, we give our results on the vaporization behavior of cesium thorate, which has not been reported so far. We also give the thermodynamic stability of the compound derived from the vaporization data.

2. Experimental

Cs_2ThO_3 was prepared by the sol–gel method through the citrate–nitrate route. The chemicals used for the preparation of the compound were CsI (99.99% purity, Aldrich, USA), thorium nitrate $\cdot\, x H_2O$ (AR grade), citric acid (AR grade), and AR grade HNO_3. Details of the preparation and characterization of the moisture sensitive compound, cesium thorate and similar other compounds are reported elsewhere [5]. A carefully controlled drying process of the citrate gel under vacuum, ignition of the dried gel and then annealing under flowing dry oxygen were used to get the crystalline product, which was characterized by chemical analysis, thermogravimetry, differential thermal analysis (TG-DTA) and X-ray diffraction (XRD) studies. The

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total carbon content in the prepared compound was also analyzed and found to be 0.08 wt%. The thermogravimetric analysis showed a single step of weight loss from the prepared compound at 1000 K. The weight loss could be accounted for by considering the volatilization of the cesium from the sample as $Cs_2O(g)$. The residue from TGA was analyzed by XRD and found to be $ThO_2(s)$. Residues from partially evaporated samples in TGA under inert gas flow and also in Knudsen evaporation condition were analyzed. XRD analysis revealed them to be a mixture of two condensed phases, namely Cs_2ThO_3 and ThO_2 only. To substantiate the weight loss as $Cs_2O(g)$ in TGA, an analysis was made for relative amounts of the reported cesium bearing species [6] in the vapor under Knudsen equilibrium at the working temperature of 1100–1254 K. The analysis showed that, among the vapor species of the cesium and cesium–oxygen systems, $Cs_2O(g)$ is the dominating one. From the analysis of the vapor species and the observed condensed phases in equilibrium with the vapor, it was considered that the following chemical path predominantly governs the evaporation of Cs_2ThO_3:

$$Cs_2ThO_3(s) = ThO_2(s) + Cs_2O(g). \tag{1}$$

The vapor pressure over the mixture of two condensed phases, namely, $Cs_2ThO_3(s)$ and $ThO_2(s)$, was measured by using the Knudsen effusion collection technique. The apparatus used and the experimental details involving the measurement of temperature and collection of vapor of Cs_2O on targets are given in Refs. [7,8]. The compound from vacuum seal was transferred within a thoroughly degassed Knudsen cell of molybdenum having a platinum liner all along the inner wall including the knife edged orifice. The liner was applied to avoid the reduction of Cs_2O vapor by molybdenum. The loaded cell was immediately positioned within the Knudsen assembly and evacuated under a dynamic vacuum of 5×10^{-4} Pa.

Before starting the collection of the effusate sufficient degassing time was given for removal of traces of moisture in the sample as well as the cell up at a temperature slightly above the highest working temperature. This was done to minimize the transport of cesium in the effusate in the form of CsOH(g) by the residual water vapor in the system. Exploratory runs of vapor collection at a fixed temperature (1250 K) established the time for complete degassing. The analysis of the collected vapor indicated that the rate of effusion of cesium bearing species steeply falls and settles to a constant value within a few minutes. To this constant value, the contribution of CsOH(g) due to a constant ingress of water vapor into the cell from the background pressure of 5×10^{-4} Pa is negligible. Considering the steady-state dynamics of effusion through the cell-orifice it is estimated that the CsOH(g) content in the effusate of Cs_2O vapor is less than 1% within the working temperatures of the present study.

The final collection experiment was carried out at ten different temperatures ($1100 \leqslant T/\mathrm{K} \leqslant 1254$). The first five settings of temperatures were done successively from the highest value to the lowest one and then the other five settings were done in the increasing direction of temperatures. The vapor deposits on the ten targets of tantalum were analyzed chemically by bringing them into an aqueous solution and measuring the cesium concentration by atomic emission spectrometry with proper standards.

3. Results and discussion

The experimentally obtained data of the effusate at different temperatures and duration were treated in the following way to compute the corresponding vapor pressures of $Cs_2O(g)$ species over the two phase mixtures, $Cs_2ThO_3(s)$ and $ThO_2(s)$. The vapor pressure expression for Cs_2O in the Knudsen cell obtained using the kinetic theory of the gases and the geometry of vapor collection is given by the relation

$$p(Cs_2O) = (1/A)(w_{Cs_2O}/t)\left[\left(r^2+d^2\right)/r^2\right] \times [2\pi RT/M_{Cs_2O}]^{-1/2}, \tag{2}$$

where W_{Cs_2O} is the mass of Cs_2O deposited on the target during the time t, A the area of cross-section of the orifice from which the vapor is effusing out, R the gas constant and T is the temperature of the Knudsen cell during the vapor collection. M_{Cs_2O} is the molar mass of Cs_2O, $[(r^2+d^2)/r^2]$ the geometric factor, r being the radius of the collimator for the target collection and d is the vertical separation between the orifice and the collimator. Typical values of the parameters A, d, and r used in the experiments were 8.3×10^{-7} m², 0.07 m and 0.01 m, respectively. The vapor pressures of Cs_2O were calculated from the experimentally determined parameters involved in Eq. (2) and are represented in Table 1. The linear least square fit of $\ln p(Cs_2O)$ vs $1/T$ for the experimental results can be represented by the relation

$$\ln\left(p(Cs_2O)/\mathrm{Pa}\right)(\pm 0.36) = -32102.4/T + 27.49, \quad (1100 \leqslant T/\mathrm{K} \leqslant 1254). \tag{3}$$

The experimental datapoints as well as the linear fit are shown in Fig. 1.

The incongruent vaporization of Cs_2ThO_3 yielding $Cs_2O(g)$ and $ThO_2(s)$ is given by Eq. (1). Therefore, the Gibbs energy change for the vaporization reaction can be expressed as

Table 1
Vaporization data and the Gibbs energy of formation of $Cs_2ThO_3(s)$

Temperature (K)	Time (s)	Mass collected $w(Cs_2O) \times 10^9$ (kg)	Pressure (Pa)	$\Delta_f G^\circ(Cs_2ThO_3, s)$ (kJ/mol)
1100	1200	8.48	0.191	−1299.4
1111	1020	9.54	0.255	−1294.6
1125	900	14.84	0.452	−1288.5
1159	840	22.26	0.737	−1273.6
1173	720	20.14	0.782	−1267.5
1188	720	31.81	1.244	−1260.9
1195	600	51.95	2.444	−1257.9
1223	480	50.89	3.028	−1245.6
1247	300	69.97	6.726	−1235.2
1254	300	78.45	7.563	−1232.1

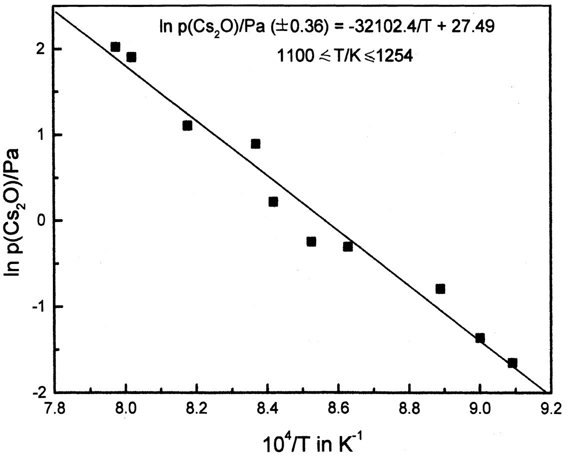

Fig. 1. $\ln p(Cs_2O)/Pa$ vs reciprocal temperature.

$$\Delta_r G^\circ = \Delta_f G^\circ(Cs_2O, g) + \Delta_f G^\circ(ThO_2, s) - \Delta_f G^\circ(Cs_2ThO_3, s), \qquad (4)$$

where $\Delta_f G^\circ$s are the Gibbs energies of formation of the respective compounds from the elements in their standard states at 1.01325×10^5 Pa pressure and $\Delta_r G^\circ$ is the standard Gibbs energy of the reaction in Eq. (1). The standard Gibbs energy of reaction can equated to $-RT \ln[p(Cs_2O)]$ since the values of $p(Cs_2O)$ given in Eq. (3) represent the equilibrium values. Eq. (4) can be rearranged and the standard Gibbs energy of formation of Cs_2ThO_3 is written as

$$\Delta_f G^\circ(Cs_2ThO_3, s) = \Delta_f G^\circ(ThO_2, s) + \Delta_f G^\circ(Cs_2O, g) + RT \ln p(Cs_2O). \qquad (5)$$

The values of the standard Gibbs energies of formation of $\Delta_f G^\circ(ThO_2, s)$ and $\Delta_f G^\circ(Cs_2O, g)$ required in Eq. (5) were obtained from literature [9]. Therefore, the standard Gibbs energy of formation of Cs_2ThO_3 could be calculated using Eqs. (3) and (5). The equation describing the temperature dependence of the Gibbs energy of formation of Cs_2ThO_3 is thus given by

$$\Delta_f G^\circ(Cs_2ThO_3, s)\ (\pm 20\ \text{kJ/mol}) = -1780.1 + 0.437T \quad (1100 \leqslant T/\text{K} \leqslant 1254). \qquad (6)$$

There is no previous report on the thermodynamic properties of this compound to compare with our data.

4. Conclusion

The Gibbs energy of formation of Cs_2ThO_3 derived from the vapor pressure measurements in this investigation can be used to predict the partial pressure of iodine gas in the fuel-clad gap of thoria based fuel. The calculated partial pressure of $I(g)$ at 1000 K and at an oxygen potential of −375 kJ/mol was found to be of the order of 10^{-8} Pa, which is far below the threshold value required for the stress corrosion cracking of the Zircaloy clad.

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References

[1] T.M. Chen, S.M. Kauzearich, J.D. Corbett, J. Nucl. Mater. 151 (1988) 225.
[2] P. Hofmann, J. Spino, J. Nucl. Mater. 127 (1985) 205.
[3] R. Kohli, W. Lacom, IAEA Tech. Committee Meeting on Fuel Rod Internal Chemistry and Fission Products Beha-

viour, Karlshruhe, Germany, 11–15 November 1985 (IWGFPT/25).

[4] O. Götzmann, J Nucl. Mater. 107 (1982) 185.

[5] R. Mishra, M. Ali (Basu), S.R. Bharadwaj, D. Das, J. Therm. Anal. (2001), in press.

[6] R.H. Lamoreaux, D.L. Hildenbrand, J. Phys. Chem. Ref. Data 13 (1984) 1514.

[7] R. Mishra, M. Ali (Basu), S.R. Bharadwaj, A.S. Kerkar, D. Das, S.R. Dharwadkar, J. Alloys Compounds 290 (1999) 97.

[8] D. Das, M.S. Chandrasekharaiah, High Temp. Sci. 21 (1987) 161.

[9] I. Barin, Thermochemical Data of Pure Substances, 3rd Ed., VCH, Weinheim, 1995.