

## Vaporization behavior and Gibbs energy of formation of $\text{Rb}_2\text{ThO}_3$

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### Abstract

The thermodynamic stability of rubidium thorate,  $\text{Rb}_2\text{ThO}_3(\text{s})$ , was determined from vaporization studies using the Knudsen effusion forward collection technique.  $\text{Rb}_2\text{ThO}_3(\text{s})$  vaporized incongruently and predominantly as  $\text{Rb}_2\text{ThO}_3(\text{s}) = \text{ThO}_2(\text{s}) + 2\text{Rb}(\text{g}) + 1/2\text{O}_2(\text{g})$ . The equilibrium constant  $K = p_{\text{Rb}}^2 \cdot p_{\text{O}_2}^{1/2}$  was evaluated from the measurement of the effusive flux due to Rb vapor species under the oxygen potential governed by the stoichiometric loss of the chemical component  $\text{Rb}_2\text{O}$  from the thorate phase. The Gibbs energy of formation of  $\text{Rb}_2\text{ThO}_3$  derived from the measurement and other auxiliary data could be given by the equation,  $\Delta_f G^\circ(\text{Rb}_2\text{ThO}_3, \text{s}) = -1794.7 + 0.42T \pm 5.0 \text{ kJ mol}^{-1}$  ( $1058 \leq T/\text{K} \leq 1187$ ).

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### 1. Introduction

The nuclear energy program in India envisages the use of thorium-based fuels in Advanced Heavy Water Reactors. For predicting the performance of the fuels, information on the thermochemistry of various fission products produced inside the fuel matrix is important. The fission product rubidium can react in presence of oxygen with the matrix forming the reported compound  $\text{Rb}_2\text{ThO}_3$  [1]. However, the thermodynamic stability of this compound is not reported so far. The stability data of rubidium thorate will be useful in predicting its chemical state inside the irradiated fuel/clad. Like the case of cesium [2–4] the possible other chemical states are their oxo-compounds with urania, and zirconia, and iodide by reaction with the fission product iodine. This study aimed at generating thermodynamic data of rubidium thorate from the vaporization behavior of the compound.

### 2. Experimental

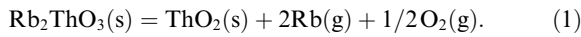
$\text{Rb}_2\text{ThO}_3$  was prepared from 2:1 mixture of  $\text{RbNO}_3$  and  $\text{ThO}_2$  by solid state reaction. The chemicals used for the preparation of the compound were  $\text{Rb}_2\text{CO}_3$  (99.975% purity, Aldrich, USA),  $\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$  (99.99%, Indian Rare Earths Ltd.) and AR grade  $\text{HNO}_3$ .  $\text{RbNO}_3$  was prepared by reacting  $\text{Rb}_2\text{CO}_3$  with nitric acid and then evaporating the solution to dryness.  $\text{RbNO}_3$  crystals were mixed with freshly prepared  $\text{ThO}_2$  powder (obtained by decomposition of  $\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$  in air at 700 K) in a Pt crucible and heated at 673 K for 1 h under Ar flow. Then under the inert gas blanket, the temperature was raised to 1173 K and the mixture was heated for 1 h for pyrolysis of the nitrate and formation of the thorate. The XRD pattern of the resulting product indicated lines due to  $\text{Rb}_2\text{ThO}_3$  (JCPDS 24-974) and  $\text{ThO}_2$  (JCPDS 4-556). The prepared sample was stored in vacuum for subsequent studies.

Thermogravimetric analysis carried out with the prepared compound showed a single step of weight loss at 1125 K. The residue from the TGA was analyzed by XRD and found to be  $\text{ThO}_2(\text{s})$ . Moreover, the residues

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from partially evaporated samples in TGA under inert gas flow and also under Knudsen evaporation conditions were analyzed. The XRD analysis revealed them to be a mixture of two condensed phases, namely  $\text{Rb}_2\text{ThO}_3(\text{s})$  and  $\text{ThO}_2(\text{s})$  only. The weight loss of the Rb bearing vapor species in TGA and in Knudsen effusion could be understood from reported thermodynamic data of the Rb–O system [5,6], which suggests that the volatilization of the sample under the prevailing low partial pressure of oxygen ( $\approx 5 \times 10^{-4}$  Pa) in the experiments was largely due to  $\text{Rb}(\text{g})$ . The predominant chemical path for the evaporation that involves the two condensed phases  $\text{Rb}_2\text{ThO}_3$  and  $\text{ThO}_2$  could be represented by



The equilibrium constant of reaction (1) is given by

$$K_p = p_{\text{Rb}}^2 \cdot p_{\text{O}_2}^{1/2} \quad (2)$$

$p_{\text{Rb}}$  and  $p_{\text{O}_2}$  are respectively the equilibrium vapor pressures of  $\text{Rb}(\text{g})$  and  $\text{O}_2(\text{g})$ . To derive the thermodynamic property of  $\text{Rb}_2\text{ThO}_3$  from the effusion technique, the knowledge of the oxygen partial pressure was thus essential.

The oxygen pressure within the Knudsen cell was controlled by the stoichiometric loss of the chemical component  $\text{Rb}_2\text{O}$  from the thorate and therefore by the effusion fluxes of the total Rb bearing species and  $\text{O}_2(\text{g})$  in their molar ratio of 4:1. The consideration of available thermodynamic data of the other Rb bearing gaseous species, namely,  $\text{Rb}_2\text{O}$ ,  $\text{RbO}$  and  $\text{Rb}_2$  showed that the effusion loss of the total Rb was mainly as  $\text{Rb}(\text{g})$ . The effusion flux of the total Rb could be approximated to that of  $\text{Rb}(\text{g})$ . By the kinetic theory of gases, the flux of a species being directly proportional to its vapor pressure within the cell and inversely to the square root of its molecular weight, the flux ratio of 1:4 of  $\text{Rb}(\text{g})$  and  $\text{O}_2(\text{g})$  leads to

$$p_{\text{Rb}} : p_{\text{O}_2} = 4(M_{\text{Rb}}/M_{\text{O}_2})^{1/2}. \quad (3)$$

The above equation is valid under the assumption that the effusion fluxes were hardly modified by the background pressure of oxygen ( $\approx 1 \times 10^{-4}$  Pa). In the working temperature range of this study, the partial pressures of  $\text{O}_2(\text{g})$  and  $\text{Rb}(\text{g})$  being orders of magnitude larger than the background pressure, Eq. (3) could be employed in the evaluation of  $p_{\text{O}_2}$ . The necessary data of  $p_{\text{Rb}}$  were obtained from the collection rate of total Rb in the forward vapor-collection technique.

The Knudsen effusion forward vapor collection apparatus used and the experimental details on the vapor collection on targets and the temperature measurement are given in Refs. [7,8]. The compound from the 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 loaded cell was immediately positioned within the Knudsen assembly and evacuated under a dynamic vacuum of  $5 \times 10^{-4}$  Pa.

Before starting the collection of effusate sufficient, degassing time was given for removal of traces of moisture in the sample as well as the cell at a temperature slightly above the highest working temperature. This was done to minimize the transport of Rb in the effusate in the form of  $\text{RbOH}(\text{g})$  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 in the exploratory run indicated that the rate of effusion of Rb bearing species steeply falls and settles to a constant value within a few minutes. To this constant value, the contribution of  $\text{RbOH}(\text{g})$  due to a constant ingress of water vapor into the cell from the background pressure of  $5 \times 10^{-4}$  Pa was negligible. Considering the steady-state dynamics of effusion through the cell-orifice it is estimated that the  $\text{RbOH}(\text{g})$  content in the effusate of  $\text{Rb}(\text{g})$ ,  $\text{RbO}(\text{g})$  and  $\text{Rb}_2\text{O}(\text{g})$  is less than 1% within the working temperatures of the present study.

The final effusion experiments were carried out at ten different settings of vapor collections within the working temperature range ( $1058 \leq T/\text{K} \leq 1187$ ). To avoid systematic errors, the isothermal vapor collections were carried out with increase as well as with decrease of temperatures. The vapor deposited on water-cooled tantalum targets was chemically analyzed by bringing it into aqueous medium and measuring the Rb 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 equilibrium constant  $K$  of reaction (1). The vapor pressure expression for  $\text{Rb}(\text{g})$  in the Knudsen cell obtained by using the kinetic theory of the gases and the geometry of vapor collection, could be given by the relation

$$p_{\text{Rb}} = (1/A) \times (N_{\text{Rb}}/t) \times [(r^2 + d^2)/r^2] \times [2\pi RTM_{\text{Rb}}]^{1/2}. \quad (4)$$

In Eq. (4),  $N_{\text{Rb}}$  are the moles of  $\text{Rb}(\text{g})$  with molecular mass  $M_{\text{Rb}}$  collected on the target during time  $t$  in the effusion experiment.  $A$  is the cross-section area of the orifice,  $R$  is the gas constant and  $T$  is the temperature of the Knudsen cell during the vapor collection. The quantity  $[(r^2 + d^2)/r^2]$  is the geometric factor,  $r$  being the radius of the collimator for the target collection and  $d$  the vertical separation between the orifice and the

collimator. Typical values of the parameters  $A$ ,  $d$  and  $r$  used in the experiments were  $7.85 \times 10^{-7} \text{ m}^2$ ,  $0.0696$  and  $0.011 \text{ m}$ , respectively. The values of the equilibrium constant  $K_p$  of reaction (1) were obtained with its pressure unit expressed in Pascal at different temperatures by considering Eq. (4) along with (3). The values are given in Table 1 along with values of the other data of the effusion experiments. The second law plot of  $\ln K_p$  versus  $1/T$  is included in Fig. 1. Linear least-squares fit of the plotted second-law data can be given by

$$\ln K_p = -69139/T + 58.1 \pm 0.3 \quad (1058 \leq T/K \leq 1187). \quad (5)$$

The standard Gibbs energy change for the incongruent vaporization of  $\text{Rb}_2\text{ThO}_3$  through the predominant reaction (1) can be expressed as

$$\Delta_r G^\circ = 2\Delta_r G^\circ(\text{Rb}, \text{g}) + 1/2 \Delta_r G^\circ(\text{O}_2, \text{g}) + \Delta_r G^\circ(\text{ThO}_2, \text{s}) - \Delta_r G^\circ(\text{Rb}_2\text{ThO}_3, \text{s}), \quad (6)$$

where  $\Delta_r G^\circ$  is the Gibbs energy of formation of the respective compounds from the elements in their standard states at  $1.01325 \times 10^5 \text{ Pa}$  pressure. The value of  $\Delta_r G^\circ(\text{O}_2, \text{g})$  is zero and so is for the value of  $\Delta_r G^\circ(\text{Rb}, \text{g})$  for the present working temperature range of  $1058$ – $1187 \text{ K}$ , which is above the boiling point of  $968 \text{ K}$  of  $\text{Rb}$  liquid [9]. The standard Gibbs energy of the reaction can be equated to  $-RT \ln K^0$ ,  $K^0$  being the value of the equilibrium constant of reaction (1) expressed with reference to  $1.01325 \times 10^5 \text{ Pa}$  pressure of  $\text{Rb}(\text{g})$  and  $\text{O}_2(\text{g})$ . Thus  $K^0$  was evaluated from  $K_p$  given in Eq. (5) as  $K^0 = K_p / (1.01325 \times 10^5)^{5/2}$ . Eq. (6) can be rearranged and the standard Gibbs energy of formation of  $\text{Rb}_2\text{ThO}_3$  is written as

$$\begin{aligned} \Delta_r G^\circ(\text{Rb}_2\text{ThO}_3, \text{s}) &= \Delta_r G^\circ(\text{ThO}_2, \text{s}) + RT \ln K^0 \\ &= -1794.7 + 0.42T \pm 3.8 \text{ kJ mol} \\ &(1058 \leq T/K \leq 1187). \end{aligned} \quad (7)$$

Table 1

Vaporization data and the derived equilibrium constant  $K_p$ 

Serial no.	Temperature (K)	Time (s)	Rb collected ( $10^{-9} \text{ kg}$ )	$K_p = p_{\text{Rb}}^2 \cdot p_{\text{O}_2}^{1/2}$ ( $p$ in Pa)
1	1058	1800	3.4	$6.95 \times 10^{-4}$
2	1067	1800	4.9	$1.75 \times 10^{-3}$
3	1087	1200	4.4	$3.77 \times 10^{-3}$
4	1087	1800	6.0	$2.97 \times 10^{-3}$
5	1091	1800	8.0	$6.13 \times 10^{-3}$
6	1103	1080	5.0	$6.88 \times 10^{-3}$
7	1107	1200	8.0	$1.72 \times 10^{-2}$
8	1125	900	7.0	$2.58 \times 10^{-2}$
9	1156	900	16.0	0.211
10	1187	600	19.0	0.923

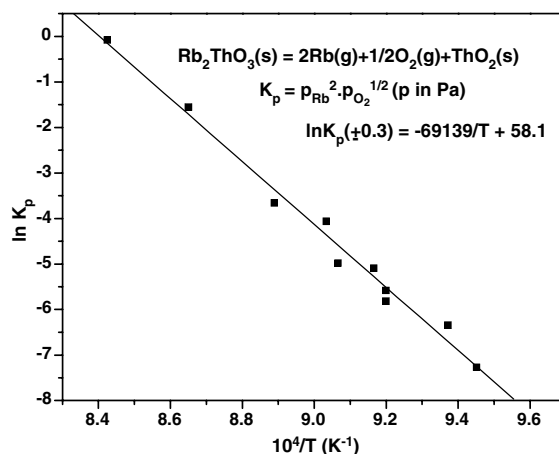
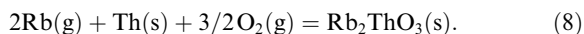


Fig. 1.  $\ln K_p$  versus reciprocal temperature for the reaction  $\text{Rb}_2\text{ThO}_3(\text{s}) = \text{ThO}_2(\text{s}) + 2\text{Rb}(\text{g}) + 1/2 \text{O}_2(\text{g})$ .

The  $\Delta_r G^\circ$  expression refers to the formation reaction



The  $\Delta_r G^\circ(\text{ThO}_2, \text{s})$  values required in the above evaluation of  $\Delta_r G^\circ(\text{Rb}_2\text{ThO}_3, \text{s})$  was taken from the literature [9]. From Eq. (7), the second-law values of standard enthalpy and entropy of reaction (8) are seen to be  $-1794.7 \text{ kJ mol}^{-1}$  and  $-420 \text{ J K}^{-1} \text{ mol}^{-1}$ , respectively, at the mean working temperature of  $1123 \text{ K}$ . The values were extrapolated to  $298 \text{ K}$  using the reported standard heat capacity data [9] of thoria,  $\text{Rb}(\text{g})$  and oxygen, and estimated heat capacity of rubidium thorate. The estimation was based on Kopp's rule of additivity of heat capacities of the constituent oxides, i.e.,  $\text{ThO}_2(\text{s})$  and  $\text{Rb}_2\text{O}(\text{s})$  [9]. As  $\text{Rb}_2\text{O}(\text{s})$  is not a stable phase above the temperature of  $778 \text{ K}$ , extrapolated values of the heat capacity of the solid phase was employed between  $778$  and  $1123 \text{ K}$ . The enthalpy and entropy values for reaction (8) at  $298.15 \text{ K}$  thus worked out to be  $-1830.5 \text{ kJ mol}^{-1}$  and  $-487.8 \text{ J K}^{-1} \text{ mol}^{-1}$ , respectively. From this result the values of  $\Delta_r H^0(\text{Rb}_2\text{ThO}_3, 298.15 \text{ K})$  and

$S^0(\text{Rb}_2\text{ThO}_3, 298.15 \text{ K})$  worked out to be  $-1668.7 \text{ kJ mol}^{-1}$  and  $213.5 \text{ JK}^{-1} \text{ mol}^{-1}$ , respectively. Considering the uncertainty of the equilibrium data of reaction (1) as given in Eq. (5), and also the uncertainties of the auxiliary data used the derived values of the standard enthalpy and entropy of formation of  $\text{Rb}_2\text{ThO}_3(\text{s})$  at 298.15 K have the overall uncertainties of  $\pm 25 \text{ kJ mol}^{-1}$  and  $\pm 20 \text{ JK}^{-1} \text{ mol}^{-1}$ , respectively.

The standard value of the enthalpy of formation of rubidium thorate from its constituent oxides,  $\text{ThO}_2(\text{s})$  and  $\text{Rb}_2\text{O}(\text{s})$ , was calculated from Eq. (7) at the mean working temperature of 1123 K. Barin's [9] thermochemical table for  $\text{Rb}_2\text{O}(\text{s})$  gives the data for three solids (Sol-C, Sol-B and Sol-A) with transition temperatures at 543 K (Sol-C to Sol-B), 613 K (Sol-B to Sol-A) and the melting point of Sol-A at 778 K. Therefore, for calculating the standard value of the enthalpy of formation of rubidium thorate from its constituent oxides,  $\text{ThO}_2(\text{s})$  and  $\text{Rb}_2\text{O}(\text{s})$ , the extrapolated data of the reported high temperature solid phase (Sol-A, [9]) of  $\text{Rb}_2\text{O}$  was employed. The enthalpy of formation from the constituent oxides at 1123 K worked out to be  $-110.5 \text{ kJ mol}^{-1}$ . The corresponding value at 298.15 K worked out to be  $-103.3 \text{ kJ mol}^{-1}$ . The enthalpy of formation from constituent oxides value at 1123 K compares well with the corresponding value of  $-118 \text{ kJ mol}^{-1}$  for  $\text{Cs}_2\text{ThO}_3$  derivable from its reported thermodynamic data [10]. The reported basicity of  $\text{Rb}_2\text{O}(\text{s})$  and  $\text{Cs}_2\text{O}(\text{s})$  based on statistical analysis [11] on several Rb and Cs based compounds suggests that the stabilities of thorates of Rb and Cs should be similar as derived from this study.

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