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Letter to the Editors

Gibbs energy of formation of thorium molybdate ($ThMo_2O_8$) by the transpiration technique

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Abstract

The Gibbs energy of formation of $ThMo_2O_8$ (s) was determined from its vapour pressure measured by the transpiration technique. $ThMo_2O_8$(s) vapourized incongruently according to the reaction $n\mathrm{ThMo_2O_8(s)} = n\mathrm{ThO_2(s)} + 2(\mathrm{MoO_3})_n\mathrm{(g)}$, $n = 3$, 4 and 5. The Gibbs energy of formation of $ThMo_2O_8$(s) derived from the vapour pressure of $(MoO_3)_3$ could be expressed by the relation $\Delta_f G° = -2682.6 + 0.595T \pm 12.8$ kJ mol^{-1} ($1195 \leqslant T/K \leqslant 1291.5$). The standard enthalpy of formation ($\Delta_f H°298.15$ K) of solid $ThMo_2O_8$ derived from the enthalpy of formation at the mean temperature of the measurements using estimated values for the heat capacity of the compound was found to be $\Delta_f H° = -(2737.4 \pm 15.0)$ kJ mol^{-1} at 298 K.

1. Introduction

The increasing interest in utilization of thorium for production of nuclear energy in the third phase of Indian nuclear power reactors [1] necessitates the study of the thermochemistry of a number of thorium compounds formed in the multicomponent systems involving thorium dioxide and the oxides of several major fission products produced in the fission of heavy nuclei. The thermochemical information on various phases formed is needed in the prediction of formation of such compounds during fuel irradiation and its subsequent influence on the fuel performance. In this paper we report our results on the vapour pressure and Gibbs energy of formation of $ThMo_2O_8$ as a prelude to our detailed investigations on the thermochemistry of thorium compounds containing some of the major fission products and having relevance in nuclear technology.

2. Experimental

The compound $ThMo_2O_8$ was prepared by heating a thoroughly ground mixture of ThO_2 and MoO_3 in 1:2 molar ratio at 925 K as reported in the literature [2]. The procedure involves heating the mixture in a platinum boat at the rate of 2 K min^{-1} to the desired temperature in flowing argon and holding for 48 h with intermittent grinding. The completion of the reaction was confirmed from the X-ray powder diffraction of the product. The stoichiometry was also independently established by chemical analysis. $ThMo_2O_8$ vaporized incongruently according to the reaction

$$n\ \mathrm{ThMo_2O_8(s)} = n\ \mathrm{ThO_2(s)} + 2(\mathrm{MoO_3})_n\mathrm{(g)},$$
$$n = 3, 4 \text{ and } 5. \quad (1)$$

The stoichiometry of the reaction was established from the X-ray diffraction pattern of the partially vaporized $ThMo_2O_8$ and the X-ray and the chemical analysis of the condensate obtained in the cooler region of the reaction tube. The vapour pressure of the Mo bearing species over $ThMo_2O_8$(s) was measured using the novel thermogravimetric transpiration apparatus described elsewhere [3]. The experimental details involving the measurement of temperature and flow rate are given in

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Refs. [4,5]. The mass loss of the sample per unit volume of the carrier gas (oxygen) swept over it was monitored as a function of flow rate at 1241 K. It was found to remain constant in the range of flow rates between 3 and 3.5 l/h indicating thereby the saturation of the carrier gas by the vapour. The plot of apparent pressure of the molybdenum bearing species as a function of the flow rate at 1241 K is shown in Fig. 1. The measurements at different temperatures were carried out employing the flow rate of 3.35 l h^{-1}.

3. Results and discussion

It is known that $MoO_3(s)$ vapourizes predominantly as $(MoO_3)_n$ in one atmosphere oxygen partial pressure [6] according to the reaction n MoO_3 (s) = $(MoO_3)_n$, where $n = 3$, 4 and 5. The molybdenum bearing species over the mixture of $ThMo_2O_8$ (s) and ThO_2 (s) (Eq. (1)) were assumed to be identical to those over pure $MoO_3(s)$.

The apparent pressure p^{app} of molybdenum bearing species in equilibrium with $ThMo_2O_8(s)$ was calculated from the mass loss of the sample per unit volume of the carrier gas swept over it from the relation

$$p^{app} = (W/V_c)\,(RT_c/M), \tag{2}$$

where W is the mass transported, V_c is the total volume of the carrier gas passed over the sample, T_c is the ambient temperature (in the present case, (299 ± 0.5) K) at which the volume of the carrier gas is measured and M is the molecular weight of the vapourising species. In the present calculation, the molecular weight of vapourising species was assumed to be that of $(MoO_3)_3$ in order to obtain the apparent vapour pressure p_3^{app}. The vapour species consist predominantly of $(MoO_3)_3$ in addition to the lesser amounts of $(MoO_3)_4$ and $(MoO_3)_5$ [6]. The chemical analysis of the condensate deposited on the cooler part of the walls of the hang down tube showed the presence of MoO_3 (s) only. From the apparent pressure of the trimer derived from the experimental data, the equilibrium pressure of the trimer was obtained using the following treatment. The apparent pressure of the trimer can be written as

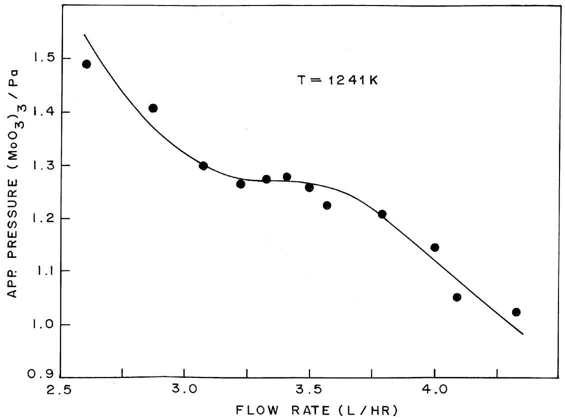

Fig. 1. Apparent pressure of the molybdenum bearing species $(MoO_3)_3$ as a function of the flow rate at 1241 K.

$$p_3^{app} = p_3 + 4/3p_4 + 5/3p_5, \tag{3}$$

where p_3, p_4 and p_5 are the equilibrium partial pressures of the trimer, tetramer and pentamer of the molybdenum trioxide species in the vapour phase. The equilibria between the trimer, tetramer and pentamer could be expressed by the following equations:

$$4(MoO_3)_3 = 3(MoO_3)_4, \quad K_1 = p_4^3/p_3^4, \tag{4}$$

$$5(MoO_3)_3 = 3(MoO_3)_5, \quad K_2 = p_5^3/p_3^5, \tag{5}$$

where K_1 and K_2 are the equilibrium constants for the reactions given in Eqs. (4) and (5), respectively.

The relation between the apparent pressure and the equilibrium pressure of the trimer could be expressed as

$$p_3^{app} = p_3 + 4/3K_1^{1/3}p_3^{4/3} + 5/3K_2^{1/3}p_3^{5/3}. \tag{6}$$

The equilibrium pressures of the trimer was calculated from the apparent pressure employing the relation given in Eq. (6). The constants K_1 and K_2 could be obtained from the data compiled by Brewer and Lamoreaux [6]. The values of the apparent vapour pressure of $(MoO_3)_3$ calculated from the measured mass loss due to vaporization of $ThMo_2O_8$ at different temperatures are listed in Table 1.

The equilibrium pressure of $(MoO_3)_3$ derived from the apparent pressure considering the presence of tetramers and pentamers in the vapour phase, as a function of temperature, could be expressed by the relation

$$\ln p(MoO_3)_3/\mathrm{Pa} = -41579.0/T + 33.81 \pm 0.04. \tag{7}$$

The plot of the logarithm of the trimer pressure vs. reciprocal of temperature is given in Fig. 2.

The compound $ThMo_2O_8$ is reported to undergo a phase transformation [7] at 1223 K. We could confirm this phase transition from the DTA of the compound recorded in oxygen atmosphere at 5 K min^{-1} heating rate. The phase transformation temperature recorded from DTA was 1213 K in fairly good agreement with that reported in the literature [7]. The enthalpy of this transition derived from the DTA curve was about 2 kJ mol^{-1} whereas the error in the enthalpy of formation of $ThMo_2O_8$ derived from the pressure measurements worked out to be about 12 kJ mol^{-1}. The plot of ln $p(MoO_3)_3$/Pa vs. $1/T$ (Fig. 2) does not show any break at the transition temperature as the enthalpy change for this transition is very low. Subsequently, the enthalpy change for this phase transformation was not taken into

Table 1
Standard Gibbs energy of formation $\Delta_f G°\mathrm{ThMo_2O_8(s)}$

Temperature (K)	Mass loss (mg l^{-1})	$p_3^{\mathrm{app}}(\mathrm{MoO_3})_3$ (Pa)	$p_3(\mathrm{MoO_3})_3$ (Pa)	$\Delta_f G°\mathrm{ThMo_2O_8(s)}$ (kJ $\mathrm{mol^{-1}}$)
1195.0	0.073	0.42	0.39	−1974.04
1205.0	0.088	0.51	0.48	−1968.75
1214.0	0.120	0.69	0.64	−1963.11
1228.0	0.178	1.02	0.95	−1954.81
1238.0	0.233	1.34	1.24	−1948.92
1249.0	0.306	1.76	1.62	−1942.56
1257.0	0.414	2.38	2.18	−1937.20
1266.5	0.545	3.14	2.87	−1931.38
1283.0	0.734	4.23	3.86	−1922.44
1291.5	0.968	5.57	5.05	−1916.95

consideration during the calculation of the standard enthalpy of formation for this compound at 298.15 K using the second-law enthalpy at the mean temperature of the measurement.

The Gibbs energy of formation for $\mathrm{ThMo_2O_8}$ can be obtained from the reaction

$$3\mathrm{ThMo_2O_8(s)} = 3\mathrm{ThO_2(s)} + 2(\mathrm{MoO_3})_3(\mathrm{g}).$$

The standard Gibbs energy change for this reaction can be expressed by

$$\Delta_r G° = 3\Delta_f G°\mathrm{ThO_2(s)} + 2\Delta_f G°(\mathrm{MoO_3})_3(\mathrm{g}) - 3\Delta_f G°\mathrm{ThMo_2O_8(s)}. \quad (8)$$

From this $\Delta_f G°$ of $\mathrm{ThMo_2O_8(s)}$ can be written as

$$3\Delta_f G°\mathrm{ThMo_2O_8(s)} = 3\Delta_f G°\mathrm{ThO_2(s)} + 2\Delta_f G°(\mathrm{MoO_3})_3(\mathrm{g}) - \Delta_r G° \quad (9)$$

i.e.

$$3\Delta_f G°\mathrm{ThMo_2O_8(s)} = 3\Delta_f G°\mathrm{ThO_2(s)} + 2\Delta_f G°(\mathrm{MoO_3})_3(\mathrm{g}) + 2RT\ \ln p_3. \quad (10)$$

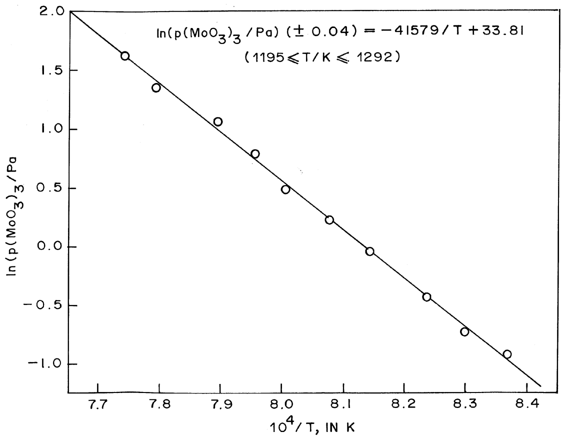

Fig. 2. ln $p(\mathrm{MoO_3})_3$ of $\mathrm{ThMo_2O_8}$ vs. reciprocal temperature.

The values of $\Delta_f G°\mathrm{ThO_2(s)}$ and $\Delta_f G°(\mathrm{MoO_3})_3(\mathrm{g})$ are taken from the compilation of Knacke et al. [8]. The $\Delta_f G°\mathrm{ThMo_2O_8(s)}$ derived from Eq. (10) could be expressed by the equation

$$\Delta_f G°\mathrm{ThMo_2O_8(s)} = -2682.6 + 0.595T \pm 12.8\ \mathrm{kJ\ mol^{-1}} \quad (1195 \leqslant T/\mathrm{K} \leqslant 1291.5) \quad (11)$$

and Table 1 presents $\Delta_f G°\mathrm{ThMo_2O_8(s)}$ values at the temperatures of this measurement.

4. Conclusion

The Gibbs energy of formation of $\mathrm{ThMo_2O_8}$ reported in this paper was obtained from the vapour pressure of the compound measured in the temperature range $1195 \leqslant T/\mathrm{K} \leqslant 1292$. There are no other data available in the literature on the thermodynamic stability of this compound. The standard enthalpy of formation of $\mathrm{ThMo_2O_8}$ derived from these measurements using the estimated value for the heat capacity of the compound was found to be $\Delta_f H° = -(2737.4 \pm 15.0)\ \mathrm{kJ\ mol^{-1}}$ at 298.15 K. This is in excellent agreement with the value of $-(2726.0 \pm 15.0)\ \mathrm{kJ\ mol^{-1}}$ estimated using the model proposed recently by Zhuang et al. [9] for determining the standard enthalpy of formation of ternary compounds from their binary oxide components. The calorimetric experiments are in progress to check the value of the standard enthalpy of formation derived from vapour pressure measurements.

References

[1] R. Chidambaram, in: M. Srinivasan, I. Kimura (Eds.), Proceedings of the Indo-Japan Seminar on Thorium Utilization, 10–13 December 1990, Bombay, India, p. 7.
[2] J. Thoret, Rev. Chim. Miner. 11 (1974) 237.
[3] S.R. Dharwadkar, A.S. Kerkar, M.S. Samant, Thermochim. Acta 217 (1993) 175.

[4] S.R. Dharwadkar, M.S. Samant, A.S. Kerkar, in: P.V. Ravindran, M. Sudersanan, S.R. Bharadwaj, S.R. Dharwadkar (Eds.), Proceedings of the Ninth Symposium on Thermal Analysis, 8–10 November 1993, Goa University, Goa, India, p. 590.
[5] O.M. Sreedharan, S.R. Dharwadkar, M.S. Chandrasekharaiah, BARC Internal Report No. I-239, 1973.
[6] L. Brewer, R.H. Lamoreaux, R. Ferro, R. Marazza, K.Girgis, in: L. Brewer (Ed.), Molybdenum: Physico-Chemical Properties of its Compounds and Alloys, IAEA Review, Special Issue No. 7, IAEA, Vienna, 1980.
[7] J. Thoret, A. Rimsky, W. Freundlich, C.R. Acad. Sci. Ser. C 267 (1968) 1682.
[8] O. Knacke, O. Kubaschewski, K. Hesselmann (Eds.), Thermochemical Properties of Inorganic Substances, Springer, Berlin, 1991.
[9] W. Zhuang, J. Liang, Z. Quiao, J. Shen, Y. Shi, G. Rao, J. Alloys Compounds 267 (1998) 6.