The standard molar enthalpy of formation of $ThMo_2O_8$

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Abstract

The molar enthalpies of solution of $ThMo_2O_8$, Mo, and ThF_4 in (10 mol dm^{-3} HF(aq) + 4.41 mol dm^{-3} H_2O_2(aq)) have been measured using an isoperibol calorimeter. From these results and other auxiliary data, the standard molar enthalpy of formation of $ThMo_2O_8$ has been calculated to be $\Delta_f H_m^0(298.15\ K) = (-2742.2 \pm 4.5)$ kJ mol^{-1}. This value of enthalpy of formation of $ThMo_2O_8$ is consistent with the second law enthalpy of formation of $ThMo_2O_8$ determined in this laboratory by transpiration technique. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The increasing interest in utilisation of thorium in the third phase of Indian nuclear power reactors necessitates the study of thermochemistry of a number of thorium compounds formed in the multicomponent systems involving thorium dioxide and the oxides of several major fission products produced during the fission of heavy nuclei. The thermochemical information on the various phases formed is needed in the prediction of formation of such compounds during fuel irradiation and its subsequent influence on the fuel performance. Recently, we investigated the vaporization behaviour of thorium molybdate ($ThMo_2O_8$) and reported its Gibbs energy of formation [1]. In the present paper, we report the enthalpy of formation of the ternary compound $ThMo_2O_8$ obtained using solution calorimetry.

2. Experimental

$ThMo_2O_8$ was prepared by heating a mixture of ThO_2 (99.9% pure, Metallurgy Division, BARC) and MoO_3 (AR grade, Mallinkrodt Chemicals, USA) in the required stoichiometric 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 air and holding for 48 h with intermittent grinding. The complete formation of $ThMo_2O_8$ was confirmed by X-ray diffraction (XRD) and chemical analysis. Thorium was determined by precipitating as oxalate which was then ignited and weighed as the dioxide. The observed Th content of the compound was 42.11 ± 0.15 mass% as against the calculated 42.04. Molybdenum was determined by spectrophotometric method by complexing with hydrogen peroxide. The observed Mo content of the compound was 34.39 ± 0.50 mass% as against the calculated 34.77. ThF_4 (99.9% pure) was obtained from Fuel Chemistry Division, BARC.

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The enthalpies of solution were measured in an isoperibol calorimeter which is a modified version of the instrument reported earlier [3,4]. Briefly, the calorimeter was made from a glass Dewar of 0.300 dm^3 capacity, which was enclosed in a nickel plated copper container. The annular space between the Dewar flask and the container was packed with fine glass wool. The copper container was covered with a flange having a O-ring grove. The flange had leak-tight fittings for introducing a glass stirrer, a sample bulb, a heater and a thermistor. The heater was fabricated by winding Teflon coated manganin wire over a Teflon disk and the leads of the heater were taken through a twin bore alumina tube of 3 mm diameter. The resistance of the heater was $(5.300 \pm 0.001)\ \Omega$. Stirring at seven revolutions per second was achieved using a synchronous motor. The calorimeter was kept in a constant-temperature bath having a control accuracy of ± 0.5 K. The temperature of the bath was kept at 298.15 K during the experiments. A control unit consisting of a stabilised power-supply unit, a heater power-supply unit, a bridge amplifier and quartz timer was fabricated for calibrating and recording the calorimeter signals. The output of the control unit was fed to a recorder (Rika Denki, Model No. R-56-53).

The performance of the calorimeter was tested using NBS KCl (SRM 1655) which had been heated at 800 K to remove occluded water, cooled and stored in a dessiccator. Each dissolution of KCl was carried out with 0.100 dm^3 of distilled water. Each dissolution of ThMo$_2$O$_8$, ThF$_4$ and Mo was done with 0.100 dm^3 of solution containing (10 mol dm^{-3} HF(aq) + 4.41 mol dm^{-3} H$_2$O$_2$(aq)). The glass Dewar flask, stirrer, heater and the thermistor were given a uniform coating of polyethylene to prevent the attack by hydrofluoric acid. The sample was weighed in a gelatin capsule and introduced into the solution only after a steady state signal was obtained on the strip chart recorder. The energy equivalent of the calorimeter was determined by electrical calibration using standard resistance, before and after each experiment. In case of ThMo$_2$O$_8$ and ThF$_4$ dissolution the length of the main period was less than 5 min. Therefore, in these two cases the temperature change ΔT during the reaction was corrected by the method of Kubaschewski and Alcock [5] and was used for the evaluation of the enthalpy of the reaction. In case of Mo dissolution the length of the main period was

about 30 min. As a short main period did not occur in case of Mo dissolution, the corrected temperature increase was obtained by the method of Fitzsimmons and Kirkbride [6]. The temperature T of the reaction vessel was carefully adjusted until $\mathrm{d}T/\mathrm{d}t < 10^{-5}$ K min^{-1}. A gelatin capsule, and not the usual glass bulb, was used for introducing the samples, and therefore, the correction for evaporation of water is insignificant in the case of ThF$_4$. A correction of 0.65 KJ mol^{-1} was applied for evaporation of water in case of ThMo$_2$O$_8$ and Mo dissolutions where 1 mol of oxygen and 1 mol of hydrogen are evolved, respectively, per mole of the solute. The necessary data were obtained from [7,8] for computing this value. Corrections were applied for the dissolution of gelatin capsule in the solvent.

3. Results and discussion

The molar enthalpies of solution $\Delta_{\mathrm{sol}}H_{\mathrm{m}}$ of KCl corresponding to the reaction:

$$\mathrm{KCl} + v\mathrm{H_2O} = \mathrm{KCl} \cdot v(\mathrm{H_2O})$$
$$(v = 3500 \rightarrow 5000)$$
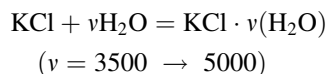
were used with the Debye-Hückel limiting law [9] to calculate the molar enthalpy of solution at infinite dilution: $\Delta_{\mathrm{sol}}H_{\mathrm{m}}^{\infty}(\mathrm{KCl}, \ 298.15\ \mathrm{K}) = (17.18 \pm 0.07)$ kJ mol^{-1}. This value agrees within the uncertainty bounds with values reported by Sahanuja and Cesari [10]: (17.206 ± 0.092) kJ mol^{-1}, and the NBS: (17.241 ± 0.018) kJ mol^{-1} [11]. These results give the precision and accuracy of the present calorimetric measurements.

The results of the enthalpies of solution of ThMo$_2$O$_8$, ThF$_4$ and Mo are given in Table 1. Here m denotes the mass of the sample dissolved. ΔH is the measured energy change and $\Delta_{\mathrm{sol}}H_{\mathrm{m}}$ is the enthalpy of solution per mole of the solute. The thermochemical cycle from which the standard molar enthalpy of formation of ThMo$_2$O$_8$ has been derived is given in Table 2. The molar enthalpies of solution of ThMo$_2$O$_8$(s), Mo(s) and ThF$_4$(s) in (10 mol dm^{-3} HF(aq) + 4.41 mol dm^{-3} H$_2$O$_2$(aq)) have been measured to be (-374.19 ± 0.61) kJ mol^{-1}, (-672.23 ± 1.08) kJ mol^{-1} and (-3.3 ± 0.31) kJ mol^{-1}, respectively. In case of ThMo$_2$O$_8$ and Mo, corrections for evaporation of water have been incorporated. The

Table 1
The molar enthalpy of solution of $ThMo_2O_8(s)$, $Mo(s)$ and $ThF_4(s)$ in 0.100 dm^3 of (4.41 mol dm^{-3} H_2O_2 + 10 mol dm^{-3} HF) at 298.15 K

	m(solute) (g)	ΔH (J)	$\Delta_{sol}H_m$ (kJ mol^{-1})
$ThMo_2O_8(s)$	0.0677	−45.78	−373.21
$M = 551.9133$	0.0466	−31.60	−374.26
	0.0554	−37.52	−373.79
	0.0583	−39.39	−372.90
			average:−373.54 ± 0.61[a]
			Evaporation correction: −0.65
			Corrected value: −374.19 ± 0.61
$Mo(s)$	0.0879	−615.60	−671.91
$M = 95.94$	0.0758	−529.45	−670.12
	0.0928	−650.68	−672.70
	0.1483	−1038.10	−671.58
			average: −671.58 ± 1.08[a]
			Evaporation correction: −0.65
			Corrected value −672.23 ± 1.08
$ThF_4(s)$	0.1068	−1.08	−3.11
$M = 308.0317$	0.1123	−1.09	−2.99
	0.2134	−2.36	−3.41
	0.1091	−1.30	−3.67
			Average: −3.30 ± 0.31[a]

[a] Uncertainties are standard deviations of the mean; M: molar mass in g mol^{-1}.

enthalpies of solution of HF(40% aq), (i.e. HF·2H$_2$O), H$_2$O$_2$(30% aq), (i.e. H$_2$O$_2$·5H$_2$O) and H$_2$O(l) in the solvent (i.e.(10 mol dm^{-3} HF(aq) + 4.41 mol dm^{-3} H$_2$O$_2$(aq))) have also been measured and found to be (-0.95 ± 0.08) kJ mol^{-1}, (-0.23 ± 0.03) kJ mol^{-1} and (-0.61 ± 0.05) kJ mol^{-1}, respectively. These values have been combined with other auxiliary data such as the standard molar enthalpy of formation of ThF$_4$(s) (-2098.04 ± 2.09) kJ mol^{-1} [12], HF·2H$_2$O (-320.21 ± 0.65) kJ mol^{-1} [13,14], H$_2$O$_2$·5H$_2$O

(-190.95 ± 0.85) kJ mol^{-1} [15], and H$_2$O(l) (-285.83 ± 0.04) kJ mol^{-1} [14], to derive the standard molar enthalpy of formation $\Delta_f H_m^0$(298.15 K) of ThMo$_2$O$_8$(s) = (-2742.2 ± 4.5) kJ mol^{-1}. There are no previous reports on this quantity.

The scheme given in Table 2 was arrived at in the following manner. A mixture of HF and H$_2$O$_2$ was employed as the solvent for the dissolution experiments. It was found that MoO$_3$ could be dissolved only in alkali medium where ThMo$_2$O$_8$ could not be dis-

Table 2
Reaction scheme for the standard molar enthalpy of formation of $ThMo_2O_8(s)$ sln = 0.100 dm^3 of (4.41 mol dm^{-3} H_2O_2 + 10 mol dm^{-3} HF) solution $\Delta H_{11} = -\Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 - \Delta H_5 + \Delta H_6 + \Delta H_7 + \Delta H_8 + \Delta H_9 + \Delta H_{10}$[a]

Reaction	ΔH_m^0 (kJ mol^{-1})
1. $ThMo_2O_8(s) + [9HF + 7H_2O_2] (sln) = H_3Th(O_2)_3F(s) + [2[MoO(O_2)F_4]^{2-} + 4H^+ + 8H_2O](sln) + O_2(g)$	−374.19 ± 0.61
2. $ThF_4(s) + 3H_2O_2 (sln) = H_3Th(O_2)_3F(s) + 3HF(sln)$	−3.30 ± 0.31
3. $2Mo(s) + [8HF + 6H_2O_2](sln) = [2[MoO(O_2)F_4]^{2-} + 4H^+ + 6H_2O](sln) + 2H_2(g)$	−1344.46 ± 2.16
4. $4HF(aq) = 2H_2(g) + 2F_2(g)$	1280.84 ± 2.60
5. $4HF(aq) + (sln) = 4HF(sln)$	−3.80 ± 0.32
6. $Th(s) + 2F_2(g) = ThF_4(s)$	−2098.04 ± 2.09
7. $2H_2(g) + 2O_2(g) = 2H_2O_2(aq)$	−381.90 ± 1.70
8. $2H_2O_2(aq) + (sln) = 2H_2O_2(sln)$	−0.46 ± 0.06
9. $2H_2(g) + O_2(g) = 2H_2O(l)$	−571.66 ± 0.08
10. $2H_2O(l) + (sln) = 2H_2O(sln)$	−1.22 ± 1.00
11. $Th(s) + 2Mo(s) + 4O_2(g) = ThMo_2O_8(s)$	−2742.21 ± 4.5

[a] HF(aq) = HF·2H$_2$O and H$_2$O$_2$(aq) = H$_2$O$_2$·5H$_2$O.

solved in the same medium. A method was, therefore, devised which does not involve MoO_3 dissolution. We tried to dissolve Mo metal in HF but found that it could be dissolved only in a mixture of $HF + H_2O_2$. The species formed by the dissolution of $ThMo_2O_8$ in $HF + H_2O_2$ mixture was deduced as follows. It should be noted that $ThMo_2O_8$ also does not completely dissolve in $HF + H_2O_2$ mixture. Cotton and Wilkinson [16] state that addition of hydrogen peroxide to Th^{4+} salts gives a highly insoluble white precipitate of variable composition which contains an excess of anions in addition to peroxide. In our attempts to dissolve $ThMo_2O_8$ in $HF + H_2O_2$ mixture also we observed this white precipitate. Cotton and Wilkinson [16] give the approximate formula for this precipitate as $Th(O_2)_{3.2}X_{0.5}{}^-O_{0.15}{}^{2-}$. We have assumed the composition of the precipitate to be $H_3Th(O_2)_3F$ so that a suitable thermochemical cycle can be set up which gives the final reaction as formation of $ThMo_2O_8$ from the elements in their standard state. As this compound gets cancelled out in the thermochemical cycle, we are justified in making this assumption regarding the composition of the precipitate. It was clear that the molybdenum part of $ThMo_2O_8$ dissolved in the solvent as we could see the clear yellow supernatant liquid which is characteristic of $[MoO(O_2)F_4]^{2-}$. Earlier work [17] had established that compounds such as $K_2[MoO(O_2)F_4]$ could be prepared by dissolving MoO_3 in $HF + H_2O_2$ mixture and then by adding K salts and crystallizing the compound.

4. Conclusions

The standard enthalpy of formation $\Delta_f H^0$ (298.15 K) of $ThMo_2O_8$ (-2742.2 ± 4.5) kJ mol^{-1} obtained in this work is the first calorimetric value reported for this compound. The value of (-2737.4 ± 15.0) kJ mol^{-1} derived from vapour pressure measurements on this compound in the temperature range $1195 < T/K < 1291.5$ [1] is consistent with the present value.

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