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The standard molar enthalpy of formation of $HfTe_3O_8$

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Abstract

The molar enthalpies of solution of $HfTe_3O_8$, TeO_2 and HfF_4 in 10 mol dm^{-3} HF(aq) have been measured using an isoperibol-type calorimeter. From these results and other auxiliary data, the standard molar enthalpy of formation of $HfTe_3O_8(s)$ has been calculated to be $\Delta_f H^0_m(298.15\ K) = -2129.1 \pm 10.1$ kJ mol^{-1}. This value of enthalpy of formation of $HfTe_3O_8$ is consistent with the free energy of formation of $HfTe_3O_8$ determined in this laboratory by the transpiration technique.

Keywords: Molar enthalpies; Transpiration technique

1. Introduction

The standard molar free energies of formation of compounds such as $ZrMo_2O_8$, $HfMo_2O_8$, $ZrTe_3O_8$ and $HfTe_3O_8$ [1–4] were recently determined in our laboratory using the transpiration technique. $ZrMo_2O_8$ and $HfMo_2O_8$ are isostructural crystallographically and are expected to have similar chemical properties. The thermodynamic measurements on these compounds [1,2,5,6], however, indicate that $HfMo_2O_8$ is marginally more stable compared with $ZrMo_2O_8$. A similar conclusion was drawn from the vapour pressure measurements on $ZrTe_3O_8$ and $HfTe_3O_8$ [3,4], in which the standard molar free energy of the latter compound was found to be significantly more negative than that of the former.

A survey of enthalpies of formation of zirconium and hafnium compounds indicates that the enthalpies of formation of hafnium compounds are always more negative than their zirconium counterparts (Table 1) [7]. In this paper, we present our results on the determination of the standard molar enthalpy of formation of $HfTe_3O_8$ by isoperibol solution calorimetry and compare it with the $\Delta_f H^0_m(298.15\ K)$ of $ZrTe_3O_8$ obtained by the same method [8].

Table 1
Molar enthalpies of formation of some ternary oxides of zirconium and hafnium

Compound	$\Delta_f H°_{298}$ (kJ mol^{-1})	Reference
$CaZrO_3$	-1766.5 ± 9.6	[7]
$CaHfO_3$	-1779.9 ± 10.0	[7]
$SrZrO_3$	-1767.3 ± 14.6	[7]
$SrHfO_3$	-1783.6 ± 12.1	[7]
$BaZrO_3$	-1769.0 ± 5.9	[7]
$BaHfO_3$	-1789.9 ± 12.6	[7]
Li_2ZrO_3	-1762.3 ± 7.1	[7]
Li_2HfO_3	-1774.0 ± 5.4	[7]
$ZrTe_3O_8$	-2119.2 ± 9.6	[8]
$HfTe_3O_8$	-2129.1 ± 10.1	This work

2. Experimental

$HfTe_3O_8$ was prepared by heating a mixture of HfO_2 (99.9%, Metallurgy Division, BARC) and TeO_2 (99.999%, Kochlight, UK) in the required stoichiometric ratio at 923 K for 3 h. The details of optimization of temperature and time to obtain a pure compound from the stoichiometric mixture of the component oxides are described elsewhere [9]. The complete formation of $HfTe_3O_8$ was confirmed by X-ray diffraction and chemical analysis. Hafnium was determined by precipitating with mandelic acid as mandelate, which is then ignited and weighed as the dioxide [10]. The observed hafnium content of the compound was $25.63 \pm 0.20\%$, as against the calculated 25.89%. Tellurium was determined by atomic absorption spectroscopy. The observed tellurium content of the compound was $55.17 \pm 0.50\%$ as against the calculated 55.54%. HfF_4 (99.9% pure) was obtained from Fuel Chemistry Division, BARC.

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Table 2
The molar enthalpy of solution $HfTe_3O_8(s)$, $TeO_2(s)$ and $HfF_4(s)$ in 100 cm^3 of 10 mol dm^{-3} at 298.15 K

	m (solute) (g)	ΔH (J)		$\Delta_{sol}H_m$ (kJ mol^{-1})
$HfTe_3O_8(s)$	0.1408	−33.84		−165.66
M=689.2852	0.1335	−32.29		−166.72
	0.1368	−32.65		−164.51
	0.1248	−29.92		−165.25
	0.1144	−27.56		−166.06
	0.1150	−27.59		−165.37
			Average:	−165.60±0.75 [a]
$TeO_2(s)$	0.1648	−40.94		−39.65
M=159.5988	0.1863	−46.72		−40.02
	0.1673	−41.25		−39.35
	0.1724	−42.86		−39.68
			Average:	−39.68±0.27 [a]
$HfF_4(s)$	0.1705	2.86		4.27
254.4836	0.2269	3.28		3.68
	0.2715	4.03		3.78
	0.2759	4.06		3.74
			Average:	3.87±0.27 [a]
$H_2O(1)$	1.0	−27.41		−0.49
M=18.01528	1.0	−30.71		−0.55
			Average:	−0.52±0.04 [a]

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

The enthalpies of solution were measured in an isoperibol calorimeter operated at 298.15 K. The description of the instrument and the procedures for calibration and measurements have already been reported [11,12]. The calorimeter performance was tested using N.B.S. KCl (SRM 1655) and the results are given in our earlier publication [8]. 10 mol dm^{-3} hydrofluoric acid was used for the dissolution experiments. The glass Dewar flask, stirrer, heater and the thermistor were given a coating of polyethylene to prevent 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 in the strip chart recorder. The energy equivalent of the calorimeter was determined by electrical calibration using standard resistance, before and after each experiment. The temperature change ΔT during the reaction was corrected by the method of Kubaschewski and Alcock [12] and was used for the evaluation of the enthalpy change of the reaction. As the gelatin capsule, and not the usual glass bulb, was used for introducing the sample, the correction for evaporation of water is insignificant in these experiments. A correction was applied for dissolution of the gelatin capsule in HF(aq).

3. Results and discussion

The results of the enthalpy of solution measurements are given in Table 2. Here m denotes the mass of the sample dissolved, ΔH is the measured energy change and $\Delta_{sol}H_m$ is the molar enthalpy of solution. The thermochemical cycle from which the standard molar enthalpy of formation of $HfTe_3O_8(s)$ has been derived is given in Table 3. The molar enthalpies of solution of $HfTe_3O_8(s)$, $HfF_4(s)$, $TeO_2(s)$ and $H_2O(l)$ in 10 mol dm^{-3} HF(aq) have been measured to be −165.60±0.75 kJ mol^{-1}, 3.87±0.27 kJ mol^{-1}, −39.68±0.27 kJ mol^{-1} and −0.52±0.04 kJ mol^{-1} respectively. These values have been combined with other auxiliary data, such as the standard molar enthalpy of formation of $HfF_4(s)$ (−1930.50±3.56 kJ mol^{-1}) [13], $TeO_2(s)$ (−321.0±3.0 kJ mol^{-1}) [14], HF(aq) (−321.67±0.65 kJ mol^{-1}) [15] and $H_2O(l)$ (−285.83±0.04 kJ mol^{-1}) [16] to derive the standard molar enthalpy of formation $\Delta_f H^0_m$(298.15 K) of $HfTe_3O_8(s)$ is −2129.1±10.1 kJ mol^{-1}. There are no previous reports on this quantity.

We have recently determined the standard molar free energy of formation of $HfTe_3O_8(s)$ from the transpiration measurements [4], which could be represented

Table 3
Reaction scheme for the standard molar enthalpy of formation of $HfTe_3O_8(s)$:
$\Delta H_9 = -\Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 - \Delta H_5 + \Delta H_6 + \Delta H_7 + \Delta H_8$

Reaction	$\Delta H°_m$/kJ
1. $HfTe_3O_8(s) + 16HF(sln) = \{HfF_4 + 3TeF_4 + 8H_2O\}(sln)$	−165.60±0.75 [a]
2. $HfF_4(s) + (sln) = HfF_4(sln)$	3.87±0.27
3. $Hf(s) + 2F_2(g) = HfF_4(s)$	−1930.50±3.56
4. $3TeO_2(s) + 12HF(sln) = \{3TeF_4 + 6H_2O\}(sln)$	−119.04±0.81
5. $2H_2(g) + 2F_2(g) + (sln) = 4HF(sln)$	−1286.68±2.60
6. $3Te(s) + 3O_2(g) = 3TeO_2(s)$	−963.00±9.00
7. $2H_2(g) + O_2(g) = 2H_2O(l)$	−571.66±0.08
8. $2H_2O(l) + (sln) = 2H_2O(sln)$	−1.04±0.08
9. $Hf(s) + 3Te(s) + 4O_2(g) = HfTe_3O_8(s)$	−2129.1±10.1

[a] The stoichiometry of the reaction of $HfTe_3O_8(s)$ with HF(aq) was arrived at in an indirect way. ZrF_6^{-2} and TeF_5^- have been shown to be the species in HF(aq) and in a solution of TeO_2 in 40% HF containing CsF respectively [18,19]. In analogy with Zr, HfF_4 has been assumed.

as

$$\Delta_f G^0\langle \mathrm{HfTe_3O_8}\rangle$$
$$(\pm 18.3\ \mathrm{kJ\ mol^{-1}}) = -2180.7 + 0.789T\ (\mathrm{K}) \qquad (1)$$

where $1014 \leqslant T/K \leqslant 1158$.

$HfTe_3O_8$(s) vaporizes incongruently according to the reaction

$$\mathrm{HfTe_3O_8(s) = HfO_2(s) + 3TeO_2(g)} \qquad (2)$$

Eq. (1) was derived from the measured vapour pressure of TeO_2(g) over $HfTe_3O_8$(s), using other auxiliary data such as free energies of formation of HfO_2(s), TeO_2(s) and vapour pressure of TeO_2(g) over pure TeO_2(s).

The second law enthalpy at 298.15 K was derived from this equation by using the heat capacity values for $HfTe_3O_8$(s) estimated by the Neumann–Kopp rule [13]. The heat capacities for Hf(s), Te(s,l) and O_2(g) were taken from Refs. [14] and [17]. The second law enthalpy at 298.15 K from Eq. (1) is -2168.9 ± 22.0 kJ $\mathrm{mol^{-1}}$. Considering the large uncertainties involved in the second law evaluation using estimated heat capacities it may be concluded that the calorimetric results are in fair agreement with the transpiration measurements.

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