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The standard molar enthalpy of formation of $HfMo_2O_8$

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Abstract

The molar enthalpies of solution of $HfMo_2O_8$, Mo and HfF_4 in (10 mol HF(aq) + 4.41 mol H_2O_2(aq)) dm^{-3} have been measured using an isoperibol type calorimeter. From these results and other auxiliary data, the standard molar enthalpy of formation of $HfMo_2O_8$(s) has been calculated to be $\Delta_f H_m(298.15\ K) = -2605.8 \pm 5.9\ kJ\ mol^{-1}$. This value of enthalpy of formation of $HfMo_2O_8$ is consistent with the second law enthalpy of formation of $HfMo_2O_8$ determined in this laboratory by transpiration technique.

Keywords: Free energy of formation; Molybdate; Enthalpy of formation; Tellurate

1. Introduction

The standard molar free energies of formation of compounds such as $ZrMo_2O_8$, $HfMo_2O_8$, $ZrTe_3O_8$ and $HfTe_3O_8$ were recently determined in our laboratory using the transpiration technique [1–4]. The standard molar enthalpies of formation of $ZrTe_3O_8$, $HfTe_3O_8$ and $ZrMo_2O_8$ were also determined by isoperibol calorimetry [5–7]. The calorimetric enthalpies were consistent with the second law enthalpies derived from vapour pressure measurements by transpiration technique. In continuation of this series of investigations, in this paper we present the results of the determination of standard molar enthalpy of formation of $HfMo_2O_8$ by isoperibol solution calorimetry.

2. Experimental

$HfMo_2O_8$ was prepared by heating a mixture of HfO_2 (99.9 mass%, Metallurgy Division, BARC) and MoO_3 (AR grade, Mallinkrodt Chemicals, USA) in the required stoichiometric ratio at 923 K in air until the reaction was complete. The details of optimization of temperature and time to obtain pure compound from the stoichiometric mixture of the component oxides are described elsewhere [8]. The complete formation of $HfMo_2O_8$ 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 [9]. The observed hafnium content of the compound was 35.63 ± 0.20 mass% as against the calculated 35.82 mass%. Molybdenum was determined by atomic absorption spectroscopy. The observed molybdenum content of the compound was 38.85 ± 0.50 mass% as against the calculated 38.50 mass%. HfF_4 (99.9 mass% pure) was obtained from Fuel Chemistry Division, BARC.

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 [10,11]. The calorimeter performance was tested using N.B.S. KCl (SRM 1655) and the results are given in Ref. [5]. A mixture of 50 ml of 40% HF(aq) and 50 ml of 30% H_2O_2(aq) was used for the dissolution experiments. This amounts to 100 ml of (10 mol HF(aq) + 4.41 mol H_2O_2(aq)) dm^{-3}. 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

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steady state signal was obtained in the strip chart recorder. The energy equivalent of the calorimeter was determined by electrical calibration using a 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 a gelatin capsule, and not the usual glass bulb, was used for introducing the sample, the correction for evaporation of water is insignificant in the case of $HfMo_2O_8$ and HfF_4 dissolutions. A correction of 0.65 kJ mol^{-1} was applied for evaporation of water in the case of molybdenum dissolution, as hydrogen gas is evolved in this reaction. The necessary data were obtained from literature [13,14] for computing this value. Corrections were applied for dissolution of gelatin capsules in the solvent.

3. Results and discussion

The results of the enthalpy of solution measurements are given in Table 1. 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 $HfMo_2O_8(s)$ has been derived is given in Table 2. The molar enthalpies of solution of $HfMo_2O_8(s)$, $HfF_4(s)$ and Mo(s) in (10 mol HF(aq) + 4.41 mol H_2O_2(aq)) dm^{-3} have been measured to be (-145.81 ± 60) kJ mol^{-1}, (3.10 ± 0.50) kJ

Table 1
The molar enthalpy of solution $HfMo_2O_8(s)$, Mo(s) and $HfF_4(s)$ in 100 cm^3 of [10 mol HF(aq) + 4.41 mol H_2O_2(aq)] dm^{-3} at 298.15 K

	m(solute) (g)	ΔH (J)	$\Delta_{sol}H_m$ (kJ mol^{-1})
$HfMo_2O_8(s)$	0.0829	−24.25	−145.78
$M = 498.3652$[a]	0.0644	−18.90	−146.26
	0.0737	−21.52	−145.52
	0.0635	−18.48	−145.04
	0.0525	−15.47	−146.85
	0.0569	−16.60	−145.39
Average -145.81 ± 0.60[a]			
Mo(s)	0.0879	−615.49	−671.79
$M = 95.94$[a]	0.0758	−529.41	−670.07
	0.0928	−650.60	−672.61
	0.1483	−1037.60	−671.26
Average -671.43 ± 0.92[b]			
Evaporation correction −0.65			
Corrected value -672.08 ± 0.92			
$HfF_4(s)$	0.1828	2.03	2.83
$M = 254.4836$[a]	0.1498	2.32	3.94
	0.1710	1.80	2.68
	0.1678	1.94	2.94
Average 3.10 ± 0.50[b]			

[a] M is the molar mass in g mol^{-1}.

[b] Uncertainities are standard deviations of the mean.

Table 2
Reaction scheme for the standard molar enthalpy of formation of $HfMo_2O_8(s)$
$\Delta H_9 = -\Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6 + \Delta H_7 + \Delta H_8$

Reaction	ΔH_m(kJ)
1. $HfMo_2O_8(s) + 12HF(sln) + 2H_2O_2(sln) = [\{HfF_4 + 2[MoO(O_2)F_4]^{2-} + 4H^+\} + 6H_2O](sln)$	-145.81 ± 0.60
2. $HfF_4(s) + (sln) = HfF_4(sln)$	3.10 ± 0.50
3. $2Mo(s) + 8HF(sln) + 6H_2O_2(sln) = [\{2[MoO(O_2)F_4]^{2-} + 4H^+\} + 6H_2O](sln) + 2H_2(g)$	-1344.16 ± 1.84
4. $4HF(aq) = 2H_2(g) + 2F_2(g)$	1280.84 ± 2.60
5. $4HF(sln) = 4HF(aq) + (sln)$	3.80 ± 0.32
6. $Hf(s) + 2F_2(g) = HfF_4(s)$	-1930.50 ± 3.56
7. $4H_2(g) + 4O_2(g) = 4H_2O_2(aq)$	-763.80 ± 3.40
8. $4H_2O_2(aq) + (sln) = 4H_2O_2(sln)$	-0.92 ± 0.12
9. $Hf(s) + 2Mo(s) + 4O_2(g) = HfMo_2O_8(s)$	-2605.8 ± 5.9

$HF(aq) = HF \cdot H_2O$ and $H_2O_2(aq) = H_2O_2 \cdot 5H_2O$.

mol^{-1} and (-672.08 ± 0.92) kJ mol^{-1} respectively. In the case of Mo, evaporation correction has been incorporated. The enthalpies of solution of HF(aq) (i.e. $[HF \cdot 2H_2O]$) and H_2O_2(aq) (i.e. $[H_2O_2 \cdot 5H_2O]$) in the solvent have been measured to be (-0.95 ± 0.08) kJ mol^{-1} and (-0.23 ± 0.03) 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} [15], $HF \cdot 2H_2O$ (-320.21 ± 0.65) kJ mol^{-1} [16,17] and $H_2O_2 \cdot 5H_2O$ (-190.95 ± 0.85) kJ mol^{-1} [18] to derive the standard molar enthalpy of formation $\Delta_f H_m(298.15\ K)$ of $HfMo_2O_8$(s) as (-2605.8 ± 5.9) kJ mol^{-1}. There are no previous reports on this quantity.

The scheme of reactions given in Table 2 was arrived at in the following manner. As in the case of $ZrMo_2O_8$ [7], a mixture of HF and H_2O_2 had to be used for the dissolution. The species assumed in the case of $ZrMo_2O_8$ were $[MoO(O_2)F_4]^{2-}$ and $[Zr(O_2)F_5]^{3-}$. Earlier work [19] had established that salts such as $K_2[MoO(O_2)F_4]$, $K_2[MoO(O_2)_2F_2]$, $(NH_4)3[Zr(O_2)F_5]$, etc. could be prepared by dissolving MoO_3(s) or ZrO_2(s) in $HF + H_2O_2$ mixture and then adding K salts or NH_3 solution and crystallising the salt. The species $[Zr(O_2)F_5]^{3-}$ could be proved by estimating the peroxide content of the salt crystallised from the solution. A similar test was conducted for determining the peroxide content of the precipitate, obtained by dissolving HfF_4 in the mixture of HF and H_2O_2 to which ammonia solution was added. In the case of hafnium, the precipitate did not contain a peroxy linkage. Therefore, as with the earlier publication [6], HfF_4 was assumed to be formed in the dissolution of $HfMo_2O_8$ and HfF_4 in $HF + H_2O_2$ mixture.

We have recently determined the standard molar free energy of formation of $HfMo_2O_8$(s) from transpiration measurements [2], which can be represented as

$$\Delta_f G < HfMo_2O_8 > (\pm 18.0 \text{ kJ mol}^{-1}) = -2548.8 + 0.606T \text{ (K)} \quad (1)$$

for $1023 \leq T(K) \leq 1185$.

$HfMo_2O_8$(s) vaporizes incongruently according to the reaction

$$n HfMo_2O_8(s) = n HfO_2(s) + 2(MoO_3)_n(g) \quad (2)$$

(where $n = 3, 4, 5$).

Eq. (1) was derived from the measured vapour pressure of $(MoO_3)_3$(g) over $HfMo_2O_8$(s), using other auxiliary data such as free energies of formation of HfO_2(s), MoO_3(s), MoO_3(l) and vapour pressure of $(MoO_3)_3$(g) over pure MoO_3(s) and MoO_3(l).

The second law enthalpy at 298.15 K was derived from this equation by using the heat capacity values for $HfMo_2O_8$(s) estimated by the Neumann–Kopp rule [12]. The heat capacities for Hf(s), Mo(s) and O_2(g) were taken from Refs. [15,20]. The second law enthalpy at 298.15 K from Eq. (1) is -2592.0 ± 22.0 kJ 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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