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Thermochimica Acta 296 (1997) 11–14

thermochimica acta

The standard molar enthalpy of formation of $ZrMo_2O_8$

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Received 11 November 1996; received in revised form 27 December 1996; accepted 11 January 1997

Abstract

The molar enthalpies of a solution of $ZrMo_2O_8$, Mo, and ZrF_4 in 10 mol dm^{-3} HF(aq)+4.41 mol dm^{-3} H_2O_2(aq) have been measured using an isoperibol-type calorimeter. From these results and other auxiliary data, the standard molar enthalpy of formation of $ZrMo_2O_8$ has been calculated to be $\Delta_f H^0_m$ (298.15 K) = −2588.6±4.5 kJ mol^{-1}. This value of enthalpy of formation of $ZrMo_2O_8$ is consistent with the second law of enthalpy of formation of $ZrMo_2O_8$ determined in this laboratory by the transpiration technique. © 1997 Elsevier Science B.V.

Keywords: Molar enthalpy of formation; Isoperibol calorimetry; Zirconium molybdate; $ZrMo_2O_8$; Solution calorimetry

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1. Introduction

The thermochemistry of molybdates of uranium and fission products is important in predicting the chemical state of molybdenum in the operating oxide fuel pin in nuclear reactors [1,2]. In our earlier communications from this laboratory [3–5], we had reported the standard Gibbs energy of formation of uranium molybdates and zirconium molybdate. In the present paper, we report the enthalpy of formation of the ternary compound $ZrMo_2O_8$ obtained using solution calorimetry.

2. Experimental

$ZrMo_2O_8$ was prepared by heating a mixture of ZrO_2 (99.9% Metallurgy Division, BARC) and MoO_3 (AR grade, Mallinkrodt Chemicals, USA) in the required stoichiometric ratio at 925 K for 6 h in air. The details of optimization of experimental conditions for the preparation of pure $ZrMo_2O_8$ are described elsewhere [6]. The complete formation of $ZrMo_2O_8$ was confirmed by X-ray diffraction and chemical analysis. Zirconium was determined by precipitating with mandelic acid as mandelate which was then ignited and weighed as the dioxide [7]. The observed Zr content of the compound was 22.21±0.15 mass% as against the calculated 22.19. Molybdenum was determined by atomic absorption spectroscopy. The observed Mo content of the compound was 46.39±0.50 mass% as against the calculated 46.67. ZrF_4 (99.9% pure) was obtained from the Fuel Chemistry Division, BARC.

The enthalpies of solution were measured in an isoperibol calorimeter which is a modified version of the instrument reported earlier [8,9]. Briefly, the calorimeter was made from a glass Dewar of 0.300 dm^3 capacity, which was enclosed in a

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PII S0040-6031(97)00074-9

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 an 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 (6.375± 0.001) Ω. Stirring at $7\ s^{-1}$ was achieved using a synchronous motor. The calorimeter was kept in a constant-temperature bath having a control accuracy of 0.01 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 desiccator. Each dissolution of KCl was carried out with 0.100 dm^3 of distilled water. Each dissolution of $ZrMo_2O_8$, ZrF_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_2O_2(aq). The glass Dewar flask, stirrer, heater and the thermistor were given a 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 $ZrMo_2O_8$ and ZrF_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 [10] 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 short main period did not occur in case of Mo dissolution, the corrected temperature increase was obtained by the method of Fitzsimmons and Kirkbride [11]. The temperature T of the reaction vessel was carefully adjusted until $dT/dt < 10^{-5}\ K\ min^{-1}$. 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 ZrF_4. A correction of $0.65\ kJ\ mol^{-1}$ was applied for evaporation of water in case of $ZrMo_2O_8$ and Mo dissolutions where one mole of oxygen and one mole of hydrogen are evolved, respectively, per mole of the solute. The necessary data were obtained from [12,13] 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 $\Delta_{sol}H_m$ of KCl corresponding to the reaction:

$$KCl + \nu H_2O = KCl \cdot \nu H_2O \quad (\nu = 3500\text{–}5000)$$

were used with the Debye–Hückel limiting law [14] to calculate the molar enthalpy of solution at infinite dilution:
$\Delta_{sol}H_m^{\infty}(KCl,\ 298.15\ K) = (17.18 \pm 0.07)\ kJ\ mol^{-1}$. This value agrees within the uncertainty bounds with values reported by Sahanuja and Cesari [15]: 17.206± $0.092\ kJ\ mol^{-1}$, and the NBS: 17.241±0.018 $kJ\ mol^{-1}$ [16]. These results give the precision and accuracy of the present calorimetric measurements.

The results of the enthalpies of solution of $ZrMo_2O_8$, ZrF_4 and Mo are given in Table 1. Here m denotes the mass of the sample dissolved. ΔH is the measured energy change and $\Delta_{sol}H_m$ is the enthalpy of solution per mole of the solute. The thermochemical cycle from which the standard molar enthalpy of formation of $ZrMo_2O_8$ has been derived is given in Table 2. The molar enthalpies of solution of $ZrMo_2O_8$(s), Mo(s) and ZrF_4(s) in $10\ mol\ dm^{-3}$ HF(aq) +4.41 $mol\ dm^{-3}$ H_2O_2(aq) have been measured to be −325.02±0.52, −672.23±1.08 and 2.71±0.38 $kJ\ mol^{-1}$, respectively. In case of $ZrMo_2O_8$ and Mo, corrections for evaporation of water have been incorporated. The enthalpies of solution of HF(40% aq, i.e. $HF\cdot 2H_2O$), H_2O_2 (30% aq, i.e. $H_2O_2\cdot 5H_2O$) and H_2O(l) in the solvent (i.e. $10\ mol\ dm^{-3}$ HF(aq)+4.41 $mol\ dm^{-3}$ H_2O_2(aq)) have also been measured and found to be −0.95±0.08, −0.23±0.03 and −0.61±0.05 $kJ\ mol^{-1}$, respectively. These values have been combined with other auxiliary data such as the standard molar

Table 1
The molar enthalpy of solution of $ZrMo_2O_8(s)$, Mo(s) and $ZrF_4(s)$ 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})
$ZrMo_2O_8(s)$	0.0865	−68.33		−324.74
M = 411.0992	0.0744	−58.64		−324.02
	0.0615	−48.50		−324.20
	0.0721	−56.98		−324.89
	0.0664	−52.46		−324.79
	0.0701	−55.18		−323.60
			Average: −324.37±0.52 [a]	
			Evaporation correction: −0.65	
			Corrected value: −325.02±0.52	
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	
$ZrF_4(s)$	0.2712	3.81		2.35
M = 167.2176	0.1672	3.23		3.23
	0.2379	3.96		2.78
	0.3123	4.65		2.49
			Average: 2.71±0.38 [a]	

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

Table 2
Reaction scheme for the standard molar enthalpy of formation of $ZrMo_2O_8(s)$ (sln = 0.100 dm^{-3} of 4.41 mol dm^{-3} H_2O_2+10 mol dm^{-3} HF solution; $\Delta H_{11} = -\Delta H_1+\Delta H_2+\Delta H_3+\Delta H_4-\Delta H_5+\Delta H_6+\Delta H_7+\Delta H_8+\Delta H_9+\Delta H_{10}$)

Reaction	ΔH_m^0 kJ mol^{-1}
1. $ZrMo_2O_8(s) + 13HF + 5H_2O_2 = [[ZrO_2F_5]^{3-} + 2[MoO(O_2)F_4]^{2-} + 7H^+](sln) + 8H_2O + O_2(g)$	−325.02±0.52
2. $ZrF_4(s) + HF + H_2O_2 = [[ZrO_2F_5]^{3-} + 3H^+](sln)$	2.71±0.38
3. $2Mo(s) + 8HF + 6H_2O_2 = [2[MoO(O_2)F_4]^{2-} + 4H^+] + 6H_2O + 2H_2(g)$	−1344.46±2.16
4. $4HF(aq) = 2H_2(g) + 2F_2(g)$	1290.84±2.60
5. $4HF(aq) + (sln) = 4HF(sln)$	−3.80±0.32
6. $Zr(s) + 2F_2(g) = ZrF_4(s)$	−1911.25±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. $Zr(s) + 2Mo(s) + 4O_2(g) = ZrMo_2O_8(s)$	−2588.6±4.5

HF(aq) = $HF{\cdot}2H_2O$ and $H_2O_2(aq) = H_2O_2{\cdot}5H_2O$.

enthalpy of formation of $ZrF_4(s)$ (−1911.25± 2.09 kJ mol^{-1}) [17], $HF{\cdot}2H_2O$ (−320.21± 0.65 kJ mol^{-1}) [18,19], $H_2O_2{\cdot}5H_2O$ (−190.95± 0.85 kJ mol^{-1}) [20] and $H_2O(l)$ (−285.83± 0.04 kJ mol^{-1}) [19], to derive the standard molar enthalpy of formation $\Delta_f H_m^0$ (298.15 K) of $ZrMo_2O_8(s)$ = −2588.6±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_2O_2 was employed as the solvent for the dissolution experiments. It was found that, though $ZrMo_2O_8$ could be dissolved in any acid, MoO_3 could be dissolved only in alkali 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 $ZrMo_2O_8$ in $HF+H_2O_2$ mixture was deduced as follows. Earlier work [21] had established that salts such as $K_2[MoO(O_2)F_4]$, $K_2[MoO(O_2)_2F_2]$ and $(NH_4)_3[Zr(O_2)F_5]$ could be prepared by dissolving MoO_3 or ZrO_2 in $HF+H_2O_2$ mixture and then by adding K salts or NH_3 solution and crystallizing the salt. The IR and Raman patterns of these salts have been recorded and the various frequencies have been assigned to the vibrational modes. In our laboratory, the proof for the $[Zr(O_2)F_5]^{3-}$ species was obtained as follows: ZrF_4 was dissolved in $HF+H_2O_2$ mixture and excess NH_3 was added to the solution by keeping it in an ice bath. The precipitate was filtered, washed, dried and the peroxide content was estimated by titrating against standard $KMnO_4$ solution. The observed O_2^{2-} content of the freshly prepared compound matched closely with that required for the stoichiometric $(NH_4)_3[ZrO_2F_5]$. The peroxide contents of the compound, however, decreased continuously on storage in presence of light. Brown et al. [22] made a similar observation in their study on alkali metal peroxo complexes. Therefore, it was assumed that the species in solution should be $[ZrO_2F_5]^{3-}$.

4. Conclusion

The standard enthalpy of formation Δ_fH^0(298.15 K) of $ZrMo_2O_8$ (-2588.6 ± 4.5 kJ mol^{-1}) obtained in this work is the first calorimetric value reported for this compound. The value of -2577.7 ± 18.2 kJ mol^{-1} derived from vapour-pressure measurements on this compound in the temperature range $1029 < T/K < 1142$ [5] is consistent with the present value.

Acknowledgements

Thanks are due to Dr. K.N. Roy of Fuel Chemistry Division of BARC for his help in the preparation of ZrF_4(s).

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