Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Nuclear Materials 336 (2005) 110–112
journal of nuclear materials
www.elsevier.com/locate/jnucmat

The standard molar enthalpy of formation of $CdMoO_4$

M. Ali (Basu), S.R. Bharadwaj, D. Das *

Applied Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

Received 22 June 2004; accepted 14 September 2004

Abstract

The molar enthalpies of solution of $CdMoO_4$(s), CdO(s), Na_2 MoO_4(s) and NaF(s) 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 $CdMoO_4$(s) has been calculated to be $\Delta_f H°(298.15\,K) = -(1034.3 \pm 5.7)\,kJ\,mol^{-1}$. This value of enthalpy of formation of $CdMoO_4$(s) agrees well with the estimated enthalpy of formation of this compound. There is no other report on the thermodynamic property measurements on this compound.

1. Introduction

Recently, an investigation involving the interactions between MoO_3(s) and metals Te, Cd and Sb was reported [1]. $CdMoO_4$ appears to be the only ternary oxide in the Cd–Mo–O system. Depending on the oxygen potential it is shown that $CdMoO_4$ coexists with either MoO_3(s) + MoO_2(s) or Cd(g) + MoO_2(s) below 973 K [1]. As a part of the ongoing programme of generation of thermodynamic data for several ternary oxides, the enthalpy of formation of $CdMoO_4$ was obtained using isoperibol solution calorimetry. The results are presented in this paper.

2. Experimental

$CdMoO_4$ was prepared by heating a mixture of CdO (obtained from decomposition of $CdCO_3$, Loba-Chemie, purity 99.9%) and MoO_3 (AR grade, Mallinkrodt Chemicals, USA) in equal molar proportions, in sealed quartz ampoule, at 773 K for 4 h. The complete formation of $CdMoO_4$ was confirmed by X-ray diffraction and chemical analysis. The XRD pattern of the compound was found to match with the pattern reported in JCPDS file No. (07-0209). The observed cadmium content was found to be (41.0 ± 1.5) mass % as against the calculated 41.3%. The Mo content was found to be (34.5 ± 2.0) mass % as against the calculated 35.2%.

The enthalpies of solution were measured in an isoperibol calorimeter. The calorimeter was made from a glass Dewar of 0.300 dm^3 capacity, enclosed in a copper container. The annular space between the flask and the container was packed with fine glass wool. The lid of the copper container had leak-tight fittings for introducing a glass stirrer, a sample bulb, a heater and a thermistor. The lid was fastened to the container through O-ring fittings. The heater was fabricated out of manganin wire having a resistance of (6.200 ± 0.001) Ω. 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 K during the experiments. A control unit consisting of a

---

* Corresponding author. Tel.: +91 22 550 5151; fax: +91 22 551 9613.
E-mail address: dasd@apsara.barc.ernet.in (D. Das).

0022-3115/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2004.09.006

stabilized power supply unit, a heater power-supply unit, a bridge amplifier and quartz timer were 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). This apparatus is a modified version of the instrument reported earlier [2,3].

The performance of the calorimeter was tested using NBS grade KCl (SRM1655) which was heated at 800 K to remove adsorbed moisture, cooled and stored in a desiccator. Each dissolution of KCl was carried out with 0.100 dm^3 of distilled water.

The energy equivalent of the calorimeter was determined by electrical calibration using standard resistance, before and after each experiment. The dissolution of $CdMoO_4$ was done in 0.100 dm^3 of a solvent containing 0.050 dm^3 of 10 $mol\,dm^{-3}$ HF(aq) + 0.050 dm^3 of 4.41 $mol\,dm^{-3}$ H_2O_2(aq). The other compounds chosen for completion of the thermochemical cycle were CdO(s), Na_2MoO_4(s) and NaF(s). These were also dissolved in the same solvent. The glass Dewar flask, stirrer, heater and thermistor were given a uniform coating of polyethylene to prevent the attack by hydrofluoric acid vapors. An accurately weighed quantity of the sample was taken each time in a previously weighed gelatin capsule and introduced into the solution only after a steady state signal was obtained on the strip chart recorder. Correction was applied for the dissolution of gelatin capsule in the solvent.

3. Results and discussion

The results of the enthalpies of solution of $CdMoO_4$(s), CdO(s), Na_2MoO_4(s) and NaF(s) are given in Table 1. Here *m* denotes the mass of the sample dissolved. ΔH is the measured energy change and $\Delta_{sol}H$ is the enthalpy of solution per mole of the solute. The relevant thermochemical cycle which has been used to derive the standard molar enthalpy of the formation of $CdMoO_4$ is given in Table 2. The molar enthalpies of solution of $CdMoO_4$(s), Na_2MoO_4(s), NaF(s), CdO(s), HF(l) and H_2O(l) in 10 $mol\,dm^{-3}$ HF(aq) + 4.4 $mol\,dm^{-3}$ H_2O_2(aq) have been measured and found to be (−204.5 ± 2.8) $kJ\,mol^{-1}$, (−232.5 ± 1.9) $kJ\,mol^{-1}$, (−19.9 ± 0.9) $kJ\,mol^{-1}$, (−113.9 ± 1.0) $kJ\,mol^{-1}$, (−1.0 ± 0.1) $kJ\,mol^{-1}$ and (−0.6 ± 0.1) $kJ\,mol^{-1}$, respectively. The experimental values could not be compared with any literature data since these are the first reported values of the enthalpies of dissolution of the above compounds in the above-mentioned solvent. However, calorimetric measurements with KCl (recommended standard) in distilled water gave the value of enthalpy of dissolution to be (17.22 ± 0.02) $kJ\,mol^{-1}$ as against the reported value of (17.24 ± 0.02) $kJ\,mol^{-1}$ [4]. This proves the authenticity of our data.

Table 1
The molar enthalpy of solution of $CdMoO_4$(s), Na_2MoO_4(s), NaF(s) and CdO(s) in 0.100 dm^3 of (4.41 $mol\,dm^{-3}$ H_2O_2 + 10 $mol\,dm^{-3}$ HF) at 298.15 K

Compound	m_{solute}(g)	ΔH (J)	$\Delta_{sol}H$ ($kJ\,mol^{-1}$)
$CdMoO_4$(s)	0.0755	−57.06	−205.84
M = 272.35	0.0746	−55.52	−202.69
	0.0847	−64.77	−208.26
	0.0606	−44.72	−201.00
			Ave.: −204.5 ± 2.8[a]
Na_2MoO_4(s)	0.0566	−63.23	−230.09
M = 205.96	0.0769	−87.96	−235.28
	0.0700	−78.71	−231.59
	0.0545	−61.63	−232.90
			Ave.: −232.5 ± 1.9[a]
NaF(s)	0.0425	−20.05	−19.81
M = 41.988	0.0399	−18.51	−19.48
	0.0546	−27.76	−21.35
	0.0515	−23.13	−18.86
			Ave.: −19.9 ± 0.9[a]
CdO(s)	0.0417	−36.89	−113.60
M = 128.41	0.0728	−63.88	−112.67
	0.0545	−48.97	−115.38
	0.0552	−48.92	−113.80
			Ave.: −113.9 ± 1.0[a]

[a] Uncertainties are twice the standard deviations of the mean. *M* is the molar mass in $g\,mol^{-1}$.

The auxiliary data taken from the literature are: the standard molar enthalpies of formation of CdO(s) (−259.4 ± 1.0) $kJ\,mol^{-1}$ [5], Na_2MoO_4(s) (−1467.6 ± 3.3) [6], NaF(s) (−575.4 ± 0.8) [5], HF(aq) (−320.2 ± 0.7) $kJ\,mol^{-1}$ [7] and H_2O(l) (−285.8 ± 0.1) $kJ\,mol^{-1}$ [5]. The experimentally measured quantities and the literature data are used to derive the standard molar enthalpy of formation $\Delta_f H°$(298.15 K) of $CdMoO_4$(s) as (−1034.3 ± 5.7) $kJ\,mol^{-1}$. The relevant chemical equation to obtain this quantity is Cd(s) + Mo(s) + $2O_2$(g) = $CdMoO_4$(s). The enthalpy change for this reaction is represented as ΔH°_{12} in Table 2. This is obtained from the additive enthalpy changes involved in each step of the appropriate thermochemical cycle (Table 2). There is no previous report on this quantity.

The species obtained by Na_2MoO_4 dissolution was taken to be $[MoO(O_2)F_4]^{2-}$ where Mo exists in the hexavalent state because earlier work 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 [8]. The compound Na_2MoO_4 was chosen because neither MoO_3 nor MoO_2 could be dissolved in this solvent at room temperature within a sufficiently short period of time.

An assessment of the enthalpy of formation of cadmium molybdate was made from the reported ternary phase equilibrium [1] of the compound with MoO_2(s)

Table 2
Reaction scheme for the standard enthalpy of formation of $CdMoO_4(s)$, (ΔH°_{12})

Reaction	ΔH° (kJ mol^{-1}) at 298.15 K
1. $CdMoO_4(s) + (6HF + H_2O_2)(sln) = \{CdF_2 + [MoO(O_2)F_4]^{2-} + 2H^+ + 3H_2O\}(sln)$	-204.5 ± 2.8
2. $CdO(s) + 2HF(sln) = CdF_2(sln) + H_2O(sln)$	-113.9 ± 1.0
3. $Na_2MoO_4(s) + (6HF + H_2O_2)(sln) = \{2NaF + [MoO(O_2)F_4]^{2-} + 2H^+ + 3H_2O\}(sln)$	-232.5 ± 1.9
4. $2NaF(s) + (sln) = 2NaF(sln)$	-39.8 ± 1.8
5. $2Na(s) + Mo(s) + 2O_2(g) = Na_2MoO_4(s)$	-1467.6 ± 3.3
6. $2Na(s) + F_2(g) = 2NaF(s)$	-1150.8 ± 1.7
7. $Cd(s) + 1/2O_2(g) = CdO(s)$	-259.4 ± 1.0
8. $H_2(g) + 1/2O_2(g) = H_2O(l)$	-285.8 ± 0.1
9. $H_2O(l) + (sln) = H_2O(sln)$	-0.6 ± 0.5
10. $H_2(g) + F_2(g) = 2HF(aq)$	-640.4 ± 1.3
11. $2HF(aq) + (sln) = 2HF(sln)$	-2.0 ± 0.2
12. $Cd(s) + Mo(s) + 2O_2(g) = CdMoO_4(s)$	-1034.3 ± 5.7

sln = 0.100 dm^3 of (4.41 mol dm^{-3} H_2O_2 + 10 mol dm^{-3} HF) solution. $\Delta H^\circ_{12} = -\Delta H_1 + \Delta H_2 + \Delta H_3 - \Delta H_4 + \Delta H_5 - \Delta H_6 + \Delta H_7 - \Delta H_8 - \Delta H_9 + \Delta H_{10} + \Delta H_{11}$[a]

[a] $HF(aq) = HF \cdot 2H_2O$.

and $MoO_3(s)$ at 823 K. Namboodiri et al. have shown that the most favored reaction in the MoO_3–Cd system below 973 K is $Cd(l) + 2MoO_3(s) \rightarrow MoO_2(s) + CdMoO_4(s)$ [1]. So we have considered the heterogeneous reaction $Cd(g) + MoO_3(s) + 1/2O_2(g) = CdMoO_4(s)$, where the oxygen partial pressure is controlled by the $MoO_2(s)$–$MoO_3(s)$ equilibrium and the activity as well as partial pressure of Cd is maintained by the CdO component of activity less than unity in $CdMoO_4(s)$. This gave an upper limit of $\Delta_f G^\circ$ (823 K) of $CdMoO_4(s)$. The use of this together with an estimate of S° (823 K) value of the compound based on reported standard entropy values of CdO(s) and $MoO_3(s)$ and of the other $MMoO_4$ type molybdates (M = Zn, Mn, Fe) led to the upper limit of standard enthalpy of formation of cadmium molybdate. After an approximate correction of the heat capacity the estimate resulted in the upper limit of $\Delta_f H^\circ$(298.15 K) as (-1034.0 ± 5.0) kJ mol^{-1} at 298.15 K. The calorimetrically obtained data are thus seen to corroborate to the enthalpy estimate made above from the reported ternary equilibria [1]. Further, the calorimetric data are quite consistent with the reported standard enthalpy of formation of similar molybdates such as $ZnMoO_4(s)$ [9]. The consistency was seen considering the formation enthalpies of the compounds relative to their respective constituent oxides MO(s), (M = Cd or Zn) and $MoO_3(s)$. For $CdMoO_4(s)$ the relative value is about -30 kJ mol^{-1} whereas that for $ZnMoO_4$ it is -43 kJ mol^{-1}.

4. Conclusions

The molar enthalpy of formation $\Delta_f H^\circ$(298.15 K) of $CdMoO_4$ is obtained as (-1034.3 ± 5.7) kJ mol^{-1}. There is no other report on the thermodynamic property measurements on this compound.

Acknowledgments

The authors thank Dr N.M. Gupta, Head, Applied Chemistry Division, BARC for his support and encouragement during this work. Thanks are also due to Mr A.S. Kerkar for his help in setting up the isoperibol calorimeter. The authors also thank Mr S.C. Kumar of Analytical Chemistry Division for executing prompt chemical analysis of the compound.

References

[1] P.N. Namboodiri, S.N. Tripathi, J. Phase Equilibria 23 (2002) 339.
[2] V.T. Athavale, R. Kalyanaraman, M. Sundaresan, Ind. J. Chem. 7 (1969) 386.
[3] S.P. Awasti, M. Sundaresan, Ind. J. Chem. 20A (1981) 378.
[4] K.N. Marsh, P.A.G. O'Hare (Eds.), Solution Calorimetry, Oxford Blackwell Scientific, London, 1994.
[5] O. Kubaschewski, C.B. Alcock, Metallurgical Thermochemistry, 5th Ed., Pergamon, New York, 1979.
[6] N.K. Shukla, R. Prasad, D.D. Sood, J. Chem. Thermodyn. 25 (1993) 429, and references therein.
[7] J.D. Cox, D.D. Wagman, V.A. Medvedev, CODATA Key Values for Thermodynamics, Hemisphere, New York, 1989.
[8] W. Griffith, T.D. Wickins, J. Chem. Soc. A. Pt. I (1968) 397, and references therein.
[9] M. Binnewies, E. Milke, Thermochemical Data of Elements and Compounds, 2nd Ed., Wiley-VCH, 2002.