Thermochimica Acta, 198 (1992) 259-265
Elsevier Science Publishers B.V., Amsterdam

Standard molar enthalpies of formation of sodium molybdates ($Na_2Mo_nO_{3n+1}$ with $n = 1, 2, 3$ or 4) at 298.15 K by solution calorimetry

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(Received 19 August 1991)

Abstract

Four compounds, namely Na_2MoO_4, $Na_2Mo_2O_7$, $Na_2Mo_3O_{10}$ and $Na_2Mo_4O_{13}$, were synthesised from stoichiometric quantities of sodium carbonate and molybdenum trioxide using a pyrometallurgical technique. The products were characterised by chemical and X-ray diffraction analysis and were found to be single-phase compounds. The molar enthalpies of solution of the compounds were measured at 298.15 K using an isoperibol calorimeter. The molar enthalpies of solution at infinite dilution, $\Delta_{sol}H_m^\alpha$ (298.15 K) for Na_2MoO_4, $Na_2Mo_2O_7$, $Na_2Mo_3O_{10}$ and $Na_2Mo_4O_{13}$ are -11.79 ± 0.51, -55.89 ± 0.69, -135.01 ± 0.71 and -178.94 ± 0.82 kJ mol^{-1}, respectively. These data were used to calculate the standard molar enthalpies of formation at 298.15 K and the values obtained for the compounds are -1465.87 ± 0.98, -2245.02 ± 1.81, -2989.16 ± 2.61 and -3768.58 ± 3.45 kJ mol^{-1}, respectively. The values agree closely with the previously reported values. The standard molar enthalpy of formation of $Na_2Mo_3O_{10}$ was determined for the first time.

INTRODUCTION

The thermochemical quantities of some alkali metal molybdates have been reported in literature [1-10]. There is little thermochemical data on sodium molybdates, $Na_2MoO_nO_{3n+1}$ ($n = 2$, 3 and 4). Hence the thermochemistry of alkali metal molybdates has been studied and the values for the standard molar enthalpies of formation of Na_2MoO_4 [2], $Na_2Mo_2O_7$ [2] and $Na_2Mo_4O_{13}$ [10] have been reported. In the present study the standard molar enthalpy of formation of $Na_2Mo_3O_{10}$ was determined for the first time using solution calorimetry. In addition, the standard molar enthalpies of formation of Na_2MoO_4, $Na_2Mo_2O_7$ and $Na_2Mo_4O_{13}$ have been redetermined so that a complete set of thermochemical data on sodium molybdates would be available from the same laboratory and thus

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the systematic behaviour of these compounds elucidated. This thermochemical information is necessary for any meaningful prediction of the type of interaction between liquid metal coolant sodium and the fission product molybdenum in the case of clad breach in an operating LMFBR [1,2].

EXPERIMENTAL

Sample preparation and characterisation

A series of molybdates $Na_2Mo_nO_{3n+1}$ ($n = 1$, 2, 3 or 4) have been reported and identified [11]. Four polymolybdates of sodium, which were synthesised in our laboratory for the thermochemical investigations, bear some common features in the procedure of their preparation. The starting material consisted of sodium carbonate (99.9 mass%, Ventron, Karlsruhe) and molybdenum trioxide (99.9 mass%, Mallinkrodt Chemical Corporation, USA). Stoichiometric proportions of dried sodium carbonate and molybdenum trioxide were mixed thoroughly in an agate mortar and kept in a moisture-free argon filled glove box. The charge was heated in a platinum crucible in a stream of moisture-free oxygen. Various compounds were prepared by heating their respective charges for different lengths of time. Sufficient time was given for the solid-state diffusion of the reactants by heating the charges at a comparatively lower temperature in order to avoid loss of any of the constituents by vaporisation.

A general reaction can be represented as

$$Na_2CO_3(c) + nMoO_3(c) \rightleftharpoons Na_2Mo_nO_{3n+1}(c) + CO_2(g) \quad (n = 1 \text{ to } 4)$$

The reaction product was taken out, ground in an agate mortar kept in a dry box and reheated well below the melting temperature of the compound for 2–3 h until the products were identified. As the sodium molybdates are soluble in distilled water to varying degrees, and as MoO_3 is insoluble crystallisation from water was carried out to purify the molybdates which were subsequently dried at 500 K [12]. The results of the chemical analysis of the compounds showed that the constituent elements were in the required stoichiometry. The X-ray diffraction patterns of the purified materials agreed with those reported previously for Na_2MoO_4 and $Na_2Mo_2O_7$ [13,14] and for $Na_2Mo_4O_{13}$ by Balashov and Maier [15]. The formation of $Na_2Mo_3O_{10}$ was confirmed by the absence of the constituent materials and by the adjoining phases in the phase diagram.

Calorimetric system and experimental procedure

An isoperibol calorimeter operated at 298.15 K was used to measure the enthalpies of solution. The description of the instrument and the procedure have been reported previously [16–18]. The accuracy and precision of the calorimetric measurements were tested by the dissolution of National Bureau of Standards KCl (SRM 1655) [19]. The heat capacity of the calorimeter was determined by electrical calibration both before and after the dissolution experiment. The standard enthalpy of formation of potassium chloride was calculated using the enthalpy of solution data at infinite dilution from seven experiments and the enthalpies of formation of $K^+(aq)$ and $Cl^-(aq)$, and was calculated to be -436.45 ± 0.21 kJ mol^{-1}. This value is in excellent agreement with the value of -436.68 kJ mol^{-1} reported by the National Bureau of Standards [20]. This showed that the present calorimeter was considered suitable for further measurements.

The 0.024 M NaOH solution used in the dissolution experiments with molybdates was sufficiently dilute that for the purposes of calculation it can be considered as NaOH(aq). The NaOH solution was prepared by dissolving reagent grade sodium hydroxide in distilled water and the strength of the solution was determined by titration against potassium biphthalate. This standardised NaOH solution was chosen as the reaction medium for the dissolution. The stock solution was stored in a leak-tight container.

RESULTS AND DISCUSSION

The results of the chemical analysis of the sodium molybdates are given in Table 1 and it can be seen that the compounds were very pure for

TABLE 1

Typical chemical compositions

Compound	Run No.	Mo (μmol ml^{-1})	Na (μmol ml^{-1})	Atomic ratio Na:Mo
Na_2MoO_4	2	11.9	23.9	1.975
	4	4.8	9.6	2.009
	5	15.2	30.1	1.980
	6	6.5	13.2	2.031
$Na_2Mo_2O_7$	1	8.9	8.9	1.000
	3	17.5	17.4	0.994
	4	10.7	10.6	0.991
	7	12.3	12.2	0.992
$Na_2Mo_3O_{10}$	1	15.6	10.4	0.667
	2	8.1	5.4	0.667
	5	12.8	8.5	0.664
	6	11.4	7.6	0.667
$Na_2Mo_4O_{13}$	3	6.6	3.3	0.500
	4	13.1	6.6	0.504
	6	8.7	4.4	0.506
	7	9.7	4.9	0.505

TABLE 2

Enthalpy of solution of the molybdates at 298.15 K [a]

Compound	Mass (g)	Mass Na_2MoO_4 (g)	Molality (mol kg^{-1})	$-\Delta H$ (J)	$-\Delta_{sol}H_m$ (kJ mol^{-1})	$-\Delta_{sol}H_m^{\alpha}$ (kJ mol^{-1})
Na_2MoO_4	0.35761	–	0.01158	18.17	10.46	11.58
	0.36124	–	0.01170	19.51	11.12	12.25
	0.32895	–	0.01005	16.18	10.13	11.21
	0.34752	–	0.01125	19.27	11.42	12.53
	0.31483	–	0.01019	16.30	10.66	11.71
	0.32517	–	0.01053	16.36	10.36	11.43
Average $\Delta_{sol}H_m^{\alpha} = -11.79 \pm 0.51$ kJ mol^{-1}						
$Na_2Mo_2O_7$	0.21593	0.25418	0.00823	33.58	54.41	55.36
	0.23726	0.27929	0.00904	37.50	55.30	56.29
	0.23517	0.27683	0.00896	36.22	53.89	54.88
	0.21684	0.25524	0.00826	34.19	55.16	56.11
	0.24391	0.28712	0.00930	38.26	54.88	55.89
	0.22865	0.26916	0.00871	36.49	55.84	56.82
Average $\Delta_{sol}H_m^{\alpha} = -55.89 \pm 0.69$ kJ mol^{-1}						
$Na_2Mo_3O_{10}$	0.15632	0.19556	0.00633	42.50	134.27	135.11
	0.18251	0.22833	0.00739	49.42	133.72	134.62
	0.20136	0.25191	0.00816	55.14	135.72	136.16
	0.19375	0.24239	0.00785	52.23	133.11	134.04
	0.21194	0.26515	0.00858	57.48	133.91	134.88
	0.17382	0.21746	0.00704	47.30	134.37	135.25
Average $\Delta_{sol}H_m^{\alpha} = -135.01 \pm 0.71$ kJ mol^{-1}						
$Na_2Mo_4O_{13}$	0.13787	0.17807	0.00577	38.34	177.33	178.12
	0.16345	0.21111	0.00683	45.83	178.80	179.66
	0.14893	0.19235	0.00623	41.38	177.20	178.03
	0.14386	0.18580	0.00602	40.32	178.72	179.53
	0.15218	0.19655	0.00636	42.39	177.63	178.46
	0.16179	0.20896	0.00677	45.40	178.95	179.81
Average $\Delta_{sol}H_m^{\alpha} = -178.94 \pm 0.82$ kJ mol^{-1}						

[a] The molar masses of the compounds were calculated using atomic masses of Na = 22.99, Mo = 95.94, O = 15.99 and H = 1.00.

calorimetric work. The calorimetric data for Na_2MoO_4, $Na_2Mo_2O_7$, $Na_2Mo_3O_{10}$ and $Na_2Mo_4O_{13}$ are given in Table 2. The enthalpies of solution for the compounds correspond to the general reaction

$$\mathrm{Na_2Mo}_n\mathrm{O}_{3n+1}(\mathrm{c}) + (2n-2)\mathrm{NaOH(aq)} \rightleftharpoons n\mathrm{Na_2MoO_4(aq)} + (n-1)\mathrm{H_2O} \quad (n = 1, 2, 3 \text{ and } 4). \tag{1}$$

The enthalpy of solution data were used to calculate the enthalpy of solution at infinite dilution using the reaction

$$n\mathrm{Na_2MoO_4(aq)} \overset{\alpha\mathrm{H_2O(l)}}{\rightleftharpoons} 2n\mathrm{Na^+(aq)} + n\mathrm{MoO_4^{2-}(aq)}$$

TABLE 3

Standard molar enthalpy of formation of sodium molybdates

Compound	$-\Delta_f H_m^0$ (kJ mol^{-1})
Na_2MoO_4	1465.87 ± 0.98
$Na_2Mo_2O_7$	2245.02 ± 1.81
$Na_2Mo_3O_{10}$	2989.16 ± 2.61
$Na_2Mo_4O_{13}$	3768.50 ± 3.45

The enthalpy of solution corresponding to $n = 1$, 2, 3 and 4 in the above reaction was estimated using the Debye–Hückel limiting equation [21].

The enthalpy of solution data coupled with the following literature data were used to calculate the standard molar enthalpies of formation for different compounds:

$$\Delta_f H_m^0(H_2O(l)) = -285.83 \pm 0.04 \text{ kJ mol}^{-1} \qquad [12]$$

$$\Delta_f H_m^0(Na^+(aq)) = -240.30 \text{ kJ mol}^{-1} \qquad [22]$$

$$\Delta_f H_m^0(NaOH(aq)) = -470.11 \text{ kJ mol}^{-1} \qquad [23]$$

$$\Delta_f H_m^0(MoO_4^{2-}(aq)) = -997.05 \pm 0.84 \text{ kJ mol}^{-1} \qquad [24]$$

The value of $\Delta_{sol} H_m^\alpha$ (298.15 K) obtained for Na_2MoO_4 is -11.79 ± 0.51 kJ mol^{-1} and that for $Na_2Mo_2O_7$ is -55.89 ± 0.69 kJ mol^{-1}. These values agree very well with those reported by Koehler et al. [2] and Graham and Hepler [4], respectively.

The standard enthalpies of formation for Na_2MoO_4, $Na_2Mo_2O_7$, $Na_2Mo_3O_{10}$ and $Na_2Mo_4O_{13}$ are listed in Table 3 and compared with other values from the literature in Table 4. It can be seen that for Na_2MoO_4 and $Na_2Mo_2O_7$ the values $\Delta_f H_m^0$ are in excellent agreement with those reported by Koehler et al. [2] and Graham and Hepler [4]. The S_{298}^0 values for Na_2MoO_4(s) and $Na_2Mo_2O_7$(s) have been reported in

TABLE 4

Comparison of $\Delta_f H_m^0$ (298.15 K) and data reported in the literature for sodium molybdates

Ref.	$-\Delta_f H_m^0$ (298.15 K) (kJ mol^{-1})			
	Na_2MoO_4(c)	$Na_2Mo_2O_7$(c)	$Na_2Mo_3O_{10}$(c)	$Na_2Mo_4O_{13}$(c)
2	1467.74 ± 1.26	2244.20 ± 1.68	–	–
4	1466.07	–	–	–
10	–	2242.62 ± 1.25	–	3760.58 ± 2.09
23	1468.12	–	–	–
28	1468.00	2245.00	–	–
This study	1465.87 ± 0.98	2245.02 ± 1.81	2989.16 ± 2.61	3768.50 ± 3.45

TABLE 5

The enthalpy, entropy and Gibbs free energy of formation for Na_2MoO_4 and $Na_2Mo_2O_7$

Compound	$\Delta_f H^0_m$ [a] (kJ mol^{-1})	$\Delta_f S^0_m$ [b] (kJ mol^{-1} K^{-1})	$\Delta_f G^0_m$ [b] (kJ mol^{-1})
Na_2MoO_4	−1465.87	−0.3825	−1351.83
$Na_2Mo_2O_7$	−2245.02	−0.6270	−2058.08

[a] Experimental.
[b] Ref. 24.

literature [24]. Using the values given above for $\Delta_f H^0_m$ and the S^0_{298} values for Na(s), O_2(g) and Mo(s), the entropy of formation and Gibbs free energy of formation of the molybdates were evaluated (Table 5).

The threshold oxygen level in sodium necessary for the formation of Na_2MoO_4 and $Na_2Mo_2O_7$ was calculated using the reactions

$$\mathrm{Mo(ss)} + 4\mathrm{Na_2O(c)} \rightleftharpoons \mathrm{Na_2MoO_4(c)} + 6\mathrm{Na(l)}$$

$$2\mathrm{Mo(ss)} + 7\mathrm{Na_2O(c)} \rightleftharpoons \mathrm{Na_2Mo_2O_7(c)} + 12\mathrm{Na(l)}$$

where Mo(ss) is the solid solution of Mo in stainless steel. The $\Delta_f G^0_m$ value for Na_2O and the a_{Mo} values were taken from Jansson et al. [25] and Azad et al. [26], respectively. The equations used to calculate the threshold oxygen level were

$$\Delta_f G^0_m(\mathrm{Na_2O(c}, T))(\mathrm{kJ\ mol^{-1}}) \pm 2 = -414.8 + 0.1376\ T(\mathrm{K})$$

$$\log(a_{\mathrm{Mo}})(\pm 0.05) = -4.548 + 3148.48/T(\mathrm{K})$$

where $\Delta_r G^0_m(T)$ is given by

$$\Delta_r G_m(T)(\mathrm{J\ mol^{-1}}) = RT\ \ln a_{\mathrm{Mo}} + \delta RT\ \ln(w/w_{\mathrm{sat}})$$

where δ is 4 for Na_2MoO_4 and 7 for $Na_2Mo_2O_7$ formation, and w_{sat} is the saturation solubility of oxygen in solution. The value of w_{sat} was taken from Noden [27] and is given by

$$\log_{10}(w_{\mathrm{sat}}(\mathrm{ppm\ O})) = 6.2571 - 2444.5/T(\mathrm{K})$$

The value of w_{sat} at 1000 K for the formation of Na_2MoO_4 and $Na_2Mo_2O_7$ are 9.8 and 1360 ppm, respectively. As the LMFBR specification limits the level of oxygen in sodium to be below 10 ppm, Na_2MoO_4 is likely to be formed with steel.

ACKNOWLEDGEMENTS

The authors are grateful to Dr. C.K. Gupta, Associate Director Materials Group, and Dr. D.D. Sood, Head Fuel Chemistry Division, for their constant encouragement and useful discussion during the course of this study. The authors thank Dr. M. Sundaresan, Analytical Chemistry Division, for his guidance and for making available the facilities needed for this investigation.

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