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Thermochemistry of lithium chromate Li_2CrO_4(cr) and lithium molybdate Li_2MoO_4(cr)

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The standard molar enthalpies of formation $\Delta_f H_m^\circ$ at the temperature $T = 298.15$ K of Li_2CrO_4(cr) and Li_2MoO_4(cr) have been determined using an isoperibol solution calorimeter. The value of $\Delta_{sol} H_m^\infty$ for Li_2CrO_4(cr) in water at $T = 298.15$ K was found to be $-(45.77 \pm 0.29)$ kJ·mol^{-1} and was used to obtain $\Delta_f H_m^\circ$(298.15 K) as $-(1393.7 \pm 0.3)$ kJ·mol^{-1}. The $\Delta_{sol} H_m^\circ$ of Li_2MoO_4(cr) and of {Li_2O(cr) + MoO_3(cr) in LiOH(aq, 0.1 mol·dm^{-3}) at $T = 298.15$ K were used to obtain a value of $-(1519.2 \pm 2.2)$ kJ·mol^{-1} for $\Delta_f H_m^\circ$ for Li_2MoO_4(cr).

1. Introduction

Lithium oxide and $LiAlO_2$ have respectively been proposed as a blanket and breeding material for a thermonuclear reactor.$^{(1, 2)}$ Some possible container materials for Li_2O are (iron + nickel + chromium) alloys and molybdenum-based alloys. These can react with Li_2O at high temperatures to form compounds like $LiCrO_2$, $LiCrO_4$, Li_2MoO_4, *etc.* Similarly $LiAlO_2$ can also react with these container materials to form similar compounds if $LiAlO_2$ is thermodynamically less stable than $LiCrO_2$, Li_2CrO_4, and Li_2MoO_4. A knowledge of the thermochemistry of these compounds is desirable for understanding these reactions. In the present work the standard molar enthalpies of formation at $T = 298.15$ K of Li_2CrO_4(cr) and Li_2MoO_4(cr) have been determined using an isoperibol solution calorimeter.

Calorimetric determination of $\Delta_f H_m^\circ$ of Li_2CrO_4(cr) has been reported only by Shidlovskii *et al.*$^{(3)}$ They calculated $\Delta_f H_m^\circ$ from $\Delta_{sol} H_m^\circ$ in distilled water with the mole ratio $n(H_2O)/n(Li_2CrO_4) = 800$. This can lead to an error in the extrapolation of $\Delta_{sol} H_m^\circ$ to infinite dilution which is required for calculating $\Delta_f H_m^\circ$. Hence it was decided to carry out the measurement at higher dilution to reduce the error in extrapolation.

There are three calorimetric determinations$^{(4-6)}$ of $\Delta_f H_m^\circ$ for Li_2MoO_4(cr). Thien and Zharkova$^{(4)}$ and O'Hare *et al.*$^{(5)}$ have determined $\Delta_f H_m^\circ$ by measuring the enthalpy of reaction of MoO_3 with LiOH(aq) and the enthalpy of solution of Li_2MoO_4(cr) in LiOH(aq). Suponitskii *et al.*$^{(6)}$ have determined $\Delta_f H_m^\circ$ by measuring

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the $\Delta_{sol}H^\circ_m$ of Li_2MoO_4 in LiOH(aq, 0.3 $mol \cdot dm^{-3}$). In the present work $\Delta_f H^\circ_m$(Li_2MoO_4, cr, 298.15 K) has been determined by adopting a different approach *i.e.* by measuring $\Delta_{sol}H^\circ_m$ of Li_2MoO_4(cr) and of {Li_2O(cr) + MoO_3(cr)} in the same solvent LiOH(aq, 0.1 $mol \cdot dm^{-3}$).

2. Experimental

Lithium chromate (Li_2CrO_4, anhydrous) was prepared by the addition of LiCl(aq) (purity of LiCl, 99.99 mass per cent) to a suspension containing excess of Ag_2CrO_4(cr). The precipitated AgCl(cr) and unreacted Ag_2CrO_4 were filtered and the filtrate was concentrated to obtain crystals of $Li_2CrO_4 \cdot 2H_2O$.(7) Purification was achieved by repeated crystallization. The product was dehydrated by heating at $T = 498$ K in flowing dry argon and stored in a dry-argon glove box (mass fractions: O_2, N_2: $<10^{-5}$; H_2O: $<5 \cdot 10^{-6}$). The X-ray diffraction pattern of the material agreed with that reported in the literature and the mass fraction of chromium corresponded to the formula Li_2CrO_4.

Lithium molybdate {Li_2MoO_4(cr)} was prepared by heating {0.5Li_2CO_3(cr) + 0.5MoO_3(cr)} of high purity in flowing dry argon. Li_2CO_3(cr) of purity 99.997 mass per cent, and MoO_3(cr) of purity 99.99 mass per cent, were obtained from Aldrich, U.S.A. The required amounts of reactants were loaded into a gold boat and heated at $T = 1000$ K for 18 h. The product was cooled and ground to a fine powder in an agate mortar and was recrystallized from water. The crystals were heated in dry argon at $T = 500$ K to obtain moisture-free Li_2MoO_4(cr). The product was cooled to room temperature and stored in an argon-atmosphere dry box. The X-ray diffraction pattern of the sample agreed with that reported in the literature and the chemical analysis indicated the mole ratio n(Li)/n(Mo) as 2.00.

Lithium oxide was prepared by the decomposition of Li_2CO_3(cr) under vacuum.(8) Li_2CO_3(cr) was loaded in a platinum boat and heated at $T = 1100$ K for 50 h under a vacuum of $1.33 \cdot 10^{-4}$ Pa. The product was further purified by heating in helium gas at $T = 1250$ K for 8 h and after cooling was transferred to a dry-argon box. The X-ray diffraction pattern of the sample agreed with that reported in the literature.

Lithium hydroxide solution (aq, 0.1 $mol \cdot dm^{-3}$) was prepared by dissolving high-purity $LiOH \cdot H_2O$ (99.95 mass per cent obtained from Aldrich, U.S.A.) in air-free deionized distilled water and stored in an air-tight container.

The calorimeter used has already been described.(9) Electrical calibration experiments were performed immediately before and after each measurement of enthalpy of solution/reaction. The energy equivalent of the calorimeter was obtained from the average of both the calibration experiments. The corrected temperature change was evaluated using Newton's law of cooling. The heater and thermistor were protected against possible acid or alkali attack by enclosing them in thin-walled glass tubes filled with oil.

The calorimetric samples were weighed into pre-dried glass bulbs. The performance of the calorimeter was checked by measuring the enthalpy of solution on N.B.S. KCl SRM 1655 in distilled water and of tris(β-hydroxyaminomethane) SRM 724 in HCl(aq, 0.1 $mol \cdot dm^{-3}$). The measured values were in close agreement

TABLE 1. Standard molar enthalpy of solution $\Delta_{sol}H^\circ_m$ at the temperature 298.15 K of Li_2CrO_4(cr) in water. In every run 350.0 g of water was used. Molar mass of Li_2CrO_4(cr) was taken as 129.8716 $g \cdot mol^{-1}$, $\Delta_f H^\circ_m$ values at 298.15 K for Li^+(aq, ∞) and CrO_4^{2-}(aq, ∞) were taken as −278.461 $kJ \cdot mol^{-1}$ and −882.514 $kJ \cdot mol^{-1}$, respectively. The uncertainty is equal to twice the standard deviation of the mean

Run	$m(Li_2CrO_4)$ / g	$-\Delta_{sol}H^\circ$ / J	$-\Delta_{sol}H^\circ_m$ / $kJ \cdot mol^{-1}$	$-\Delta_{sol}H^\infty_m$ / $kJ \cdot mol^{-1}$	$-\Delta_f H^\circ_m$ / $kJ \cdot mol^{-1}$
1	0.09465	33.3	45.69	46.17	1393.3
2	0.13650	46.9	44.62	45.19	1394.2
3	0.12891	44.3	44.63	45.19	1394.2
4	0.13417	46.7	45.20	45.77	1393.7
5	0.10480	36.2	44.86	45.36	1394.1
6	0.13260	46.1	45.15	45.72	1393.7
7	0.20610	72.8	45.87	46.58	1392.9
8	0.02831	9.9	45.42	45.68	1393.8
9	0.14110	49.4	45.47	46.05	1393.4
10	0.13256	46.4	45.46	46.02	1393.4

$\Delta_{sol}H^\circ_m(Li_2CrO_4$, cr, 298.15 K$) = -(45.24 \pm 0.28)\ kJ \cdot mol^{-1}$

$\Delta_{sol}H^\infty_m(Li_2CrO_4$, cr, 298.15 K$) = -(45.77 \pm 0.29)\ kJ \cdot mol^{-1}$

$\Delta_f H^\circ_m(Li_2CrO_4$, cr, 298.15 K$) = -(1393.7 \pm 0.3)\ kJ \cdot mol^{-1}$

with the N.B.S. reported values. Calorimetric experiments consisted of breaking of bulbs containing samples Li_2CrO_4, Li_2MoO_4, or (Li_2O + MoO_3) in the respective solvents. The standard molar enthalpy of solution $\Delta_{sol}H^\circ_m$ at $T = 298.15$ K of Li_2CrO_4 was measured in deionized distilled water. The $\Delta_{sol}H^\circ_m$ of MoO_3, Li_2MoO_4, and (Li_2O + MoO_3) were measured in LiOH(aq, 0.1 $mol \cdot dm^{-3}$, 298.15 K). The molar enthalpy of solution of Li_2O at $T = 298.15$ K was also measured in distilled water. Since the materials involved are hygroscopic in nature all the weighing and loading operations were performed in an argon-atmosphere dry box.

3. Results and discussion

The standard molar enthalpies of solution $\Delta_{sol}H^\circ_m$ at $T = 298.15$ K for Li_2CrO_4(cr) in water are given in table 1 along with the derived values. The enthalpy of solution of Li_2CrO_4 in water corresponds to the reaction:

$$Li_2CrO_4(cr) + 50000H_2O(l) = Li_2CrO_4 \cdot 50000H_2O(aq).$$

The enthalpy of dilution to infinite dilution $\Delta_{sol}H^\infty_m$ was calculated using the Debye-Hückel limiting law(10) and corresponds to the reaction:

$$Li_2CrO_4 \cdot 50000H_2O(aq) + \infty H_2O(l) = 2Li^+(aq, \infty) + CrO_4^{2-}(aq, \infty).$$

The standard molar enthalpy of formation was calculated from the reaction:

$$Li_2CrO_4(cr) + \infty H_2O(l) = 2Li^+(aq, \infty) + CrO_4^{2-}(aq, \infty).$$

The standard molar enthalpy of solution $\Delta_{sol}H^\circ_m$, and the standard molar enthalpy of solution at infinite dilution $\Delta_{sol}H^\infty_m$, were found to be $-(45.27 \pm 0.28)\ kJ \cdot mol^{-1}$, and $-(45.77 \pm 0.29)\ kJ \cdot mol^{-1}$, respectively. Combining $\Delta_{sol}H^\infty_m$ with the $\Delta_f H^\circ_m$ for

TABLE 2. The standard molar enthalpy of solution of MoO_3 in LiOH(aq, $0.1\ mol\cdot dm^{-3}$) at $T = 298.15$ K. In each run the mass of solvent LiOH(aq, $0.1\ mol\cdot dm^{-3}$) was taken as 350.0 g. Molar mass of MoO_3(cr) was taken as $143.9382\ g\cdot mol^{-1}$. Uncertainty is equal to twice the standard deviation of the mean

Run	$m(MoO_3)$/g	$-\Delta_{sol}H^\circ$/J	$-\Delta_{sol}H^\circ_m$/$kJ\cdot mol^{-1}$
1	0.15375	82.3	77.05
2	0.15543	83.4	77.23
3	0.15045	80.4	76.92
4	0.15210	81.4	77.03
5	0.15565	83.5	77.13
6	0.15435	82.6	77.03
$\Delta_{sol}H^\circ_m(MoO_3, cr, 298.15\ K) = -(77.06 \pm 0.09)\ kJ\cdot mol^{-1}$			

$Li^+(aq, \infty)$,[11] and $CrO_4^{2-}(aq, \infty)$,[12] $\Delta_f H^\circ_m(Li_2CrO_4$, cr, 298.15 K) was derived as $-(1393.7 \pm 0.3)\ kJ\cdot mol^{-1}$. The only reported value: $-(1394.6 \pm 1.9)\ kJ\cdot mol^{-1}$ by O'Hare *et al.*[13] based on $\Delta_{sol}H^\circ_m$ of Shidlovskii *et al.*, agrees very well with the present value.

The molar enthalpy of solution at $T = 298.15$ K of Li_2O was obtained as $-(133.01 \pm 0.20)\ kJ\cdot mol^{-1}$ in close agreement with the value $-(132.80 \pm 0.33)\ kJ\cdot mol^{-1}$ reported in the JANAF tables.[14] This confirms the purity of Li_2O used in the present study. The molar enthalpies of solution of MoO_3, Li_2MoO_4, and (Li_2O + MoO_3) at $T = 298.15$ K in LiOH(aq, $0.1\ mol\cdot dm^{-3}$) are given in tables 2, 3, and 4, respectively.

The molar enthalpy of solution of MoO_3 at $T = 298.15$ K in LiOH(aq, $0.1\ mol\cdot dm^{-3}$) was found to be $-(77.06 \pm 0.09)\ kJ\cdot mol^{-1}$ and the molar enthalpies of solution of Li_2MoO_4 and (Li_2O + MoO_3) were found to be $-(31.69 \pm 0.47)\ kJ\cdot mol^{-1}$ and $-(207.11 \pm 0.07)\ kJ\cdot mol^{-1}$ respectively. The molar enthalpies of solution of MoO_3 and Li_2MoO_4 are listed in table 5 for comparison with the literature, with which the present values are in good agreement, with the

TABLE 3. The standard molar enthalpy of solution of Li_2MoO_4(cr) at $T = 298.15$ K in LiOH(aq, $0.1\ mol\cdot dm^{-3}$). In every run 350.0 g of LiOH(aq, $0.1\ mol\cdot dm^{-3}$) was used as the solvent. Molar mass of Li_2MoO_4(cr) was taken as $173.8156\ g\cdot mol^{-1}$. Uncertainty is equal to twice the standard deviation of the mean

Run	$m(Li_2MoO_4, cr)$/g	$-\Delta_{sol}H^\circ$/J	$-\Delta_{sol}H^\circ_m$/$kJ\cdot mol^{-1}$
1	0.12260	22.9	32.43
2	0.13370	24.4	31.75
3	0.10540	19.4	31.98
4	0.13800	24.5	30.93
5	0.12870	23.5	31.80
6	0.16350	29.4	31.28
$\Delta_{sol}H^\circ_m(Li_2MoO_4, cr, 298.15\ K) = -(31.69 \pm 0.47)\ kJ\cdot mol^{-1}$			

TABLE 4. Enthalpy of reaction at $T = 298.15$ K of (Li_2O + MoO_3) in LiOH(aq, 0.1 mol · dm^{-3}). In each run 350.0 g of LiOH(aq, 0.1 mol · dm^{-3}) was used. Molar mass of Li_2O(cr) and MoO_3(cr) were taken as 29.8774 g · mol^{-1} and 143.9382 g · mol^{-1}, respectively. Uncertainty is equal to twice the standard deviation of the mean

Run	$m(Li_2O + MoO_3)$ / g	$-\Delta_r H^\circ$ / J	$-\Delta_r H_m^\circ$ / kJ · mol^{-1}
1	0.10384	123.7	207.05
2	0.10559	125.8	207.08
3	0.11100	132.3	207.17
4	0.11548	137.6	207.11
5	0.12153	144.9	207.24
6	0.12234	145.7	207.00
7	0.29082	346.6	207.15
8	0.29495	351.8	207.32
9	0.29710	353.8	206.99
10	0.30278	360.6	207.01

$\Delta_r H_m^\circ(Li_2O + MoO_3$, cr, 298.15 K$) = -(207.11 \pm 0.07)$ kJ · mol^{-1}

exception of the value reported by Thien and Zharkova. This confirms the accuracy of our method.

The enthalpy of formation of Li_2MoO_4 from solid oxides, $\Delta_{f,\,oxide} H_m^\circ$, at $T = 298.15$ K using the reaction:

$$Li_2O(cr) + MoO_3(cr) = Li_2MoO_4(cr),$$

was obtained as the difference of enthalpy of solution of Li_2MoO_4 from that of (Li_2O + MoO_3) in the same solvent: LiOH(aq, 0.1 mol · dm^{-3}):

$$\begin{aligned}\Delta_{f,\,oxides} H_m^\circ(Li_2MoO_4, \text{cr}, 298.15\ \text{K}) &= \\ &\Delta_{sol} H_m^\circ\{(Li_2O + MoO_3), \text{cr}, 298.15\ \text{K})\} - \\ &\qquad \Delta_{sol} H_m^\circ(Li_2MoO_4, \text{cr}, 298.15\ \text{K}).\end{aligned}$$

The standard molar enthalpy of formation from oxides was obtained as $-(175.42 \pm 0.47)$ kJ · mol^{-1}. The thermochemical cycle to derive the standard molar enthalpy of formation from elements at $T = 298.15$ K is given in table 6. The molar enthalpy change for the reaction:

$$2Li(cr) + \tfrac{1}{2}O_2(g) = Li_2O(cr),$$

was taken as $-(598.73 \pm 2.09)$ kJ · mol^{-1} from the JANAF tables(14) and for the

TABLE 5. Comparison of $\Delta_r H_m^\circ$ values of MoO_3(cr) and Li_2MoO_4(cr) in LiOH(aq) at $T = 298.15$ K

Authors	$-\Delta_r H_m^\circ$/(kJ · mol^{-1})	
	MoO_3(cr)	Li_2MoO_4(cr)
Present work (0.1 mol · dm^{-3})	77.06 ± 0.09	31.69 ± 0.47
O'Hare *et al.* (0.2 mol · dm^{-3})	77.57 ± 0.17	31.84 ± 0.04
Suponitskii *et al.* (0.5 mol · dm^{-3})	77.19 ± 0.54	32.25 ± 0.04
Thien and Zharkova (0.3 mol · dm^{-3})	93.47 ± 0.38	38.49 ± 0.42

TABLE 6. The thermochemical cycle to derive the standard molar enthalpy of formation $\Delta_f H^\circ_m$ at $T = 298.15$ K of Li_2MoO_4(cr). Uncertainties in reaction (3) and (4) are quoted from references 14 and 15, respectively. Uncertainty in reaction (5) is the square root of the sum of the uncertainties in reactions (1) to (4)

1. $Li_2O(cr) + MoO_3(cr) = Li_2MoO_4(cr)$; $\Delta_{f,\,oxides} H^\circ_m = -(175.42 \pm 0.47)\ \mathrm{kJ \cdot mol^{-1}}$.
2. $2Li(cr) + \frac{1}{2}O_2(g) = Li_2O(cr)$; $\Delta_r H^\circ_m = -(598.73 \pm 2.09)\ \mathrm{kJ \cdot mol^{-1}}$.
3. $Mo(cr) + \frac{3}{2}O_2(g) = MoO_3(cr)$; $\Delta_r H^\circ_m = -(745.09 \pm 0.33)\ \mathrm{kJ \cdot mol^{-1}}$.
4. $2Li(cr) + Mo(cr) + 2O_2(g) = Li_2MoO_4(cr)$; $-\Delta_f H^\circ_m = (175.42 + 598.73 + 745..09 \pm 2.2)\ \mathrm{kJ \cdot mol^{-1}} = -(1519.2 \pm 2.2)\ \mathrm{kJ \cdot mol^{-1}}$.

reaction:

$$Mo(cr) + \tfrac{3}{2}O_2(g) = MoO_3(cr),$$

as $-(745.09 \pm 0.33)\ \mathrm{kJ \cdot mol^{-1}}$ from Wagman *et al.*(15) The $\Delta_f H^\circ_m$ value for Li_2MoO_4(cr) was derived as $-(1519.3 \pm 2.2)\ \mathrm{kJ \cdot mol^{-1}}$ and is in good agreement with the literature values as seen from table 7. The value reported by Thien and Zharkova is about $9\ \mathrm{kJ \cdot mol^{-1}}$ more negative than the rest of the results and as already pointed out by O'Hare *et al.*(5) it seems to have calorimetric bias (enthalpy of solution of both MoO_3 and Li_2MoO_4 are 20 per cent more negative). Further the value $-(1522.5 \pm 0.8)\ \mathrm{kJ \cdot mol^{-1}}$ reported by Suponitskii *et al.* is based on the enthalpy of solution of Li_2MoO_4(cr) in LiOH(aq, $0.3\ \mathrm{mol \cdot dm^{-3}}$) and the enthalpy of formation of the ions $Li^+(aq, \infty)$ and $MoO_4^{2-}(aq, \infty)$, where hydrolysis will affect the result. To account for this hydrolysis effect we have measured the enthalpy of solution of lithium molybdate in water and from the difference of enthalpy of solution of lithium molybdate in LiOH(aq, $0.1\ \mathrm{mol \cdot dm^{-3}}$) and in water we obtained a value of $3.25\ \mathrm{kJ \cdot mol^{-1}}$ as the enthalpy of hydrolysis. The result of Suponitskii *et al.*(6) when corrected for the enthalpy of hydrolysis, yielded a value of $-(1519.3 \pm 0.8)\ \mathrm{kJ \cdot mol^{-1}}$ which is also in excellent agreement with the present value.

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TABLE 7. $\Delta_f H^\circ_m$ values of Li_2MoO_4(cr) at $T = 298.15$ K

Authors	$-\Delta_f H^\circ_m/(\mathrm{kJ \cdot mol^{-1}})$
Thien and Zharkova	$1528.2 + 0.8$
O'Hare *et al.*	1519.8 ± 0.5
Suponitskii *et al.*	1522.5 ± 0.8
	1519.3 ± 0.8[a]
CATCH Table	1518.5 ± 4.4
Present work	1519.2 ± 2.2

[a] $\Delta_f H^\circ_m$ value of Li_2MoO_4(cr) after correcting for the enthalpy of hydrolysis as determined in the present work.

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