Conference paper

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Thermodynamic properties of molybdate ion: reaction cycles and experiments

Abstract: Standard molar quantities of molybdate ion entropy, S^0_m, enthalpy of formation, $\Delta_f H^o_m$, and Gibbs energy of formation, $\Delta_f G^o_m$, are key data for the thermodynamic properties of molybdenum compounds and complexes, which are at present investigated by an OECD NEA review project. The most reliable method to determine $\Delta_f H^o_m$ of molybdate ion and alkali molybdates directly consists in measuring calorimetrically the enthalpy of dissolution of crystallized molybdenum trioxide and anhydrous alkali molybdates in corresponding aqueous alkali metal hydroxide solutions. Solubility equilibria of sparingly soluble alkaline earth molybdates and silver molybdate lead to trustworthy data for $\Delta_f G^o_m$ of molybdate ion. Thereby the Gibbs energies of the metal molybdates and the corresponding metal ions are combined with the Gibbs energies of dissolution. As reliable values are available for $\Delta_f G^o_m$ of the relevant metal ions the problem reduces to select the best values of solubility constants and $\Delta_f G^o_m$ of alkaline earth molybdates and silver molybdate. There are two independent possibilities to achieve the latter task. (1) $\Delta_f H^o_m$ for alkaline earth molybdates and silver molybdate have been determined by solution calorimetry. Entropy data of molybdenum have been compiled and evaluated recently. CODATA key values are available for S^o_m of the other elements involved. Whereas $S^o_m(CaMoO_4, cr)$ is well known since decades, low-temperature heat capacity measurements had to be performed recently, but now reliable values for S^o_m of Ag_2MoO_4(cr), $BaMoO_4$(cr) and $SrMoO_4$(cr) are available. (2) $\Delta_f H^o_m(BaMoO_4, cr)$, for example, can be obtained from high temperature equilibria also, but the result is less accurate than that of the first method. Once Gibbs energy of formation, $\Delta_f G^o_m$, and enthalpy of formation, $\Delta_f H^o_m$, of molybdate ion are known its standard entropy, S^o_m, can be calculated.

Keywords: enthalpy; entropy; ISSP-16; molybdate ion; thermodynamics.

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Present status of $\Delta_f H^o$, $\Delta_f G^o$ and $S^o(MoO_4^{2-})$

Thermodynamic standard data of MoO_4^{2-} are listed in Table 1. Latimer's [1] values are clearly obsolete compared to those selected by Dellien et al. [2] and Wagman et al. [3]. While enthalpies and Gibbs energies of formation of [2] and [3] agree quite well the entropies differ by more than 10 $J \cdot K^{-1} \cdot mol^{-1}$, thus a re-evaluation within the framework of the OECD NEA Review Project on "Chemical Thermodynamics of Molybdenum" seemed appropriate. The final deliverable of Phase III of this Thermodynamic Data Base project is the "Chemical Thermodynamics of Iron, Part 1" [4], which is freely downloadable from the Internet. In sections Background, Focus of the review and Review procedure and results of this and the other chemical thermodynamics

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Table 1 Present status of $\Delta_f H^o$, $\Delta_f G^o$, S^o (MoO_4^{2-}) at T_{ref} = 298.15 K.

References	$\Delta_f H^o$/kJ·mol^{-1}	$\Delta_f G^o$/kJ·mol^{-1}	S^o/J·K^{-1}·mol^{-1}
Latimer [1]	−1063.99	−915.46	58.60
Dellien et al. [2]	−997.05	−838.47	37.70
Wagman et al. [3]	−997.9	−836.3	27.2

volumes background and procedure of the OECD-NEA reviews are explained. Thermodynamic properties of molybdate ion investigated and evaluated in this work are key data controlling solution chemistry of molybdenum compounds.

Standard molar enthalpy of formation of molybdate ion and alkali molybdates

Enthalpy of dissolution of molybdenum trioxide in dilute aqueous alkali hydroxide

Graham and Hepler [5] constructed a high precision calorimeter and derived $\Delta_f H^o$ (Na_2MoO_4, cr, 298.15 K) as well as $\Delta_f H^o$ (MoO_4^{2-}, 298.15 K) by measuring the enthalpies of solution of the following reactions.

$$MoO_3(cr) + 2\,NaOH\,(0.531\ mol\ dm^{-3}) = soln.\ I + H_2O(l) \quad (1)$$

$$soln.\ I = Na_2MoO_4(cr) \quad (2)$$

$$MoO_3(cr) + 2\,NaOH\,(0.531\ mol\ dm^{-3}) = Na_2MoO_4(cr) + H_2O(l) \quad (1) + (2) = (3)$$

A detailed calorimetric balance is given in Table 2. Interconversion between amount ratio (mole ratio) $r(H_2O/B)$ and molality m_B is achieved by eq. (4), where M_{H_2O} is the molar mass of H_2O.

$$r(H_2O/B) = 1/(M_{H_2O} m_B) \quad (4)$$

$$\Delta_f H^o_m(MoO_4^{2-}) = \Delta_{2r6} H^o_m + \Delta_f H^o_m(MoO_3, cr)[6] + 2\Delta_f H^o_m(OH^-)\,(Tab.\ 14) - \Delta_f H^o_m(H_2O,l)\,(Tab.\ 14)$$
$$\Delta_f H^o(MoO_4^{2-})/kJ\cdot mol^{-1} = -(997.42 \pm 1.13) \quad (5)$$

The value for $\Delta_f H^o$(MoO_3, cr, 298.15 K) has been compiled and evaluated recently [6], for this and all other auxiliary data used see section "Auxiliary data". The values for $\Delta_{2r4} H^o$ and $\Delta_{2r5} H^o$ in Table 2 have been derived from [3], see Figs. 1a, b and 2. Enthalpies of dilution for Na_2MoO_4 have not been determined experimentally, but have been estimated by assuming analogue behavior as observed with Na_2SO_4 ($\Delta_{2r5} H^o$). At ≈ 0.2 mol·dm^{-3}

Table 2 Calorimetric determination of $\Delta_f H^o$(MoO_4^{2-}, 298.15 K), $r(H_2O/NaOH)$ = 104.4, m(NaOH) ≈ 0.53 mol·kg^{-1} [5].

Reaction	($\Delta_r H^o \pm \delta\Delta_r H^o$)/kJ·mol^{-1}
MoO_3(cr) + 50 ($NaOH\cdot 104.4H_2O$) = $Na_2MoO_4\cdot 48NaOH\cdot 5221H_2O$	−78.868 ± 0.837 (2r1)
$Na_2MoO_4\cdot 48NaOH\cdot 5221H_2O$ = $Na_2MoO_4\cdot 208.84H_2O$ + 48($NaOH\cdot 104.42H_2O$)	0 ± 0.40 (2r2)
48($NaOH\cdot 104.42H_2O$) = 48($NaOH\cdot 104.4H_2O$) + 0.96H_2O(l)	0 ± 0.021 (2r3)
2($NaOH\cdot\infty H_2O$) = 2($NaOH\cdot 104.4H_2O$) + (∞ −208.8)H_2O(l)	0.938 ± 0.10 (2r4)
$Na_2MoO_4\cdot 208.84H_2O$ + (∞ −208.84)H_2O(l) = $Na_2MoO_4\cdot\infty H_2O$	−0.309 ± 0.20 (2r5)
MoO_3(cr) + 2($NaOH\cdot\infty H_2O$) = $Na_2MoO_4\cdot\infty H_2O$ + H_2O(l)	
MoO_3(cr) + 2OH^- = MoO_4^{2-} + H_2O(l)	−78.239±0.954(2r6)

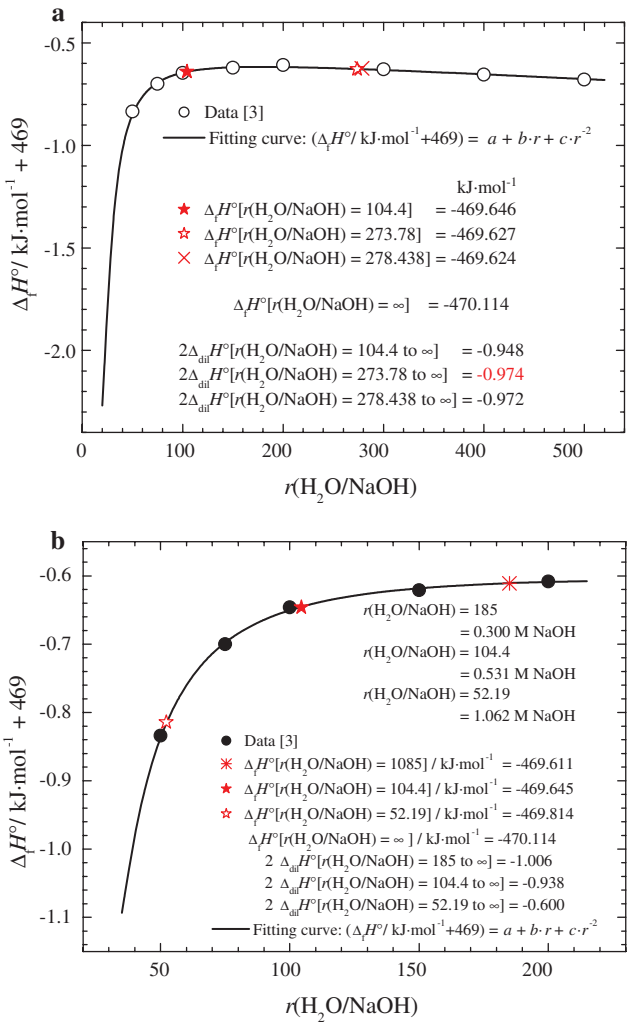

Fig. 1 (a) Calculation of $\Delta_f H^\circ_m[r(H_2O/NaOH)]$ for $50 \le r \le 500$. (b) Calculation of $\Delta_f H^\circ_m[r(H_2O/NaOH)]$ for $50 \le r \le 200$.

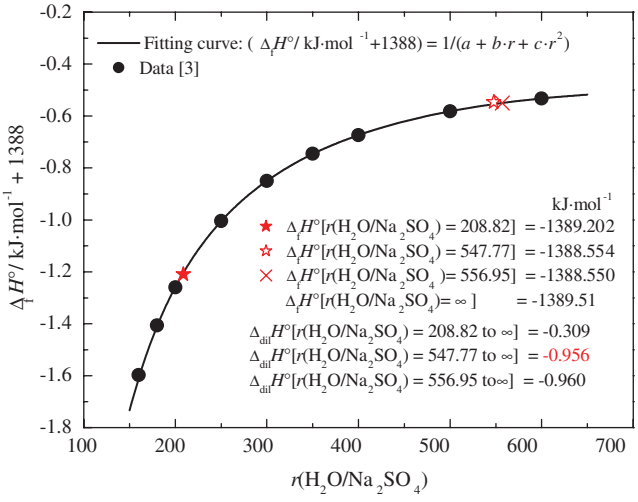

Fig. 2 Calculation of $\Delta_f H^\circ_m[r(H_2O/Na_2SO_4)]$. For $160 \le r \le 600$.

NaOH ($r(H_2O/NaOH = 273.8$, $r(H_2O/Na_2SO_4 = 547.8)$ corresponding values for $\Delta_{r4}H^o$ and $\Delta_{r5}H^o$ practically cancel each other, see the numerical values in red in Figs. 1a and 2.

Crouch-Baker and Dickens [7] dissolved MoO_3(cr) in 0.20 mol·kg^{-1} NaOH, thus there is only a minute difference between the recalculated values of $\Delta_{r1}H^o$ and $\Delta_{r6}H^o$, see Table 3.

O'Hare and his coworkers determined Δ_fH^o (MoO_4^{2-}, 298.15 K) as well as Δ_fH^o (Ma_2MoO_4, 298.15 K), where Ma = Cs, Rb or Li, by measuring the enthalpy of solution of MoO_3(cr) and Ma_2MoO_4(cr) in ≈ 0.24 mol·dm^{-3} CsOH [8], ≈ 0.2 mol·dm^{-3} RbOH [9], and ≈ 0.2 mol·dm^{-3} LiOH [10]. In each case a detailed calorimetric balance of the reaction cycle analogous to Table 2 was presented. Enthalpies of dilution for Cs_2MoO_4, etc. should be known. In [9] Δ_rH^o for reactions analogous to (2r2) and (2r3) were set to zero and Δ_rH^o for reactions analogous to (2r4) and (2r5) were assumed to cancel each other. The latter assumption, however, turned out to be approximately true only for sodium sulfate ($r = 547.8$). Thus corrections were applied assuming that dilution enthalpies of cesium, rubidium and lithium molybdates can be approximated by calculating the dilution enthalpies of the corresponding sulfates.

Similar experiments have been carried out by Suponitskii et al. [11] when MoO_3(cr) was dissolved in 0.32 mol·dm^{-3} NaOH. The enthalpies of solution obtained $\Delta_{r1}H^o$/kJ·mol^{-1} = −(78.01 ± 1.17) and $\Delta_{r6}H^o$/kJ·mol^{-1} = −(77.86 ± 1.25) agree quite well with the other determinations of this quantity [5, 7–10, 12]. However, the radiation correction given in Table 1 of [11] could not be assigned properly. In addition 0.32 mol·dm^{-3} NaOH equals $r(H_2O/NaOH) = 173.25$ and not $r(H_2O/NaOH) = 185$, thus $\Delta_{r6}H^o$ given in [11] was excluded from calculation of the weighted mean.

Shukla et al. [12] determined $\Delta_{sln}H^o_m$ values of MoO_3(cr), Li_2MoO_4(cr) and of [Li_2O(cr) + MoO_3(cr)] in LiOH(aq, 0.1 mol·dm^{-3}) at 298.15 K using an isoperibol solution calorimeter. From these data $\Delta_fH^o_m$ (Li_2MoO_4, cr) and $\Delta_fH^o_m$ (MoO_4^{2-}) were obtained. Results of references [5, 8–10], and [12] have been evaluated in a manner similar to that described for Na_2MoO_4(cr).

In Table 3 the weighted mean of $\Delta_{r1}H^o$ and $\Delta_{r6}H^o$ has been calculated. $\Delta_{r1}H^o$ and $\Delta_{r6}H^o$ differ only by a quarter of the 2σ values, but $\Delta_{r6}H^o$ is considered to be more reliable, and thus has been used for all further calculations.

Weighted mean: $(\Delta_{r1}H^o \pm 2\sigma)$/kJ·mol^{-1} = −(77.759 ± 0.569), $(\Delta_{r6}H^o \pm 2\sigma)$/kJ·mol^{-1} = −(77.625 ± 0.569) selected!

Equation (5) leads to the selected value:

$$\Delta_fH^o(MoO_4^{2-}, 298.15\ K)/kJ\cdot mol^{-1} = -(996.807 \pm 0.826)$$

In principle $\Delta_fH^o(MoO_4^{2-}, 298.15\ K)$ can be obtained also from eq. (6):

$$\Delta_fH^{\oplus}(MoO_4^{2-}) = -R(\partial \ln K^o_{s0}/\partial T^{-1})_p - n\Delta_fH^o(M^{2+/n}) + \Delta_fH^o(M_nMoO_4, cr) \quad (6)$$

Only K^o_{s0} of Ag_2MoO_4(cr) has been measured in a temperature range which allows to calculate $(\partial \ln K^o_{s0}/\partial T^{-1})_p$ reliably. For silver molybdate $-R(\partial \ln K^o_{s0}/\partial T^{-1})_p = (58.4 \pm 3.7)$ kJ·mol^{-1} [13], $\Delta_fH^o(Ag_2MoO_4, cr) = -(838.16 \pm 2.00)$ kJ·mol^{-1} [14]. For $\Delta_fH^o(Ag^+)$ see section "Auxiliary data". These data lead to $\Delta_fH^o(MoO_4^{2-}, 298.15\ K = -(991.3 \pm 4.2)$ kJ·mol^{-1}, and this value almost overlaps with the one determined by solution calorimetry of LiOH, NaOH, RbOH CsOH and MoO_3(s). As its uncertainty is ≈ 4.5 times higher, it was disregarded for the calculation of the weighted mean.

Table 3 Standard enthalpy of reaction MoO_3(cr) + $2OH^-$ = MoO_4^{2-} + H_2O(l).

Alkali metal	$\Delta_{r1}H^o$/kJ·mol^{-1}	$\Delta_{r6}H^o$/kJ·mol^{-1}	Reference
Li	−77.579 ± 0.661	−78.178 ± 0.661	[10]
Li	−77.091 ± 0.569	−77.718 ± 0.569	[12]
Na	−78.868 ± 0.954	−78.239 ± 0.954	[5]
Na	−78.099 ± 0.963	−78.088 ± 0.963	[7]
Rb	−77.870±0.635	−77.090±0.635	[9]
Cs	−78.025±0.655	−77.026±0.655	[8]

Standard molar enthalpy of formation of anhydrous sodium molybdate

The enthalpies of formation of alkali molybdates play an important role for the determination of formation enthalpies for silver, barium and strontium molybdate. Thus, in this section methods to obtain $\Delta_f H^o(Na_2MoO_4, cr)$ will be discussed. As pointed out in subsection "Enthalpy of dissolution of molybdenum trioxide in dilute aqueous alkali hydroxide", Graham and Hepler [5] and O'Hare et al. [8–10] determined $\Delta_f H^o$ (Ma_2MoO_4, cr, 298.15 K), where Ma = Cs, Rb, Na or Li, by measuring the enthalpy of solution of MoO_3(cr) and Ma_2MoO_4(cr) in dilute aqueous solutions of the corresponding alkali hydroxide. The detailed calorimetric balance leading to $\Delta_f H^o(Na_2MoO_4, cr)$ is given in Table 4.

$$\begin{aligned}\Delta_f H^o_m(Na_2MoO_4, cr) &= \Delta_{4r5} H^o_m - \Delta_f H^o_m(H_2O, l) + 2\Delta_f H^o_m(NaOH{\cdot}\infty H_2O)[3] + \Delta_f H^o_m(MoO_3, cr)\\ \Delta_f H^o_m(Na_2MoO_4, cr) &= -(1467.574 \pm 1.014)/kJ{\cdot}mol^{-1}\end{aligned} \quad (7)$$

As the enthalpies of dilution have been taken from [3], so was the value for $\Delta_f H^o_m(NaOH{\cdot}\infty H_2O)$, the uncertainty assigned to it was obtained by combining the values listed for $\pm\delta\Delta_f H^o_m(Na^+)$ and $\pm\delta\Delta_f H^o_m(OH^-)$ in [15].

Koehler et al. [16] adopted a different reaction scheme for the solution calorimetric determination of $\Delta_f H^o_m(Na_2MoO_4, cr)$, see Table 5:

$$\begin{aligned}\Delta_f H^o_m(Na_2MoO_4, cr) = \Delta_{5r6} H^o_m - 2\Delta_f H^o_m(HCl, r = 12.731)[3] + 2\Delta_f H^o_m(NaCl, cr)(Tab.\ 14)\\ + \Delta_f H^o_m(H_2O, l) + \Delta_f H^o_m(MoO_3, cr)\end{aligned} \quad (8)$$

The value for $\Delta_f H^o_m(HCl, r = 12.731)/kJ{\cdot}mol^{-1} = -(162.421 \pm 0.209)$ has been calculated from enthalpies of dilution listed in [3], see Fig. 3, the uncertainty was taken from [16].

As the calorimetric experiments were carried out at T = 303.15 K the authors [16] corrected $\Delta_{5r6} H^o_m$ to T = 298.15 K. This correction was accepted, but for calculating the weighted mean the uncertainty was increased by a factor of 1.5, $\delta\Delta_f H^o_m(Na_2MoO_4, cr) = \pm(1.5{\cdot}0.968)\,kJ{\cdot}mol^{-1}$.

$$\Delta_f H^o_m(Na_2MoO_4, cr, 298.15\ K)/kJ{\cdot}mol^{-1} = -(1468.593 \pm 1.452)$$

Table 4 Reaction scheme and thermochemical data of $\Delta_f H^o(Na_2MoO_4, cr, 298.15\ K)$.

Reaction [5]	$(\Delta_r H^o \pm \delta\Delta_r H^o)/kJ{\cdot}mol^{-1}$
$MoO_3(cr) + 50\,(NaOH{\cdot}104.4H_2O) = Na_2MoO_4{\cdot}48NaOH{\cdot}5221H_2O$ (r1)	
$Na_2MoO_4{\cdot}48NaOH{\cdot}5221H_2O = Na_2MoO_4(cr) + 48(NaOH{\cdot}104.42H_2O)$ (r2)	-69.141 ± 0.804 (4r1 + 4r2)
$50(NaOH{\cdot}104.42H_2O) = 50(NaOH{\cdot}104.4H_2O) + H_2O(l)$	0 ± 0.02 (4r3)
$2(NaOH{\cdot}\infty H_2O) = 2(NaOH{\cdot}104.42\ H_2O) + (\infty - 208.84)\ H_2O(l)$	0.938 ± 0.10 (4r4)
$MoO_3(cr) + 2(NaOH{\cdot}\infty H_2O) = Na_2MoO_4(cr) + H_2O(l)$ $MoO_3(cr) + 2Na^+ + 2OH^- = Na_2MoO_4(cr) + H_2O(l)$	-68.203 ± 0.810 (4r5)

Table 5 Calorimetric reaction scheme for $\Delta_f H^o_m(Na_2MoO_4, cr)$.

Eq.	Reaction [16]	$\Delta_{5r} H_{303.15}/kJ{\cdot}mol^{-1}$
(5r1)	$MoO_3(cr) + 2OH^-(sol) = MoO_4^{2-}(sol) + H_2O(sol)$	-77.188 ± 0.133
(5r2)	$2NaCl(cr) = 2Na^+(sol) + 2Cl^-(sol)$	7.448 ± 0.030
(5r3)	$26.462H_2O(l) = 26.462H_2O(sol)$	0.042 ± 0.042
(5r4)	$2Na^+(sol) + MoO_4^{2-}(sol) = Na_2MoO_4(cr)$	10.572 ± 0.043
(5r5)	$2\,Cl^-(sol) + 27.462H_2O(sol) = 2(HCl{\cdot}12.731H_2O)(l) + 2OH^-(sol)$	117.727 ± 0.575
(5r6)	$MoO_3(cr) + 2NaCl(cr) + 26.462H_2O(l) = Na_2MoO_4(cr) + 2(HCl{\cdot}12.731H_2O)(l)$	58.601 ± 0.594 $\Delta_{5r6} H_{298.15}/kJ{\cdot}mol^{-1}$ 59.897 ± 0.594

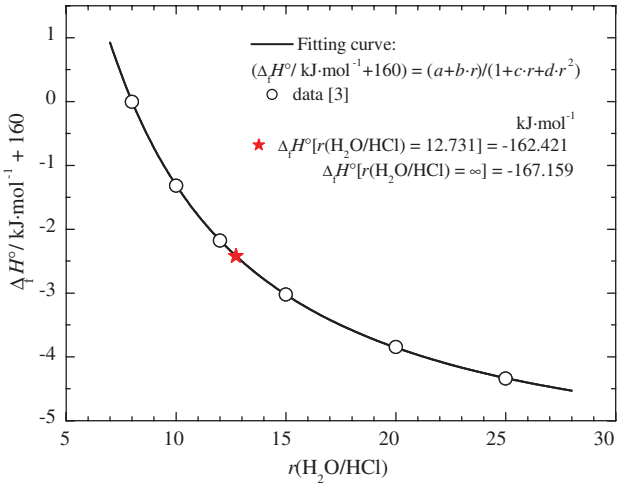

Fig. 3 Calculation of $\Delta_f H^o_m[r(H_2O/HCl)]$. for $8 \le r \le 26$.

Tangri et al. [17] synthesized Na_2MoO_4(cr) from stoichiometric quantities of sodium carbonate and molybdenum trioxide by means of a pyrometallurgical technique, and measured its molar enthalpy of solution at 298.15 K using an isoperibol calorimeter. Dash and Shukla [18] carried out similar calorimetric experiments, but prepared anhydrous sodium molybdate by heating of $Na_2MoO_4 \cdot 2H_2O$ at 450 K for 8 h under a stream of high purity argon. To convert $\Delta_{sln}H_m$ (Table 6, column 4) into $\Delta_{sln}H^o_m$ (Table 6, column 5) the Debye-Hückel limiting law according to eq. (9) was used, where v is the sum of stoichiometric numbers of ions, z_+ and z are cation and anion charge numbers, respectively, and $A_H/RT = 0.80185$ (kg·mol^{-1})$^{0.5}$ has been taken from [19].

$$\Delta_{sln}H_m = \Delta_{sln}H^o_m + A_H \frac{v}{2} |z_+ z_-| I_m^{0.5} \tag{9}$$

In [18] it is argued that at amount ratio $r(H_2O/Na_2MoO_4) > 1000$ the measured heat of solution equals the heat at infinite dilution. Table 6, however, shows that $\Delta_{sln}H^o_m\ (r = \infty) - \Delta_{sln}H_m\ (r \approx 5000) \approx -1$ kJ·mol^{-1} and $\Delta_{sln}H^o_m\ (r = \infty) - \Delta_{sln}H_m\ (r \approx 20\,000) \approx -0.5$ kJ·mol^{-1}, thus these differences are by no means negligible.

As $\Delta_{sln}H^o_m$ refers to reaction $Na_2MoO_4(cr) \leftrightharpoons 2Na^+ + MoO_4^{2-}$ the standard molar enthalpy of sodium molybdate formation can be obtained by eq. (10).

Table 6 Enthalpy of solution of Na_2MoO_4(cr).

Refs.	Na_2MoO_4 m/mol·kg^{-1}	(I_m/mol·kg^{-1})$^{0.5}$	$\Delta_{sln}H_m$ ($r > 1000$)/kJ·mol^{-1}	$\Delta_{sln}H^o_m$(r=∞)/kJ·mol^{-1}
[17]	0.01158	0.18639	−10.464	−11.575
	0.01170	0.18735	−11.122	−12.240
	0.01005	0.17364	−10.129	−11.165
	0.01125	0.18371	−11.419	−12.515
	0.01019	0.17484	−10.662	−11.705
	0.01053	0.17774	−10.361	−11.421
			($\Delta_{sln}H^o \pm 2\sigma$)/kJ·mol^{-1} = −10.693 ± 0.977	($\Delta_{sln}H^o \pm 2\sigma$)/kJ·mol^{-1} = −11.770 ± 1.022
[18]	0.003690	0.10522	−9.848	−10.475
	0.002331	0.08362	−9.684	−10.183
	0.002137	0.08006	−10.043	−10.520
	0.002914	0.09349	−10.022	−10.580
			($\Delta_{sln}H^o \pm 2\sigma$)/kJ·mol^{-1} = −9.899 ± 0.336	($\Delta_{sln}H^o \pm 2\sigma$)/kJ·mol^{-1} = −10.440 ± 0.353

$$\Delta_f H^o_m(Na_2MoO_4, cr) = 2\Delta_f H^o_m(Na^+)[15] + \Delta_f H^o_m(MoO_4^{2-}) - \Delta_{sln} H^o_m \quad (10)$$

$$\Delta_f H^o_m(Na_2MoO_4, cr)/kJ\cdot mol^{-1} = -(1465.717 \pm 2\cdot 1.320)\ [17]$$

$$= -(1467.047 \pm 0.906)\ [18]$$

The atomic ratio of anhydrous sodium molybdate Na_2MoO_4(cr) synthesized and studied by [17] r(Na/Mo) = 1.999 ± 0.052, this scatter might be the reason that in this work the value for $\Delta_f H^o_m(Na_2MoO_4, cr)$ is slightly higher than those found by [5, 16] and [18]. Thus for calculating the weighted mean the uncertainty was increased by a factor of 2, $\delta\Delta_f H^o_m(Na_2MoO_4) = \pm 2.64$ kJ·mol^{-1}.

For further calculations the weighted mean of $\Delta_f H^o_m(Na_2MoO_4, cr)$ from the results of [5, 16–18] was selected:

$$\Delta_f H^o_m(Na_2MoO_4, cr, 298.15\ K) = -(1467.423 \pm 0.597)\ kJ\cdot mol^{-1}.$$

Standard molar Gibbs energy of formation of molybdate ion

Determination of $\Delta_f G^o_m(MoO_4^{2-})$ using solubility data of crystalline calcium, strontium, barium, and silver molybdate

O'Hare et al. [10] derived $\Delta_f G^o$ (MoO_4^{2-}, 298.15 K) using K^o_{s0} data obtained from solubility equilibria, M_nMoO_4(cr) ⇋ $nM^{2/n+}$(aq) + MoO_4^{2-}(aq), and eq. (11). In the present application M_nMoO_4 stands for calcium, strontium, barium, and silver molybdate. CODATA key values [15] and NEA selected auxiliary data [20] are available for the corresponding Gibbs energies of metal ion formation $\Delta_f G^o(M^{2+/n})$. Corresponding K^o_{s0} values have been reviewed recently [13].

$$\Delta_f G^o(MoO_4^{2-}) = -RT_{ref} \ln K^o_{s0} - n\Delta_f G^o(M^{2+/n}) + \Delta_f G^o(M_nMoO_4, cr) \quad (11)$$

One way to obtain $\Delta_f G^o(M_nMoO_4, cr)$ is by eqs. (12) and (13).

$$\Delta_f S^o(M_nMoO_4, cr) = S^o(M_nMoO_4, cr) - nS^o(M, cr) - 2S^o(O_2, g) - S^o(Mo, cr) \quad (12)$$

$$\Delta_f G^o(M_nMoO_4, cr) = \Delta_f H^o(M_nMoO_4, cr) - T_{ref}\Delta_f S^o(M_nMoO_4, cr) \quad (13)$$

For S^o(M, cr) and $S^o(O_2, g)$ again CODATA key values [15] and NEA selected auxiliary data [20] are available, whereas S^o(Mo, cr) has been compiled and evaluated recently [6]. Low-temperature heat capacity measurements of Morishita and his group led to standard entropies of Ag_2MoO_4(cr) (Morishita, private communication), $BaMoO_4$(cr) (Morishita, private communication) and $SrMoO_4$(cr) [21], which differ from those accepted so far by 7–15 J·K^{-1}·mol^{-1}, see Table 7 [3, 22]. The new value of $S^o_m(CaMoO_4, cr, 298.15)$ (Morishita, private communication) agrees within experimental uncertainties with the one obtained by Weller and King [23], (122.6 ± 0.8) J·K^{-1}·mol^{-1}.

Muldrow and Hepler determined $\Delta_f H^o(Ag_2MoO_4, cr)$ [14] and $\Delta_f H^o(CaMoO_4, cr)$ [24] by measuring solution enthalpies of reactions (14r), (16r), (18r), and (20eff) in their high precision calorimeter.

Table 7 Standard molar entropies of sparingly soluble molybdates.

Solid molybdates	S^o_m/J·K^{-1}·mol^{-1}		$\Delta_f S^o_m$/J·K^{-1}·mol^{-1}
	Ref. [3]	Ref. [22]	Ref. [(Morishita, private communication), 21]	Refs. [6, 15, 20, 21, (Morishita, private communication)]
Ag_2MoO_4(cr)	213	–	220.80 ± 2.21	−303.18 ± 2.25
$BaMoO_4$(cr)	138	146.9 ± 4.6	152.69 ± 1.53	−348.62 ± 1.75
$SrMoO_4$(cr)	–	128.9 ± 5.0	136.56 ± 1.37	−358.02 ± 1.39
$CaMoO_4$(cr)	122.6	122.6 ± 1.0	121.69 ± 1.22	−358.78 ± 1.29

Silver molybdate

In the 1st series of calorimetric experiments [14] the enthalpy of reaction of crystalline Na_2MoO_4 with dilute solutions of $AgNO_3$ in excess was measured to determine the enthalpy of precipitation of Ag_2MoO_4. The calorimetric reaction has been written as eq. (14r)

$$Na_2MoO_4(cr) + AgNO_3(\text{excess dil. sln.}) = Ag_2MoO_4(cr) + AgNO_3(\text{dil. sln.}) + NaNO_3(\text{dil. sln.}) \rightarrow \Delta_{14}H^o_m \tag{14r}$$

The enthalpies of dilution of $NaNO_3$ and $AgNO_3$ have been ignored because in these dilute solutions the respective heat effects are small and tend to cancel each other. Thus the calorimetric equation used effectively can be written as

$$Na_2MoO_4(cr) + 2Ag^+ = Ag_2MoO_4(cr) + 2Na^+ \rightarrow \Delta_{14}H^o_m / \text{kJ}\cdot\text{mol}^{-1} = -(61.086 \pm 2.292),\ \text{mean of 8 data sets} \tag{14eff}$$

$$\begin{aligned} &\Delta_f H^o_m(Ag_2MoO_4, cr) = \Delta_{14}H^o_m - 2\Delta_f H^o_m(Na^+) + 2\Delta_f H^o_m(Ag^+)[15] + \Delta_f H^o_m(Na_2MoO_4, cr) \\ &\Delta_f H^o_m(Na_2MoO_4, cr, 298.15\ K) / \text{kJ}\cdot\text{mol}^{-1} = -(1467.42 \pm 0.60)\ [\text{this work}] \\ &\Delta_f H^o_m(Ag_2MoO_4, cr) / \text{kJ}\cdot\text{mol}^{-1} = -(836.246 \pm 2.378) \end{aligned} \tag{15}$$

In the 2nd series of calorimetric experiments [14] the enthalpy of reaction of excess crystalline $AgNO_3$ with dilute solutions of Na_2MoO_4 was measured to determine the enthalpy of precipitation of Ag_2MoO_4. The calorimetric reaction has been written as eq. (16r).

$$AgNO_3(cr, \text{excess}) + Na_2MoO_4(\text{dil. sln}) = Ag_2MoO_4(cr) + AgNO_3(\text{dil. sln}) + NaNO_3(\text{dil. sln}) \rightarrow \Delta_{16}H_m \tag{16r}$$

To calculate the actual value of $\Delta^{sln}_{cr}H^o_m(AgNO_3)$ subtract $\Delta_f H^o_m(AgNO_3, cr)$ [3] from $\Delta_f H^o_m(AgNO_3, sln)$ at the corresponding value of $r(H_2O/AgNO_3)$. An analytical function of $\Delta_f H^o_m(AgNO_3, sln) = f[r(H_2O)/AgNO_3)]$ can be obtained, just as the curves plotted in Figs. 1–3, by nonlinear regression of respective data listed in [3]. When the enthalpy of solution of excess $AgNO_3$(cr) had been taken into account, the calorimetric equation used effectively was simplified to

$$2AgNO_3(cr) + MoO_4^{2-} = Ag_2MoO_4(cr) + 2NO_3^- \rightarrow \Delta_{16}H^o_m / \text{kJ}\cdot\text{mol}^{-1} = -(10.84 \pm 3.34),\ \text{mean of 4 data sets} \tag{16eff}$$

$$\Delta_f H^o_m(AgMoO_4, cr) = \Delta_{16}H^o_m - 2\Delta_f H^o_m(NO_3^-)[15] + \Delta_f H^o_m(MoO_4^{2-}) + 2\Delta_f H^o_m(AgNO_3, cr)[3] \tag{17}$$

$\Delta_f H^o_m(MoO_4^{2-})$ /kJ·mol^{-1} = −(996.762 ± 0.843) [this work], uncertainty of $\Delta_f H^o_m(AgNO_3, cr)$ has been estimated by analogy to similar data in [20].

$$\Delta_f H^o_m(Ag_2MoO_4, cr)/\text{kJ}\cdot\text{mol}^{-1} = -(842.73 \pm 3.67)$$

The weighted mean of eq. (15) and eq. (17) is the revised result of [14], which is based on auxiliary data accepted at present:

$$\Delta_f H^o(Ag_2MoO_4, cr, 298.15\ K) = -(838.16 \pm 2.00)\ \text{kJ}\cdot\text{mol}^{-1}.$$

Calcium molybdate

In the 1st series of calorimetric experiments [24] the enthalpy of reaction of excess crystalline $Ca(NO_3)_2$ with dilute solutions of Na_2MoO_4 was measured to determine the enthalpy of precipitation of $CaMoO_4$. The calorimetric reaction has been written as eq. (18r)

Table 8 Calorimetric reaction scheme for $CaMoO_4$(cr).

Eq.	Reaction	$\Delta_{8r}H$/kJ·mol^{-1}
(8r1)	MoO_3(cr, 25 °C) + H_2O(sol, 73.7 °C) = MoO_4^{2-}(sol,73.7 °C) + 2H^+(sol, 73.7 °C)	−25.557 ± 0.128
(8r2)	CaO(cr, 25 °C) + 2HF(sol, 73.7 °C) = CaF_2(s, 73.7 °C) + H_2O(sol, 73.7 °C)	−232.329 ± 0.371
(8r3)	CaF_2(sol, 73.7 °C) + MoO_4^{2-}(sol, 73.7 °C) + 2H^+(sol, 73.7 °C) = $CaMoO_4$(cr, 25 °C) + 2HF(sol, 73.7 °C)	92.153 ± 0.144
(8r4)	CaO(cr, 25 °C) + MoO_3(cr, 25) = $CaMoO_4$(cr, 25)	−165.733 ± 0.418

$$Ca(NO_3)_2(cr, \text{excess}) + Na_2MoO_4(\text{dil. sln}) = CaMoO_4(cr) + Ca(NO_3)_2(\text{dil. sln}) + 2NaNO_3(\text{dil. sln}) \quad (18r)$$

The actual value of $\Delta_{cr}^{sln}H_m^o[Ca(NO_3)_2]$ was calculated by the same method as was $\Delta_{cr}^{sln}H_m^o(AgNO_3)$. When the enthalpy of solution of $Ca(NO_3)_2$(cr) had been taken into account, the calorimetric equation used effectively was simplified to

$$\begin{aligned} Ca(NO_3)_2(cr, \text{excess}) + MoO_4^{2-} &= CaMoO_4(cr) + 2NO_3^- \rightarrow \Delta_{18}H_m^o \text{ kJ·mol}^{-1} \\ &= -(12.67 \pm 2.37), \text{ mean of 3 data sets} \end{aligned} \quad (18eff)$$

$$\begin{aligned} &\Delta_f H_m^o(CaMoO_4, cr) = \Delta_{18}H_m^o - 2\Delta_f H_m^o(NO_3^-) + \Delta_f H_m^o(MoO_4^{2-}) + \Delta_f H_m^o[Ca(NO_3)_2, cr]\ [3] \\ &\Delta_f H_m^o(CaMoO_4, cr)/\text{kJ·mol}^{-1} = -(1534.17 \pm 2.94) \end{aligned} \quad (19)$$

In the 2nd series of calorimetric experiments [24] the enthalpy of reaction of crystalline Na_2MoO_4 with dilute solutions of $Ca(NO_3)_2$ was measured to determine the enthalpy of precipitation of $CaMoO_4$. The calorimetric reaction has been written as eq. (20eff).

$$Na_2MoO_4(cr) + Ca^{2+} = CaMoO_4(cr) + 2Na^+ \rightarrow \Delta_{20}H_m^o/\text{kJ·mol}^{-1} = -(7.05 \pm 0.16), \text{ mean of 4 data sets} \quad (20eff)$$

$$\begin{aligned} &\Delta_f H_m^o(CaMoO_4, cr) = \Delta_{20}H_m^o - 2\Delta_f H_m^o(Na^+) + \Delta_f H_m^o(Na_2MoO_4, cr) + \Delta_f H_m^o(Ca^{2+})[14] \\ &\Delta_f H_m^o(CaMoO_4, cr)/\text{kJ·mol}^{-1} = -(1536.793 \pm 1.182) \end{aligned} \quad (21)$$

The weighted mean of series 1 and 2 results in: $\Delta_f H_m^o$ ($CaMoO_4$, cr, 298.15 K) = − (1536.43 ± 1.10) kJ·mol^{-1}. This value agrees perfectly with the original result of [24] $\Delta_f H_m^o$ ($CaMoO_4$, cr, 298.15 K) = −(1536.79 ± 3.77) kJ·mol^{-1}. Taking into account the difference in $\Delta_{cr}^{sln}H_m^o[Ca(NO_3)_2]$ measured by preliminary experiments of [24] and given by [3] it is suggested to keep the original uncertainty.

$$\Delta_f H_m^o(CaMoO_4, cr)/\text{kJ·mol}^{-1} = -(1536.43 \pm 3.77)$$

Barany [25] determined $\Delta_f H^o$ ($CaMoO_4$, cr) by solution calorimetry using the reaction scheme given in Table 8.

$$\begin{aligned} &\Delta_f H_m^o(CaMoO_4, cr) = \Delta_{8r4}H_m^o + \Delta_f H_m^o(MoO_3, cr) + \Delta_f H_m^o(CaO, cr)[15] \\ &\Delta_f H_m^o(CaMoO_4, cr)/\text{kJ·mol}^{-1} = -(1545.635 \pm 1.156) \end{aligned} \quad (22)$$

Barium molybdate, strontium molybdate

O'Hare [26] selected for the determination of $\Delta_f H^o(BaMoO_4, cr, 298.15\ K)$ the reaction

Cs_2MoO_4(cr) + $BaCl_2$(sln, pH ≈ 10) ⇌ $BaMoO_4$(cr) + 2CsCl(sln). When alkali molybdate is added to an excess of a barium salt solution at pH ≈ 10, pure $BaMoO_4$ precipitates quantitatively. The calorimetric scheme of three sets of measurements is summarized in Table 9.

Table 9 Reaction scheme for determination of $\Delta_f H^\circ_m(BaMoO_4, cr, 298.15\ K)$.

Reaction	$(\Delta_r H^\circ \pm \delta\Delta_r H^\circ)$/kJ·mol^{-1}
$Cs_2MoO_4(cr) + 20(Ba^{2+}\cdot 2Cl^-\cdot NH_4OH\cdot 532H_2O) = BaMoO_4(cr) + (19Ba^{2+}\cdot 20NH_4OH\cdot 40Cl^-\cdot 2Cs^+\cdot 10640H_2O)$	−(11.450 ± 0.310) (9r1)
$(19Ba^{2+}\cdot 20NH_4OH\cdot 40Cl^-\cdot 2Cs^+\cdot 10640H_2O) = (19Ba^{2+}\cdot 20NH_4OH\cdot 38Cl^-\cdot 10640H_2O) + 2CsCl(cr)$	−(34.748 ± 0.070) (9r2)
$(19Ba^{2+}\cdot 20NH_4OH\cdot 38Cl^-\cdot 10640H_2O) + BaCl_2(cr) = 20(Ba^{2+}\cdot 2Cl^-\cdot NH_4OH\cdot 532H_2O)$	−(12.349 ± 0.057) (9r3)
$Cs_2MoO_4(cr) + BaCl_2(cr) = BaMoO_4(cr) + 2CsCl(cr)$	−(58.547 ± 0.323) (9r4)

$$\Delta_f H^\circ_m(BaMoO_4, cr) = \Delta_{9r4} H^\circ_m - 2\Delta_f H^\circ_m(CsCl, cr)[20] + \Delta_f H^\circ_m(BaCl_2, cr)[20] + \Delta_f H^\circ_m(Cs_2MoO_4, cr)[6] \quad (23)$$

Recalculated value:

$$\Delta_f H^\circ(BaMoO_4, cr, 298.15\ K)/kJ\cdot mol^{-1} = -(1543.50 \pm 2.81)$$

Shukla et al. [27] determined the standard molar enthalpies of formation, $\Delta_f H^\circ_m$, at $T = 298.15$ K of $BaMoO_4$(cr) and $SrMoO_4$(cr) by a quite similar method, measuring the enthalpies of precipitation of these molybdates due to the reaction between Na_2MoO_4(cr) and ammoniacal solutions of barium or strontium nitrate in an isoperibol solution calorimeter. Molybdates of barium and strontium both have very low solubilities at pH = 10 and when an alkali molybdate is added to a barium or strontium salt solution, quantitative precipitation of barium or strontium molybdate takes place. The reaction can be represented as

Na_2MoO_4(cr) + $M(NO_3)_2$(aq, pH = 10) = $MMoO_4$(cr) + $2NaNO_3$(aq), (M = Ba or Sr). This reaction was used to derive the enthalpy of formation of $BaMoO_4$ and $SrMoO_4$. The quantities required include the enthalpies of solution/reaction of $Ba(NO_3)_2$, $Sr(NO_3)_2$, $NaNO_3$, and Na_2MoO_4 in ammoniacal solutions (pH = 10) of $Ba(NO_3)_2$ or $Sr(NO_3)_2$, enthalpies of formation of these four compounds, and the enthalpies of precipitation of $BaMoO_4$ and $SrMoO_4$ from ammoniacal $Ba(NO_3)_2$ or $Sr(NO_3)_2$ solutions.

The standard molar enthalpies of formation $\Delta_f H^\circ_m$ at $T = 298.15$ K of $Ba(NO_3)_2$(cr), $Sr(NO_3)_2$(cr), and $NaNO_3$(cr) required for evaluating $\Delta_f H^\circ_m$ values of $BaMoO_4$(cr) and $SrMoO_4$(cr) are available from [3] without their uncertainties. Hence in [27] it was attempted to measure these standard enthalpies of solution at 298.15 K in distilled water.

Plotting of $\Delta_{sln} H_m$ *vs.* $I_m^{0.5}$, showed that the extrapolation to zero ionic strength was faulty, see Fig. 4. Comparison with data selected by [3] showed discrepancies of 0.3–1 kJ·mol^{-1}. Correct application of eq. (9) improved the result, but a slight discrepancy remained. In view of this analysis it was decided to

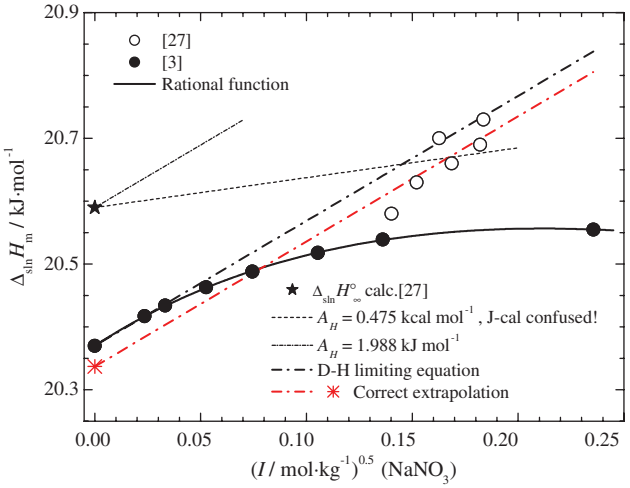

Fig. 4 Enthalpy of solution of $NaNO_3$ at 298.15 K.

take auxiliary quantities (i) $\Delta_f H^o(Sr(NO_3)_2, cr)$, and $\Delta_f H^o(NaNO_3, cr)$ as well as their uncertainties from [20], (ii) $\Delta_f H^o(Na_2MoO_4, cr)$ from this work, (iii) $\Delta_f H^o[Ba(NO_3)_2, cr]$ from [3], and the uncertainties of the latter from [27]. The reaction schemes for the determination of formation enhalpies of barium and strontium molybdate are summarized in Tables 10 and 11, respectively.

$$\Delta_f H^o_m(BaMoO_4, cr) = \Delta_{10r4} H^o_m - 2\Delta_f H^o_m(NaNO_3, cr) + \Delta_f H^o_m(Na_2MoO_4, cr) + \Delta_f H^o_m[Ba(NO_3)_2, cr]\ [3] \quad (24)$$

$$\Delta_f H^o_m(SrMoO_4, cr) = \Delta_{11r4} H^o_m - 2\Delta_f H^o_m(NaNO_3, cr) + \Delta_f H^o_m(Na_2MoO_4, cr) + \Delta_f H^o_m[Sr(NO_3)_2, cr]\ [20] \quad (25)$$

Recalculated values:

$$\Delta_f H^o_m(BaMoO_4, cr, 298.15\ K) / kJ \cdot mol^{-1} = -(1548.10 \pm 1.36)$$

$$\Delta_f H^o_m(SrMoO_4, cr, 298.15\ K) / kJ \cdot mol^{-1} = -(1548.10 \pm 1.30)$$

Standard Gibbs energies of formation have been calculated using these enthalpies of formation and the entropies of formation listed in Table 7, see Table 12.

The weighted mean of $\Delta_f H^o_m(BaMoO_4, cr)$ determined by [26] and [27] and the corresponding value of $\Delta_f G^o_m(BaMoO_4, cr)$ have been calculated, because eqs. (26) and (27) lead to independent values of $\Delta_f G^o_m(Ag_2MoO_4, cr)$ and $\Delta_f G^o_m(CaMoO_4, cr)$. The solubility products K^o_{s0} of $Ag_2MoO_4(cr)$, $CaMoO_4(cr)$, and $BaMoO_4(cr)$ are well known [13] and $\Delta_{sln} G^o_m = -RT_{ref} \ln K^o_{s0}$.

$$\Delta_f G^o_m(Ag_2MoO_4, cr) = \Delta_{sln} G^o_m(BaMoO_4) - \Delta_{sln} G^o_m(Ag_2MoO_4) - \Delta_f G^o_m(Ba^{2+}) + 2\Delta_f G^o_m(Ag^+) + \Delta_f G^o_m(BaMoO_4, cr) \quad (26)$$

$$\Delta_f G^o_m(CaMoO_4, cr) = \Delta_{sln} G^o_m(BaMoO_4) - \Delta_{sln} G^o_m(CaMoO_4) - \Delta_f G^o_m(Ba^{2+}) + \Delta_f G^o_m(Ca^{2+}) + \Delta_f G^o_m(BaMoO_4, cr) \quad (27)$$

Now the standard Gibbs energy of molybdate ion can be calculated employing eq. (11), see Table 13. Selected value:

$$\Delta_f G^o_m(MoO_4^{2-}, 298.15\ K) / kJ \cdot mol^{-1} = -(836.542 \pm 0.881)$$

This result agrees perfectly with that of O'Hare et al. [10].

Table 10 Reaction scheme for determination of $\Delta_f H^o_m(BaMoO_4, cr, 298.15\ K)$.

Reaction	$(\Delta_r H^o \pm \delta\Delta_r H^o)$/kJ·mol^{-1}
$Ba(NO_3)_2(cr) + sln\ A_1 = sln\ B_1$	(37.217 ± 0.054) (10r1)
$sln\ C_1 = 2NaNO_3(cr) + sln\ A_1$	$-(40.354 \pm 0.116)$ (10r2)
$Na_2MoO_4(cr) + sln\ B_1 = BaMoO_4(cr) + sln\ C_1$	$-(20.631 \pm 0.039)$ (10r3)
$Ba(NO_3)_2(cr) + Na_2MoO_4(cr) = BaMoO_4(cr) + 2NaNO_3(cr)$	$-(23.768 \pm 0.134)$ (10r4)

Table 11 Reaction scheme for determination of $\Delta_f H^o_m(SrMoO_4, cr, 298.15\ K)$.

Reaction	$(\Delta_r H^o \pm \delta\Delta_r H^o)$/kJ·mol^{-1}
$Sr(NO_3)_2(cr) + sln\ A_2 = sln\ B_2$	(18.388 ± 0.067) (11r1)
$sln\ C_2 = 2NaNO_3(cr) + sln\ A_2$	$-(40.510 \pm 0.101)$ (11r2)
$Na_2MoO_4(cr) + sln\ B_2 = SrMoO_4(cr) + sln\ C_2$	$-(11.359 \pm 0.012)$ (11r3)
$Sr(NO_3)_2(cr) + Na_2MoO_4(cr) = SrMoO_4(cr) + 2NaNO_3(cr)$	$-(33.481 \pm 0.122)$ (11r4)

Table 12 Calculation of standard Gibbs energies of metal molybdate formation at T_{ref} = 298.15 K.

Metal molybdate	$\Delta_f H_m^\circ$/kJ·mol^{-1}	$\Delta_f S_m^\circ$/J·K^{-1}·mol^{-1}	$\Delta_f G_m^\circ$/kJ·mol^{-1}	Refs.
Ag_2MoO_4	−838.16 ± 2.00	−303.18 ± 2.25	−747.765 ± 2.109	[14]
$BaMoO_4$	−1543.50 ± 2.81	−348.62 ± 1.75	−1439.560 ± 2.858	[26]
$BaMoO_4$	−1548.10 ± 1.36	−348.62 ± 1.75	−1444.160 ± 1.456	[27]
$BaMoO_4$ weighted mean	−1547.23 ± 1.22	−348.62 ± 1.75	−1443.387 ± 1.333	this work
$SrMoO_4$	−1548.10 ± 1.30	−358.02 ± 1.39	−1441.355 ± 1.364	[27]
$CaMoO_4$	−1545.64 ± 1.16	−358.78 ± 1.28	−1438.668 ± 1.222	[25]
$CaMoO_4$	−1536.43 ± 3.77	−358.78 ± 1.28	−1429.458 ± 3.789	[24]
$CaMoO_4$, eq. (26)	−1542.59 ± 3.14	−358.78 ± 1.28	−1437.872 ± 3.114	this work
$CaMoO_4$ weighted mean	−1544.59 ± 1.05	−358.78 ± 1.28	−1437.621 ± 1.113	this work

Table 13 Calculation of standard Gibbs energy of molybdate ion at T_{ref} = 298.15 K using eq. (11).

Metal molybdate	$\Delta_{sln} G_m^\circ$/kJ·mol^{-1}	$n\Delta_f G_m^\circ(M^{2+/n})$/kJ·mol^{-1}	$\Delta_f G_m^\circ$/ kJ·mol^{-1}	$\Delta_f G_m^\circ(MoO_4^{2-})$/ kJ·mol^{-1}
Ag_2MoO_4	66.16 ± 0.30	154.192 ± 0.312	−747.765 ± 2.109	−835.797 ± 2.153
Ag_2MoO_4, eq. (26)	66.16 ± 0.30	154.192 ± 0.312	−749.089 ± 2.627	−837.121 ± 2.663
$BaMoO_4$	48.51 ± 0.22	−557.656 ± 2.582	−1439.560 ± 2.858	−833.394 ± 3.858
$BaMoO_4$	48.51 ± 0.22	−557.656 ± 2.582	−1444.160 ± 1.456	−837.994 ± 2.973
$SrMoO_4$	45.00 ± 1.40	−563.864 ± 0.781	−1441.355 ± 1.364	−832.491 ± 2.105
$CaMoO_4$	45.69 ± 0.32	−552.806 ± 1.050	−1438.668 ± 1.222	−840.1725 ± 1.642
$CaMoO_4$	45.69 ± 0.32	−552.806 ± 1.050	−1429.458 ± 3.789	−830.962 ± 3.945
$CaMoO_4$, eq. (27)	45.69 ± 0.32	−552.806 ± 1.050	−1435.617 ± 3.113	−837.121 ± 3.301
				Weighted mean = −836.542 ± 0.881

Determination of $\Delta_f H_m^\circ(BaMoO_4, cr)$ from high-temperature equilibria

Singh et al. [28] determined the standard Gibbs energy of the reaction (I)

$$BaMoO_3(cr) + 0.5O_2(g) = BaMoO_4(cr) \quad (I)$$

by measuring the potential difference of the electrochemical cell Pt|[$BaMoO_3$(cr) + $BaMoO_4$(cr)]|CSZ|air($p(O_2)$ = 21.21 kPa)|Pt where CSZ represents zirconia stabilized with x(CaO) = 0.15, see Fig. 5. While enthalpy increment data for $BaMoO_4$(cr) are available [29], these data as well as low-temperature heat capacity data are lacking for $BaMoO_3$(cr). Thus a reliable third law analysis of reaction (I) is not feasible.

Dash et al. [30] investigated reaction (II)

$$BaMoO_3(cr) + 2Cr(cr) = Ba(g) + Mo(cr) + Cr_2O_3(cr) \quad (II)$$

by measuring the equilibrium vapor pressure of barium employing the Knudsen-effusion mass-loss technique, see Fig. 6. When the results of [28] and [30] are combined, see Fig. 7, second and third law analyses can be applied to reaction (III).

$$Ba(g) + Mo(cr) + Cr_2O_3(cr) + 0.5O_2(g) = BaMoO_4(cr) + 2Cr(cr) \quad (III)$$

Consulting the NIST-JANAF Tables [31], however, shows that $\Delta_f H_m^\circ(Cr_2O_3, cr, 298.15\,K)$/kJ·mol^{-1} = −(1134.7 ± 8.4). The second law value $\Delta_{rIII} H_m^\circ$/kJ·mol^{-1} = −(285.92 ± 2.49), see Fig. 7, thus the uncertainty of $\Delta_f H_m^\circ$ ($BaMoO_4$, cr, 298.15 K) derived from high-temperature equilibria will amount to ≈ ±9 kJ·mol^{-1}, regardless of the method of evaluation. Consequently $\Delta_f G_m^\circ(MoO_4^{2-})$ was based only on solution calorimetric experiments.

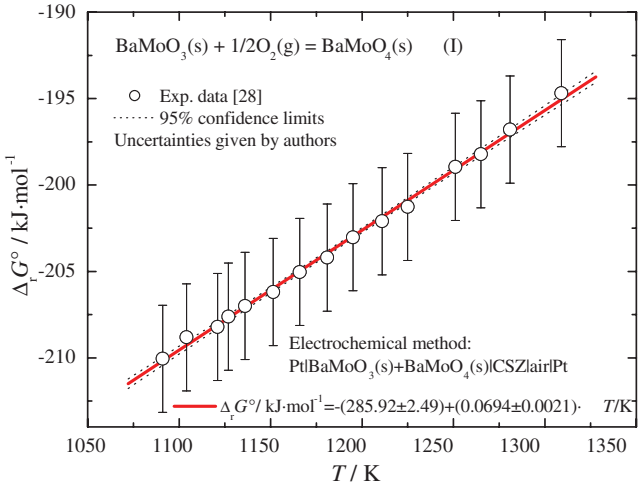

Fig. 5 Gibbs energy of reaction (I).

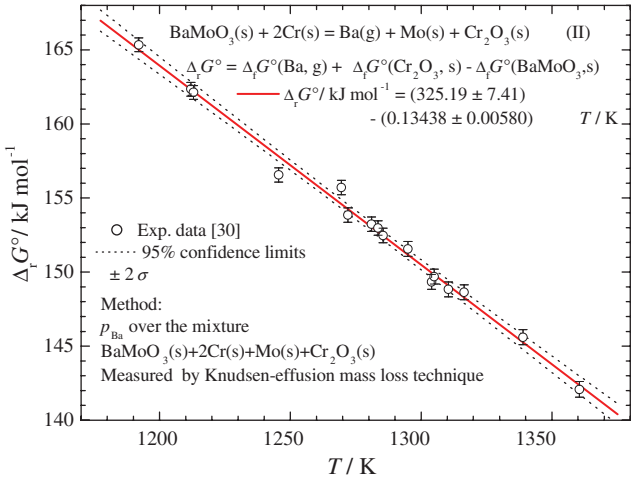

Fig. 6 Gibbs energy of reaction (II).

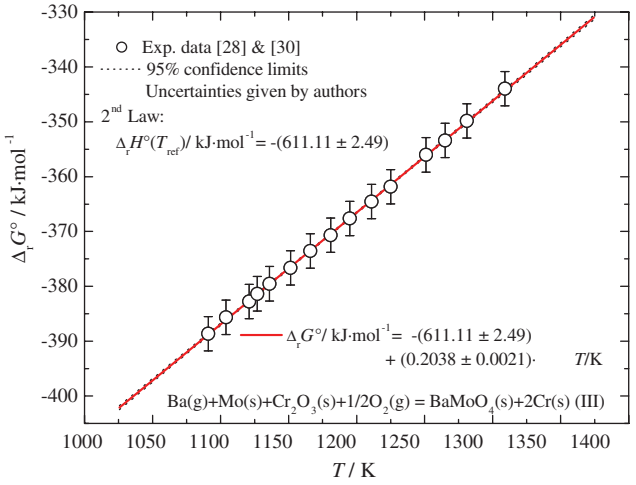

Fig. 7 Gibbs energy of reaction (III).

Calculation of $S^{\circ}_{m}(MoO_4^{2-})$

When $\Delta_f H^{\circ}_{m}(MoO_4^{2-})$, see subsection "Enthalpy of dissolution of molybdenum trioxide in dilute aqueous alkali hydroxide" and $\Delta_f G^{\circ}_{m}(MoO_4^{2-})$, see subsection "Determination of $\Delta_f G^{\circ}_{m}(MoO_4^{2-})$ using solubility data of crystalline calcium, strontium, barium, and silver molybdate" are known the calculation of $S^{\circ}_{m}(MoO_4^{2-})$ is straightforward according to eqs. (28) and (29).

$$\Delta_f S^{\circ}_{m}(MoO_4^{2-}) = [\Delta_f H^{\circ}_{m}(MoO_4^{2-}) - \Delta_f G^{\circ}_{m}(MoO_4^{2-})] / T_{ref} \tag{28}$$

$$\begin{aligned} S^{\circ}_{m}(MoO_4^{2-}) &= \Delta_f S^{\circ}_{m}(MoO_4^{2-}) + S^{\circ}_{m}(Mo, cr) + 2S^{\circ}_{m}(O_2, g) + S^{\circ}_{m}(H_2, g) \\ \Delta_f S^{\circ}_{m}(MoO_4^{2-}) / J\cdot K^{-1}\cdot mol^{-1} &= 1000\cdot[-(996.807 \pm 0.826) + (836.542 \pm 0.881)] / T_{ref} \end{aligned} \tag{29}$$

The value recommended for selection is

$$S^{\circ}_{m}(MoO_4^{2-}) / J\cdot K^{-1}\cdot mol^{-1} = (32.03 \pm 4.05)$$

Auxiliary data

Auxiliary data and references used in this work are listed in Table 14.

Selected data

Thermodynamic properties selected in this work, which will finally go in the OECD NEA Thermochemical Database (TDB) review on the inorganic compounds and aqueous complexes of molybdenum, are listed in Table 15. The data selected for Ag_2MoO_4(cr) are the weighted mean of [14] and eq. (26), see Tables 12 and 13.

Table 14 List of auxiliary data and references.

Compound/Species	$\Delta_f H^{\circ}_{m}$/kJ·mol^{-1}	Reference	Element	S°_{m}/J·K^{-1}·mol^{-1}	Reference
MoO_3(cr)	−(744.982 ± 0.592)	[6]	Mo(cr)	28.581 ± 0.050	[6]
OH^-	−(230.015 ± 0.040)	[15]	O_2(g)	205.152 ± 0.005	[15]
H_2O(l)	−(285.830 ± 0.040)	[15]	H_2(g)	130.680 ± 0.003	[15]
Na^+	−(240.340 ± 0.060)	[15]	Ag(cr)	42.55 ± 0.20	[15]
NaOH· ∞ H_2O	−(470.110 ± 0.070)	[3]	Ca(cr)	41.59 ± 0.40	[15]
NaCl(cr)	−(411.260 ± 0.120)	[20]	Sr(cr)	55.70 ± 0.21	[20]
Ag^+	(105.790 ± 0.080)	[15]	Ba(cr)	62.42 ± 0.84	[20]
$AgNO_3$(cr)	−(124.390 ± 0.500)	[3]			
$NaNO_3$(cr)	−(467.580 ± 0.410)	[20]			
$Ca(NO_3)_2$(cr)	−(938.390 ± 1.300)	[3]			
$Sr(NO_3)_2$(cr)	−(982.360 ± 0.800)	[20]			
$Ba(NO_3)_2$(cr)	−(992.070 ± 0.900)	[3]			
NO_3^-	−(206.850 ± 0.400)	[15]			
CaO(cr)	−(634.920 ± 0.900)	[15]			
Ca^{2+}	−(543.000 ± 1.000)	[15]			
Sr^{2+}	−(550.900 ± 0.500)	[20]			
Ba^{2+}	−(534.800 ± 2.500)	[20]			
$BaCl_2$(cr)	−(855.200 ± 2.500)	[20]			
CsCl(cr)	−(442.310 ± 0.160)	[20]			

Table 15 List of selected data at $T_{ref} = 298.15$ K.

Compound/Species	$\Delta_f H^\circ_m$/kJ·mol^{-1}	$\Delta_f G^\circ_m$/kJ·mol^{-1}	S°_m/J·K^{-1}·mol^{-1}
MoO_4^{2-}	−(996.807 ± 0.826)	−(836.542 ± 0.881)	32.03 ± 4.05
Na_2MoO_4(cr)	−(1467.423 ± 0.597)		
Cs_2MoO_4(cr)	−(1514.374 ± 1.206)		
Ag_2MoO_4(cr)	−(838.627 ± 1.609)	−(748.232 ± 1.743)	220.80 ± 2.21
$CaMoO_4$(cr)	−(1544.593 ± 1.045)	−(1437.621 ± 1.113)	121.69 ± 1.22
$SrMoO_4$(cr)	−(1548.100 ± 1.300)	−(1441.355 ± 1.364)	136.56 ± 1.37
$BaMoO_4$(cr)	−(1547.227 ± 1.224)	−(1443.287 ± 1.330)	152.69 ± 1.53

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References

[1] W. M. Latimer. *The Oxidation States of the Elements and Their Potentials in Aqueous Solutions*, 2nd ed., Prentice-Hall Inc., Englewood Cliffs, NJ (1952), pp. 392.
[2] I. Dellien, F. M. Hall, L. G. Hepler. *Chem. Rev.* **76**, 283 (1976).
[3] D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, R. L. Nuttall. *J. Phys. Chem. Ref. Data* **11** Suppl. 2 (1982).
[4] R. J. Lemire, U. Berner, C. Musikas, D. A. Palmer, P. Taylor, O. Tochiyama. *Chemical thermodynamics of iron*, part 1, NEA Data Bank, OECD, Ed. vol. 13, *Chemical Thermodynamics*, OECD Publications, pp. 1082, (2013).
[5] R. L. Graham, L. G. Hepler. *J. Am. Chem. Soc.* **78**, 4846 (1956).
[6] OECD NEA Mo review project, to be published.
[7] S. Crouch-Baker, P. G. Dickens. *J. Chem. Thermodyn.* **15**, 675 (1983).
[8] P. A. G. O'Hare, H. R. Hoekstra. *J. Chem. Thermodyn.* **5**, 851 (1973).
[9] P. A. G. O'Hare, H. R Hoekstra. *J. Chem. Thermodyn.* **6**, 117 (1974).
[10] P. A. G. O'Hare, K. J. Jensen, H. R. Hoekstra. *J. Chem. Thermodyn.* **6**, 681 (1974).
[11] Yu. L. Suponitskii, O. P. Proshina, M. Kh. Karapet'yants. *Russ. J. Phys. Ch.* **52**, 1699 (1978). Translated from Zhurnal Fizicheskoi Khimii **52**, 2956 (1978).
[12] N. K. Shukla, R. Prasad, K. N. Roy, D. D. Sood. *J. Chem. Thermodyn.* **24**, 897 (1992).
[13] H. Gamsjäger. *Pure Appl. Chem.* **85**, 2059 (2013).
[14] C. N. Muldrow Jr., L. G. Hepler. *J. Am. Chem. Soc.* **78**, 5989 (1956).
[15] J. D. Cox, D. D. Wagman, V. A. Medvedev, *CODATA Key Values for Thermodynamics*, Hemisphere Publ. Corp., New York (1989).
[16] M. F. Koehler, L. B. Pankratz, R. Barany. U.S. Dept.of the Interior, Bureau of Mines, Report of Investigations, No. 5973, pp. 13 (1962).
[17] R. P. Tangri, V. Venugopal, D. K. Bose. *Thermochim. Acta*, **198**, 259 (1992).
[18] S. Dash, N. K. Shukla. *J. Therm. Anal. Calorim.* **112**, 193 (2013).
[19] D. G. Archer, P. Wang. *J. Phys. Chem. Ref. Data* **19**, 371 (1990).
[20] H. Gamsjäger, T. Gajda, J. Sangster, S. K. Saxena, W. Voigt. *Chemical Thermodynamics of tin*, NEA Data Bank, OECD, Ed. vol. 12, *Chemical Thermodynamics*, pp. 55–72, OECD Publications, Tab. IV-1 (2012). *ISBN 978-92-64-99206-1.*
[21] M. Morishita and H.Houshiyama, *Mater. Trans. JIM* **56**, (2015), in press.
[22] O. Kubaschewski, C. B. Alcock, P. J. Spencer. *Materials Thermochemistry*, 6th ed., pp. 363, Pergamon Press Ltd., Oxford (1993).
[23] W. W. Weller, E. G. King. U.S. Dept.of the Interior, Bureau of Mines, Report of Investigations, No. 6147, pp. 6 (1963).
[24] C. N. Muldrow Jr., L. G. Hepler. *J. Phys. Chem.* **62**, 982 (1958).
[25] R. Barany, R. U.S. Dept.of the Interior, Bureau of Mines, Report of Investigations, No. 6143, pp. 11 (1962).
[26] P. A. G. O'Hare. *J. Chem. Thermodyn.* **6**, 425 (1974).
[27] N. K. Shukla, R. Prasad, D. D. Sood. *J. Chem. Thermodyn.* **25**, 429 (1993).
[28] Z. Singh, S. Dash, R. Prasad, V. Venugopal. *J. Alloys Comp*. **266**, 77 (1998).

[29] Z. Singh, S. Dash, R. Prasad, V. Venugopal. *J. Alloys Comp*. **279**, 287 (1998).
[30] S. Dash, Z. Singh, R. Prasad, D. D. Sood. *J. Nucl. Mater.* **207**, 350 (1993).
[31] M. W. Jr. Chase. NIST-JANAF Thermochemical Tables, 4th ed., Part II Cr-Zr, *J. Phys. Chem. Ref. Data*, Monograph No. 9 (1998).