THERMODYNAMIC PROPERTIES OF MOLYBDATE ION: REACTION CYCLES AND EXPERIMENTS

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1. Standard Gibbs energy of molybdate ion

O'Hare et al. [1] derived $\Delta_f G^\ominus(MoO_4^{2-}, 298.15\ K)$ using eq. (1):

$$\Delta_f G^\ominus(MoO_4^{2-}) = -RT_{ref} \ln K_{s0}^\ominus - n\Delta_f G^\ominus(M^{2+/n}) + \Delta_f G^\ominus(M_nMoO_4,\ cr) \quad (1)$$

The most reliable values of $K_{s0}^\ominus$ have been determined for Ag_2MoO_4(cr) and $BaMoO_4$(cr). CODATA key values [2] are available for $\Delta_f G^\ominus(Ag^+)$ and $\Delta_f G^\ominus(Ba^{2+})$. One way to obtain standard Gibbs energies of formation for Ag_2MoO_4(cr) and $BaMoO_4$(cr) is by eqs. (2) and (3).

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

$$\Delta_f G^\ominus(M_nMoO_4,\ cr) = \Delta_f H^\ominus(M_nMoO_4,\ cr) - T_{ref}\Delta_f S^\ominus(M_nMoO_4,\ cr) \quad (3)$$

CODATA key values are available for $S^\ominus(Ag,\ cr)$, $S^\ominus(Ba,\ cr)$ and $S^\ominus(O_2,\ g)$, whereas values of $S^\ominus(Mo,\ cr)$ have been compiled and evaluated recently. Low-temperature heat capacity measurements of Morishita [3] led to standard entropies of Ag_2MoO_4(cr), $BaMoO_4$(cr) and $SrMoO_4$(cr). Standard enthalpies of formation for Ag_2MoO_4(cr) and $BaMoO_4$(cr) have been determined by solution calorimetry. $\Delta_f H^\ominus$ of alkaline earth molybdates has also been obtained by 3rd law analysis of high temperature equilibrium studies, but solution calorimetry values are preferable. Thus information is complete to apply eq. (1) for the analysis of silver and barium as well as strontium and calcium molybdates which finally results in a weighted mean value of $\Delta_f G^\ominus(MoO_4^{2-}, 298.15\ K)$.

2. Standard enthalpy of molybdate ion

In principle $\Delta_f H^\ominus(MoO_4^{2-}, 298.15\ K)$ can be obtained from eq. (4) analogous to eq. (1):

$$\Delta_f H^\ominus(MoO_4^{2-}) = -R(\partial \ln K_{s0}^\ominus / \partial T^{-1})_p - n\Delta_f H^\ominus(M^{2+/n}) + \Delta_f H^\ominus(M_nMoO_4,\ cr) \quad (4)$$

Only $K_{s0}^\ominus$ of Ag_2MoO_4(cr) has been measured in a temperature range which allows to calculate $(\partial \ln K_{s0}^\ominus / \partial T^{-1})_p$ reliably. The uncertainty of the values derived using eq. (4) is approximately ±4 kJ·mol^{-1}, thus $\Delta_f H^\ominus(MoO_4^{2-}, 298.15\ K)$ determined by solution calorimetry of NaOH, MoO_3(s) and Na_2MoO_4(s) has been preferred.

3. Standard entropy of molybdate ion

Once standard Gibbs energy and standard enthalpy of MoO_4^{2-} is known the standard entropy is given by eqs. (5) and (6):

$$\Delta_f S^\ominus(MoO_4^{2-}) = \left[\Delta_f H^\ominus(MoO_4^{2-}) - \Delta_f G^\ominus(MoO_4^{2-})\right] / T_{ref} \quad (5)$$

$$S^\ominus(MoO_4^{2-}) = \Delta_f S^\ominus(MoO_4^{2-}) + S^\ominus(H_2,\ g) + 2S^\ominus(O_2,\ g) + S^\ominus(Mo,\ cr) \quad (6)$$

This approach yields the most reliable value of $S^\ominus(MoO_4^{2-}, 298.15\ K)$.

References:

[1] O'Hare P.A.G., Jensen K.J., Hoekstra, H.R., *J. Chem. Thermodyn.* **6**, (1974) 681–691.
[2] Cox J.D., Wagman D.D., Medwedev, V.A., *CODATA Key Values for Thermodynamics*, Hemisphere Publ. Corp., New York (1989) 271 p.
[3] Morishita M., Gamsjäger H., Hoshiyama H., Fukushima M., in preparation.