

1. Poos, G. I., Arth, G. E., Beyler, E. R. and Sarett, L. H. *J. Am. Chem. Soc.* **75** (1953) 422.
2. Holum, I. R. *J. Org. Chem.* **26** (1961) 4814.
3. Reich, H., Crane, K. F. and Sanfilippo, S. J. *J. Org. Chem.* **18** (1953) 822.
4. Cheronis, N. D. and Entrikin, J. B. *Semi-micro Qualitative Organic Analysis*, Interscience Publ., New York 1957, p. 730.

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## On Equilibria in Polymolybdate Solutions

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A few years ago, we published together with Ingvar Lindqvist<sup>1</sup> a short preliminary report on an investigation of the equilibria  $\text{MoO}_4^{2-} - \text{H}^+$  in 3 M (Na)ClO<sub>4</sub> medium at 25°C which indicated the presence of the complexes:  $\text{HMoO}_4^-$  ( $\text{HL}^-$ ),  $\text{H}_2\text{MoO}_4$  ( $\text{H}_2\text{L}$ ),  $\text{Mo}_7\text{O}_{24}^{6-}$  ( $\text{H}_8\text{L}_7^{6-}$ ),  $\text{HMo}_7\text{O}_{24}^{5-}$  ( $\text{H}_9\text{L}_7^{5-}$ ),  $\text{H}_2\text{Mo}_7\text{O}_{24}^{4-}$  ( $\text{H}_{10}\text{L}_7^{4-}$ ). Afterward, we have measured data over a still broader range, and added solubility data. The "MESAK" analysis<sup>2</sup> of the data gave a ( $\bar{p}$ ,  $\bar{q}$ ) diagram which indicated strongly the presence of only mono- and heptanuclear molybdates up to a value for  $Z$  (average number of  $\text{H}^+$  bound per  $\text{L}^{2-}$ ) of around 1.4. It also gave evidence for the complex  $\text{H}_{11}\text{L}_7^{3-}$  and for one larger complex. The solubility measurements indicated the presence, in acidic solutions, of a cation of charge +1.

The data have been treated by means of gradually improving versions of our computer program LETAGROP.<sup>3</sup> As a matter of fact, the difficulty of adjusting six and more equilibrium constants by

simultaneous variation was one of the chief incentives for inventing LETAGROP. Since it may still take some time until we get the final results ready for publication and the constants have been quoted repeatedly in the meantime, we think it may be helpful to publish our present preliminary results, which may still be refined somewhat.

As usual,  $\beta_{pq}$  stands for the equilibrium constants for the reaction  $p \text{H}^+ + q \text{L}^{2-} \rightleftharpoons \text{H}_p\text{L}_q^{(2q-p)-}$ , and the limits correspond to  $3\sigma$ .

$$\log \beta_{1,1} = 3.89 \pm 0.09; \log \beta_{2,1} = 7.50 \pm 0.17;$$

$$\log \beta_{3,7} = 57.74 \pm 0.03; \log \beta_{8,7} = 62.14 \pm 0.06;$$

$$\log \beta_{10,7} = 65.68 \pm 0.06; \log \beta_{11,7} = 68.21 \pm 0.07.$$

Among the various formulas hitherto tested for the large complex,  $\log \beta_{34,19} = 196.30 \pm 0.26$  gives the best agreement; however the measurements are in a fairly unfavorable range for deciding on the formula. For the cation, the agreement was improved by assuming  $\log \beta_{2,2} \approx 19$  ( $< 19.3$ ) although this formula (e.g.  $\text{HMo}_2\text{O}_6^+$ ) is not the only one possible.

A full report will be published later.<sup>4</sup>

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1. Sasaki, Y., Lindqvist, I. and Sillén, L. G. *J. Inorg. Nucl. Chem.* **9** (1959) 93.
2. Sillén, L. G. *Acta Chem. Scand.* **15** (1961) 1981.
3. Ingri, N. and Sillén, L. G. *Acta Chem. Scand.* **16** (1962) 173; *Arkiv Kemi* (1964). *In press.*
4. For references to other work on molybdate equilibria, see *Stability constants of metal-ion complexes, inorganic ligands*, *Chem. Soc. Spec. Publ.* **7** (1958) and **17** (1964).

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