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. *Semimicro Qualitative Organic Analysis*, Interscience Publ., New York 1957, p. 730.

Received April 23, 1964.

On Equilibria in Polymolybdate Solutions

YUKIYOSHI SASAKI* and LARS GUNNAR SILLÉN

Department of Inorganic Chemistry, Royal Institute of Technology (KTH), Stockholm 70, Sweden

A few years ago, we published together with Ingvar Lindqvist [1] a short preliminary report on an investigation of the equilibria $MoO_4^{2-} - H^+$ in 3 M (Na)ClO_4 medium at 25°C which indicated the presence of the complexes: $HMoO_4^-$ (HL^-), H_2MoO_4 (H_2L), $Mo_7O_{24}^{6-}$ ($H_6L_7^{6-}$), $HMo_7O_{24}^{5-}$ ($H_9L_7^{5-}$) $H_2Mo_7O_{24}^{4-}$ ($H_{10}L_7^{4-}$). Afterward, we have measured data over a still broader range, and added solubility data. The "MESAK" analysis [2] 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 $\bar{Z}$ (average number of H^+ bound per L^{2-}) of around 1.4. It also gave evidence for the complex $H_{11}L_7^{3-}$ 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.[3] 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 resuls 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, β_{pq} stands for the equilibrium constants for the reaction $p\ H^+ + q\ L^{2-} \rightleftharpoons H_pL_q^{(2q-p)-}$, and the limits correspond to 3σ.

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

log $\beta_{8,7} = 57.74 \pm 0.03$; log $\beta_{9,7} = 62.14 \pm 0.06$;

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 $\beta_{*2} \approx 19$ (< 19.3) although this formula (*e.g.* $HMo_2O_6^+$) is not the only one possible.

A full report will be published later.[4]

This research was supported by the *United States Air Force* under grant No. AF-EOAR-63-8.

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).

Received April 30, 1964.

* Present address: Department of chemistry, University of Tokyo, Japan.