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Molybdate chemistry in hydrothermal solutions: UV spectroscopic measurements.

Z. Minubayeva and T.M. Seward

Institute of Mineralogy and Petrology, ETH-Zurich, Switzerland (zminubayeva@erdw.ethz.ch / Fax: +41 1 6321088 / Phone: +41 1 6323743)

The aqueous chemistry for molybdenum in many natural hydrothermal systems where the concentration of molybdenum is less than 1×10^{-4} m is generally considered to be dominated by the simple molybdic acid species (molybdic acid itself, i.e. H_2MoO_4, and its deprotonation products, i.e. $HMoO_4^-$ and MoO_4^{2-}). Previous studies have exhibited a considerable scatter in the values of the deprotonation constants even at ambient temperature, whereas at the high temperatures, there are almost no data for this system at all. These inconsistencies in available data can in some cases be explained by different experimental conditions (i.e. total Mo concentrations, ionic strength and temperature), but in most cases the reasons for the differences in various data sets remain unsolved.

We have determined the values of K_1 and K_2, the deprotonation constants of molybdic acid at ambient temperature. Ultraviolet spectra of Mo-containing solutions with different concentrations (within the interval 1×10^{-4} - 1×10^{-5} mol/dm^3) at zero ionic strength were measured at 20^0C. The values of K_1 and K_2 were obtained from the UV-spectra using a computational technique based on singular value decomposition of the absorbance matrix. It is presumed that some polynuclear species already exist in solutions containing 10^{-4} mol/dm^3 of total molybdenum. To avoid this possibility, further experiments were conducted with lower concentrations (i.e. down to 10^{-5} mol/dm^3). At ambient temperature we also measured spectra for Mo-containing solutions over a range of constant ionic strength. Sodium molybdate was used for preparation of molybdate solutions; pH values and ionic strength of the sample solutions were adjusted with perchloric acid and sodium perchlorate respectively.

High-temperature experiments were conducted with 5×10^{-5} mol/dm^{3}Mo-containing

solutions. Spectra in the ultraviolet region were measured from 50 to 300^0C using high-temperature flow-through spectrophotometric cell.