3.6.21

A small volume, flow through optical cell for hydrothermal UV-VIS spectroscopy: Application to boric acid ionisation

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Recent developments in modern uv-vis spectrophotometers (xenon flash lamps, reference beam attenuation , very sensitive detectors, fiber optics etc) have made possible the design of miniature cells for high pressure high temperature uv-vis spectroscopy. A small volume, portable, low cost cell has been designed and tested up to 400 C and 1000 bar. The body of the cell is body of the SITEC AG double valve made out of the Hastelloy or titanium. The only one machined part is a small titanium mounting for the optical window. Because of the small size of the mounting, the sapphire window was not held by the screwed cup, but was brazed into thin wall shell of the mounting. The brazing was done using a Ag-Cu eutectic alloy in a high vacuum furnace. After brazing, the seal was then plated with gold. The sealing of the mounting with the window into the cell body was facilitated by a Graflex (flexible graphite) gasket using a Bridgman type of the seal based on the “unsupported area” principle. The volume of the cell is about 0.4 cm^3. Positioning of the cell in the spectrophotometer sample compartment was done using goniometer head supplied with a water cooled copper plate. The cell is currently being used to study of the pressure dependence of the boric acid dissociation with thymol blue as an indicator. Some of these results will be presented.

3.6.22

Spectrophotometric determination of the deprotonation of molybdic acid (H_2MoO_4) up to 400^0C

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For many natural hydrothermal fluids at temperatures up to 400^0C and near neutral pH’s, the concentration of molybdenum is $\leq 1\times10^{-4}$ m and the aqueous chemistry is generally considered to be dominated by the simple molybdic acid species. At 25^0C and molybdenum concentration $<1\times10^{-4}$ m, molybdic acid (H_2MoO_4) and its deprotonation products ($HMoO_4^{-}$ and MoO_4^{2-}) predominate. However, a slight increase in total amount of molybdenum leads to appearance of polynuclear species, first of all $Mo_7O_{24}^{6-}$ and $Mo_8O_{26}^{4-}$(1,2).

Previous studies (1,2,3) have reported quite different values for the K1 and K2 at ambient temperature, which can be explained by different experimental conditions (i.e. total Mo concentrations, ionic strength and temperature).

We have determined the values of K_1 and K_2, the deprotonation constants of molybdic acid at ambient temperature (at zero ionic strength). Ultraviolet spectra of $1*10^{-4}$ and $5*10^{-5}$ mol/dm^3 Mo-containing solutions were measured at 20^0C. Sodim molybdate was used for preparation of molybdate solutions and the pH values of the sample solutions from 2.2 to 7.2 were adjusted with perchloric acid. The ionic strength was not adjusted. Perchloric acid was used because it has no effective absorption above 200 nm when the concentrations are lower than 0.1 mol/dm^3 (2).

The values of K_1 and K_2 were obtained from the UV-spectra using a computational technique involving factor analyses with the MATLAB platform. It’s presumed that in solutions containing 10^{-4} mol/dm^3 of total molybdenum some polynuclear species already exist. To avoid this possibility experiments with lower concentrations (i.e. down to 10^{-5} mol/dm^3 were also conducted.experiments at tempeartures up to 400^0C are also underway.

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