

The Hydrolysis of As(III) and Sb(III) in Hydrothermal Solutions to 300°C

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Arsenic and antimony occur ubiquitously in fluids throughout the earth's crust but the hydrothermal geochemistry of these elements is not well known. The lack of thermodynamic data means that the reliable modelling of arsenic and antimony transport and mineral deposition in hydrothermal systems is fraught with uncertainty.

The aim of this study has therefore been to obtain data on the weak acid ionization constants for the both arsenious and antimonious acid from 25 to 300°C at saturated vapour pressures. The dissociation constants of H_3AsO_3 and H_3SbO_3 (i.e. the hydroxo complexes) from 25 to 300°C are obtained by means of high temperature UV spectrophotometry. Absorbance measurements were carried out in a flow-through Ti-Pd alloy cell with windows of uv-quality fused silica. Spectra were collected using a Cary 5E double beam spectrophotometer. In order to maintain single phase conditions, pressure was held at 15 bar above the saturated water vapour pressure and controlled by means of Dynamax SD-300 HPLC pump and back pressure regulator. The concentration range of the total dissolved arsenic(III) was 1×10^{-4} to 2×10^{-4} mol/dm³ and the pH was varied from 7 to 11 by addition of sodium hydroxide. The concentration range for Sb(III) in solution was from 2×10^{-5} to 8×10^{-5} mol/dm³ and the pH was varied from 7 to 12.

Solution preparation and handling as well as pH determination were carried out in such a way as to exclude any contact

with air. All spectra were corrected at each temperature for the background absorption of the silica windows and water solvent. Total arsenic concentrations were determined by atomic absorption. Rank analysis of the absorbance matrix indicated the presence of the three species in solution, one of which could be ascribed to the hydroxide ion charge-transfer-to-solvent transition. The other two absorbing species are H_3AsO_3 and H_2AsO_3^- . The resulting spectra permitted the refinement of the first dissociation constant of H_3AsO_3 by a non-linear least squares approach. The algorithm utilises an analytical correction of the spectra for OH^- absorbance and uses the robust Tikhonov regularization method for the solution of overdetermined systems of linear equations on each iteration. pK_1 for H_3AsO_3 was found to decrease from 9.25 to 7.11 of the temperature range, indicating that the H_2AsO_3^- becomes a more important arsenic-containing species in near-neutral, geothermal fluids at 300°C. More difficulties were encountered in the study of the Sb(III) system, mainly because of the limiting solubility of Sb_2O_3 at 25°C and 1 bar. However, the pK_1 for H_3SbO_3 was found to change from 11.88 to 8.95 as temperature increases from 25 to 300°C.

These data are prerequisite to our on-going studies which will involve the determination of the stabilities and stoichiometry of thioarsenite and thioantimonites in high temperature aqueous solutions.