

Stibnite ($\text{Sb}_2\text{S}_{3(s)}$) solubility in acid to neutral sulphide solutions at 300°C , P_{sat} : The neutral $\text{Sb}(\text{OH})_3^0_{(\text{aq})}$ species is dominant

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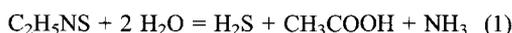
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The fact that neutral antimony hydroxocomplex is the main Sb(III) aqueous species in low sulphur hydrothermal solutions in throughout the important for geochemistry range of pH, Eh, pressure and temperature (Popova, Khodakovskiy, 1975, Shikina and Zotov, 1988, 1990). Our calculation (Akinfiyev *et al.*, 1993) demonstrated that $\text{Sb}(\text{OH})_3^0_{(\text{aq})}$ is also dominant in acid sulphide solution at $250\text{--}350^\circ\text{C}$. However, R. Krupp (1988) interpreted his experimental stibnite solubility data in $\text{H}_2\text{S}\text{--}\text{H}_2\text{O}$ solutions at $\text{pH} = 3.0\text{--}7.6$, $T = 275\text{--}350^\circ\text{C}$ and total free sulphur concentrations $0.01\text{--}0.1$ mol/kg only using $\text{Sb}_2\text{S}_2(\text{OH})_2^0_{(\text{aq})}$ species. Consequently, the present study focuses on experimental and calculational examination of the role of $\text{Sb}(\text{OH})_3^0_{(\text{aq})}$ in $\text{H}_2\text{S}\text{--}\text{H}_2\text{O}$ solutions in a broad range of H_2S concentrations.

Experimental

Aqueous stibnite solubility was measured as a function of H_2S concentration at 300°C under saturated vapour pressure (P_{SAT}). Experiments were carried out in titanic alloy pressure vessels which were filled under Ar atmosphere. Natural crystalline $\text{Sb}_2\text{S}_{3(s)}$ was used. The purity of stibnite was checked chemically and using X-ray diffraction. Distilled water or 0.001 m HCl (in order to control pH of solution) were used. Solutions were purified with Ar to remove air. H_2S was injected into a pressure vessel: 1) using a calibrated syringe and H_2S saturated solution; 2) bubbling H_2S through a solution in a pressure vessel to saturation; 3) H_2S was forming in the pressure vessel as a result of thioacetamide hydrolysis according to reaction:



It was found in preliminary experiment that presence of acetic acid and ammonia had no effect on the solubility of $\text{Sb}_2\text{S}_{3(s)}$. Total Sb concentration in solution was determined by mass loss technique and AAS. H_2S content in solutions was calculated from

amount of Sb_2S_3 and $\text{C}_2\text{H}_5\text{NS}$ that are dissolved in terms of the ligand sulphur concentration and controlled by iodometric titration. pH was measured at room temperature.

Results and discussion

Experimental $\text{Sb}_2\text{S}_{3(s)}$ solubility (in log scale) at 300 and 306°C is shown in Fig. 1 as a function of $m_{\text{H}_2\text{S}}$. Decrease of the experimentally determined $\text{Sb}_2\text{S}_{3(s)}$ solubility ($\log m_{\text{Sb}}$) as a function of $\log m_{\text{H}_2\text{S}}$ (Fig. 1) may be approximated by straight lines with the slopes of -1.41 ± 0.07 (26 points at 300°C) and -1.30 ± 0.08 (12 points at 306°C). Consequently,

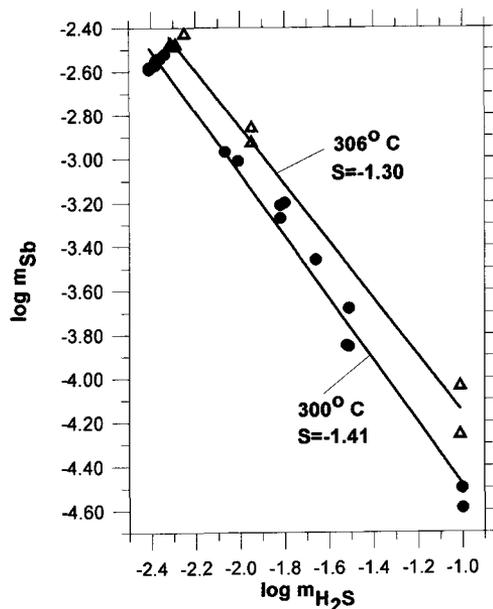


Fig. 1. Stibnite solubility ($\log m_{\text{Sb}}$, mol/kg) as a function of logarithm of H_2S equilibrium concentration (mol/kg) at 300 and 306°C and saturated vapour pressure.

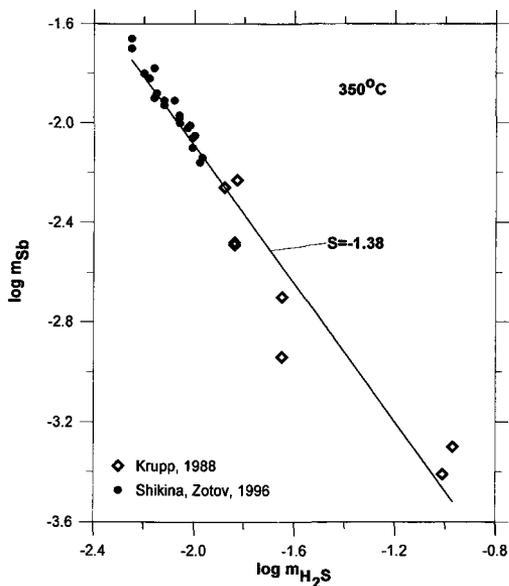
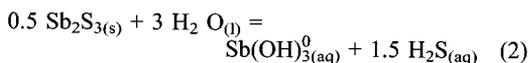
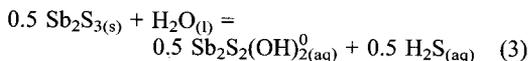


FIG. 2. Sb concentration ($\log m_{\text{Sb}}$, mol/kg) in an equilibrium with stibnite as a function of logarithm of H_2S concentration (mol/kg) at 350°C and saturated vapour pressure.

$\text{Sb}_2\text{S}_3(\text{s})$ solubility may be described according to equation:



with the slope of -1.5 , close to our experimental values. Krupp (1988) described his experimental data according to the equation:



which corresponds to a slope of only -1 . Experimental $\text{Sb}_2\text{S}_3(\text{s})$ solubility at 350°C , P_{SAT} from Krupp (1988) and our previous data (Shikina and Zotov, 1996) are plotted in Fig. 2 as a function of $\log m_{\text{H}_2\text{S}}$. The calculated slope for this figure was found as -1.38 , that corresponds to a slope of equation (2) as in our experiments at 300°C . Hence $\text{Sb}(\text{OH})_3(\text{aq})$ is dominant in hydrothermal solutions in a wide range of H_2S concentration at $300\text{--}350^\circ\text{C}$.

Thermodynamic constants for reaction (2) calculated from our data at 300 and 306°C ($\log K_{300}^0 = -12.17 \pm 0.07$, $\log K_{306}^0 = -11.73 \pm 0.15$) are plotted

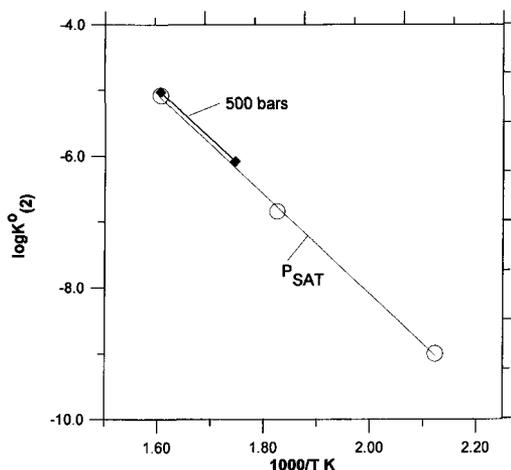


FIG. 3. Logarithm of the equilibrium constant for reaction (2) as a function of reciprocal temperature in $^\circ\text{K}$ at saturated vapour pressure (solid line) and 500 bars (dashed line).

in Fig. 3 as a function of $1/T$ together with our previously data (Akinfiev *et al.*, 1993; Shikina, Zotov, 1996; Shikina, Zotov, in press). Refinement of the thermodynamic properties for $\text{Sb}(\text{OH})_3(\text{aq})$ species from the data for $\text{Sb}(\text{III}) - \text{H}_2\text{O}$ and $\text{Sb}(\text{III}) - \text{S}(\text{II}) - \text{H}_2\text{O}$ systems is in progress.

Acknowledgements

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