

Stability of gold sulphide species ($\text{AuHS}^0_{(\text{aq})}$) and $\text{Au}(\text{HS})_2^-_{(\text{aq})}$) at 300, 350°C and 500 bar: experimental study

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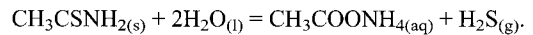
The hydrosulphide complexes AuHS^0 and $\text{Au}(\text{HS})_2^-$ are the predominant species transporting gold in hydrothermal solutions. However, literature values of the stability constants and other thermodynamic properties for AuHS^0 (Renders and Seward, 1989; Hayashi and Ohmoto, 1991; Gibert *et al.*, in press) and those for $\text{Au}(\text{HS})_2^-$ complex (Shenberger and Barnes, 1989; Seward, 1973; Benning and Seward, 1996) are in sufficient inconsistency.

Therefore, the aim of present study was to obtain new experimental data for Au-S-O-H system to calculate thermodynamic properties for gold hydrosulphide complexes.

Methods

The solubility of metallic gold have been measured at 300, 350°C and 500 bar in water, HCl (0.0002–0.2 m) and NaOH (0.05 m) solutions with H_2S concentration of 0.1 m. Experiments were carried out in titanium autoclaves. In order to prevent the H_2S oxidation the argon was bubbled through solution in an autoclave before sealing. Thioacetic

acid amid was used as a source of H_2S in 300°C experiments. It was introduced into the autoclave as a weighed solid substance, but hydrolysed under heating:



For 350°C experiments, hydrogen sulphide solutions were prepared by saturating the acid solutions and water with H_2S gas at 1 bar directly in the autoclave. A known amount of metallic aluminium was introduced in the autoclave to evolve hydrogen. Hydrogen pressure in several controlling runs was measured immediately after quenching. These pressure values were in good agreement with those calculated from the reaction of aluminium with water.

Duration of the experiments was 4 to 14 days. After water quenching, total gold concentration was measured by flameless AAS.

The pH, m_{HS^-} and $m_{\text{H}_2\text{S}(\text{aq})}$ values were calculated with the computer code GIBBS (Shvarov, 1992) using the thermodynamic properties of HCl^0 from Tagirov *et al.* (1997) and those for other aqueous

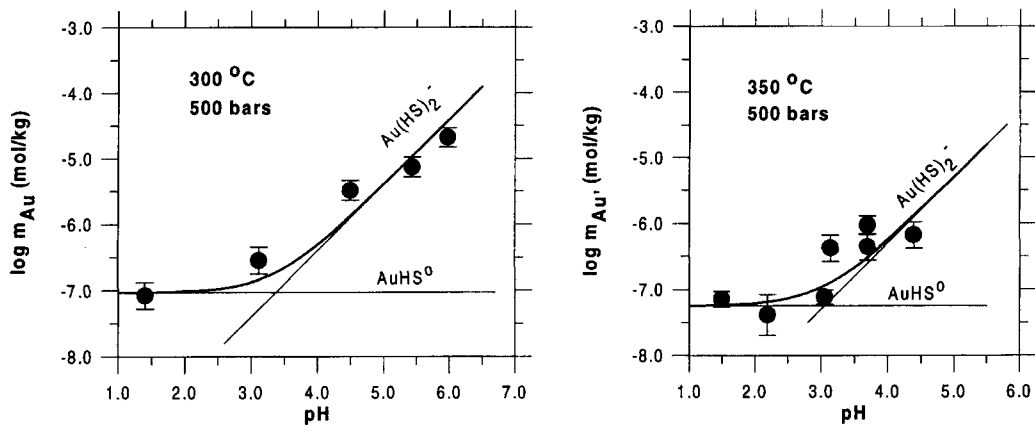


FIG. 1. Measured (the symbols) and calculated (the thick lines) gold solubility as a function of pH. The concentrations of gold species (the thin lines) are calculated using the constants from Table 1.

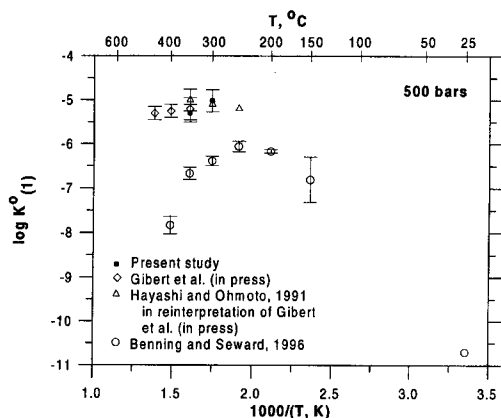


FIG. 2. Logarithm of equilibrium constants for the reaction (1) as a function of reciprocal temperature at 500 bar. The symbols represent experimental data taken from the references given in the figure.

species from SUPCRT 92 (Johnson *et al.*, 1992).

Ammonia and acetate ions are formed by hydrolysis of thioacetic acid amid. Ammonia complexes of gold are known to be stable only at very high concentration of NH_4NO_3 (10 m) at 25°C (Skibsted and Bjerrum, 1974). Up to date there is no any information on the stability of gold acetate complexes. During the calculations the possible contribution of ammonia and acetate complexes to total gold content was neglected.

Results

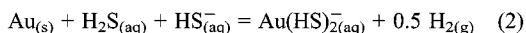
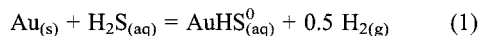
Experimental data are shown in Fig. 1 as a function of calculated pH. Solubility values obtained in this study correspond to total sulphide concentration of

TABLE 1. The logarithms of the standard constants of the reactions (1) and (2) at infinite dilution

$T^\circ\text{C}$	$\log K^\circ_{(1)}$	$\log K^\circ_{(2)}$
300	-5.02 ± 0.25	-0.25 ± 0.20
350	-5.30 ± 0.20	0.29 ± 0.30

0.1 m, and hydrogen fugacity of 105 and 46 bar at 300 and 350°C, respectively. Figure 1 demonstrates that the AuHS° is the dominate gold species in the solutions of acid $\text{pH} < 3$, whereas $\text{Au}(\text{HS})_2^-$ complex became important in low acid and near neutral solutions.

The calculated equilibrium constants for the reactions



at 300, 350°C and 500 bar are presented in Table 1. $\log K^\circ_{(1)}$ from Table are shown in Fig. 2 together with literature data. It is seen from this figure that $\log K^\circ_{(1)}$ values determined in the present study are in good agreement with data of Gibert *et al.* (in press) and Hayashi and Ohmoto (1991). However, the $\log K^\circ_{(2)}$ values (Table 1) are 1–1.5 units higher than that proposed by Shenberger and Barnes (1989); Benning and Seward (1996). The values of $K^\circ_{(2)}$ may be calculated more precisely using the new values of the first dissociation constant of H_2S (Suleimenov and Seward, 1997).

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