

# EXPERIMENTAL DETERMINATION OF STABILITY OF $\text{Au}_2\text{S}_{(\text{cr})}$ AND Au-HS AQUEOUS COMPLEXES AT 25°C, 1 bar VIA MEASUREMENTS OF SOLUBILITY OF GOLD AND Ag-Au SULPHIDES

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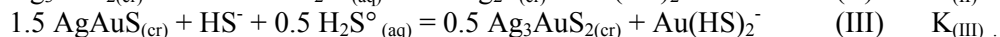
**Key words:** gold, solubility, hydrosulphide complexes, thermodynamic properties

Literature data on stability of Au hydrosulphide complexes ( $\text{AuHS}^\circ_{(\text{aq})}$  and  $\text{Au}(\text{HS})_2^-$ ) at ambient temperature are based on  $\text{Au}_2\text{S}_{(\text{cr})}$  solubility experiments [1]. However, thermodynamic properties of  $\text{Au}_2\text{S}_{(\text{cr})}$  are subjected to high uncertainty (e.g.  $\Delta_f G^\circ_{298}(\text{Au}_2\text{S}_{(\text{cr})})$  values reported in [2] and [3] are  $28.7 \pm 10.5$  kJ/mol and  $10.8 \pm 8.4$  kJ/mol, respectively). Therefore, the aim of the present study is to determine  $\Delta_f G^\circ_{298}$  for metastable  $\text{Au}_2\text{S}_{(\text{cr})}$  and Au-HS complexes via solubility measurements of metallic gold and Ag-Au sulphides whose thermodynamic properties were recently determined [4].

99.95% Au net and foil, 99.99% Ag foil and 99.99% S were used for solubility experiments and synthesis of sulphides (synthesis was carried out by E. Osadchii, IEM RAS).  $\text{Ag}_2\text{S}$  was synthesized from elements in a sealed evacuated silica glass tube at 120-140°C. XRD pattern for synthesized  $\text{Ag}_2\text{S}$  corresponded to acanthite (JCPDS card 14-0072).  $\text{AgAuS}$  (petrovskaitite) and  $\text{Ag}_3\text{AuS}_2$  (uytenbogaardite) were prepared in batches of 1-1.2 g by reacting Ag-Au alloys (electrum) and sulphur. Electrum of necessary compositions was synthesized by fusing a mixture of small pieces of gold and silver in a silica-glass ampoule in hot oxy-gas flame. The obtained alloy was flattened to ~0.2mm of thickness and then cut into small pieces ~0.5×2 mm. A weighed amount of these pieces of electrum was loaded together with stoichiometric mass of sulphur into a silica-glass tube. The synthesis was performed in horizontal tube furnaces. The sulphur was allowed to react at ~400°C for 2-3 days and then the charge was kept at ~520°C for about 1-2 days. Then the ampoule was cooled together with the furnace and opened. To eliminate possible heterogeneities this presynthesized material was ground, loaded into a silica-glass tube together with 1-5 mg of sulphur, and the synthesis procedure was repeated. The remaining sulphur crystallized on the free end of the ampoule while cooling. The obtained products were examined by XRD. The powder patterns corresponded to JCPDS cards 19-1146 for petrovskaitite and 20-461 for uytenbogaardite.

Three series of solubility experiments were performed using (i) metallic gold, (ii) mixtures of crystalline  $\text{Ag}_2\text{S}$ - $\text{Ag}_3\text{AuS}_2$ , and (iii)  $\text{Ag}_3\text{AuS}_2$ - $\text{AgAuS}$ . Experiments were performed in IGEM RAS (Moscow) and LMTG (Toulouse, France). Solubility was measured in sulfide solutions ( $m(\text{H}_2\text{S}) \sim 0.03$ -0.12) at  $24 \pm 2^\circ\text{C}$  and pH 4.7-7.5 using glass ampoules sealed in Ar atmosphere. It is necessary to reliably control Red-Ox conditions in metallic gold dissolution experiments (series i). These conditions may be affected by precipitation of trace amounts of sulfur during ampoules loading/sealing. To determine whether presence of elemental sulfur has an effect on Au solubility, experiments in series (i) were performed in 3 sub-series: in  $\text{H}_2\text{S}$  saturated solutions with and without crystalline sulfur added, and in solutions with sulfur deposited during sealing on air.

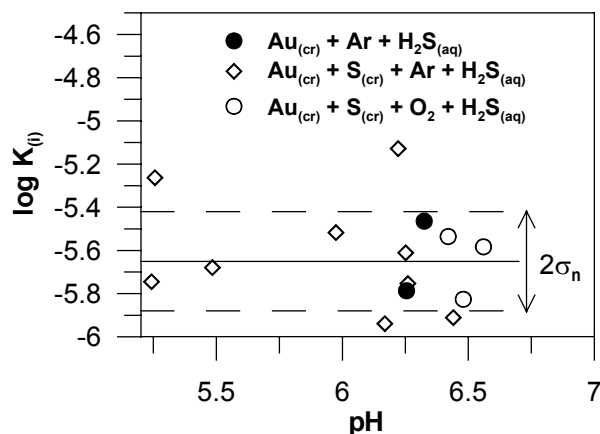
The following equilibrium reaction constants were determined:



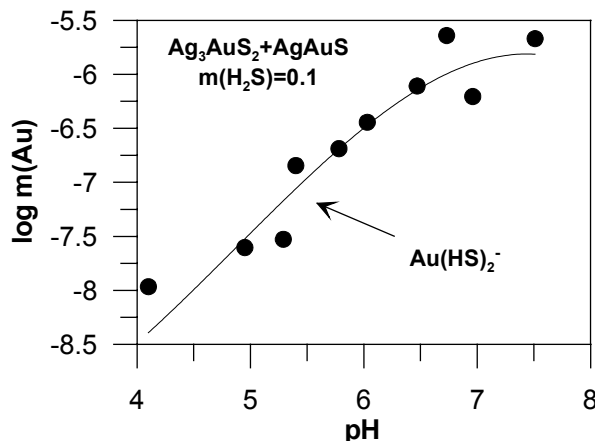
$\text{H}_2$  concentration necessary to calculate  $K_{(\text{i})}$  was deduced from gold solubility according to the stoichiometry of this reaction. Values of  $K_{(\text{i})}$  and concentration of gold in equilibrium with  $\text{Ag}_3\text{AuS}_2$ - $\text{AgAuS}$  mixture as a function of pH are shown in Fig. 1 and 2, respectively. Figure 1 demonstrates that presence of elemental sulfur has no effect on  $K_{(\text{i})}$  values and, therefore, proves correct method of calculation of  $\text{H}_2$  concentration. Independence of calculated  $K_{(\text{i})}$  values on solution pH (Fig. 1) and the shape of the solubility curve observed for series (iii) (Fig. 2) strongly suggest that stoichiometries of reactions (i) and (iii) are correct.

It was found that  $\log K_{(\text{i})} = -5.65 \pm 0.25$ ,  $\log K_{(\text{ii})} = -4.47 \pm 0.30$ , and  $\log K_{(\text{iii})} = -4.03 \pm 0.25$ . Values of  $K_{(\text{ii})}$  and  $K_{(\text{iii})}$  determined in two different laboratories (IGEM and LMTG) agree within 0.1 log unit. Combination of thermodynamic properties for Ag-Au sulphides from [4] with  $K_{(\text{ii})}$  and  $K_{(\text{iii})}$  determined in the present study yields  $\log K_{(\text{Au}(\text{HS})_2^-)} = -5.19 \pm 0.40$  and  $-5.31 \pm 0.35$ , respectively. Therefore,

a close agreement is observed between  $K_{(\text{Au}(\text{HS})_2^-)}$  derived from solubility of gold and Ag-Au sulphides. Accordingly, results of three experimental series (involving metallic gold (i) and Ag-Au sulphides (ii) and (iii)) yield the average value  $\log K_{(\text{Au}(\text{HS})_2^-)} = -5.38 \pm 0.25$ . This value, combined with  $\text{Au}_2\text{S}_{(\text{cr})}$  solubility products ( $\text{Au}_2\text{S}_{(\text{cr})} + 3 \text{HS}^- + \text{H}^+ = 2 \text{Au}(\text{HS})_2^-$  and  $\text{Au}_2\text{S}_{(\text{cr})} + \text{HS}^- + \text{H}^+ = 2 \text{AuHS}_{(\text{aq})}^0$  measured at 25°C in [1]), yields  $\Delta_f G_{298}^0(\text{Au}_2\text{S}_{(\text{cr})}) = 19.41 \pm 1.50 \text{ kJ/mol}$  and  $\log K_{(\text{AuHS}^0)} = -10.98 \pm 0.25$  for the reaction



**Fig. 1.** Logarithm of equilibrium (i) constant (series i) as a function of pH. Symbols represent values calculated from experimental solubility data, solid line is the average  $\log K_{(i)}$ , interval shown by dashed lines corresponds to standard deviation ( $\pm 0.25 \log$  units).



**Fig. 2.** Au concentration measured in equilibrium with  $\text{Ag}_3\text{AuS}_2\text{-AgAuS}$  mixture (series (iii)) carried out in Toulouse),  $m(\text{H}_2\text{S}) \sim 0.1$ . Symbols represent experimental data, solid line was calculated using  $\log K_{(iii)} = -4.03$ .

Stability constants of  $\text{AuHS}_{(\text{aq})}^0$  and  $\text{Au}(\text{HS})_2^-$  generated in the present study will further be compiled with those available in the literature for higher pressures and temperatures in order to calculate thermodynamic properties of these species.

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