# KINETICS AND CHEMISTRY OF GOLD DISSOLUTION IN H_2S-CONTAINING SOLUTIONS IN THE PRESENCE OF THE DISSOLVED SULFUR $S_8°$(aq) AT 200 AND 250°C

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The recent reviews and experimental investigations of gold solubility in the sulfide containing solutions (in the form of $Au(HS)°$(aq) and $Au(HS)_2^-$(aq)) at the elevated temperatures are still inconsistent with the experimental data [1-2]. This is largely true of the temperature interval below 300°C. The kinetic retard of hydrothermal reactions in this area hinders a good use of both the mineral buffers and the known sulfide-sulfate equilibrium in solutions [2]. Our method allows for the creation of red-ox conditions (approximated to H_2S/SO_4^{2-} equilibrium) through partial hydrogen sulfide oxidation up to the elementary sulfur (the dissolved form $S_8°$(aq). The equilibrium at the studied temperatures (200 and 250°C; P=150-200 bar) is established sufficiently fast by analogy with the method of gas mixtures for dry systems. The regularities of gold behavior in the conditions corresponding to physico-chemical parameters of ore deposition at the bottom of ocean basins additionally stimulate geochemical interest. It seems that hydrogen sulfide solution and ocean water mixing (followed by sulfide sulfur oxidation by the dissolved oxygen) is the main geochemical barrier to precipitate sulfides and concentrate noble metals. Fig.1 shows migratory ability of gold in the subacid sulfide solutions. It peaks between pyrite-pyrrhotine and pyrite-hematite buffers. This relationship is constructed on the data of the calculated modeling with the use of HCh software package [4] and UNITHERM database.
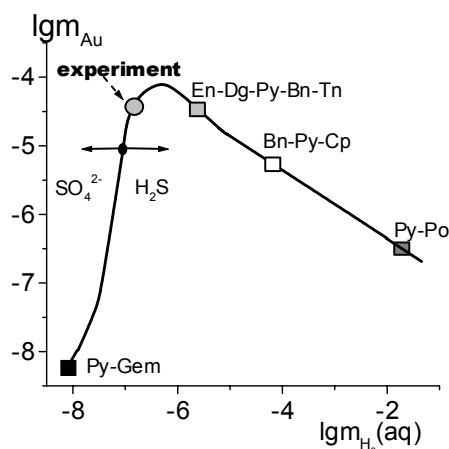
Fig.1. Calculated Au solubility in the solution $0.1mH_2S + 0.17mNaCl$, pH = 3.8, t = 200°C, P=150bar in relation to the equilibrium contents H_2(aq). The dots corresponding to the gold solubility in the presence of buffer mineral associations: Py-Gem – pyrite-hematite; En-Dg-Py-Bn-Tn – enargite – digenite – pyrite – bornite – tennatite; Bn-Py-Cp – bornite – pyrite – chalcopyrite; Py-Po – pyrite – pyrrhotine. The dot corresponding to the experimental conditions – "experiment". The arrows divide the area, where sulfate and sulfide sulfurs prevail.

Experimental results. The experiments have been carried out by autoclave procedure in titanium autoclaves with teflon insert at 200 and 250°C (P=150-200 bar). The autoclaves rotated on the cross axis. The duration of the experiments varied from 2 to 30 hours. The degree of hydrogen sulfide oxidation in the solution (0.1 m H_2S + 0.17 m NaCl) has been regulated by the addition of the dosed amounts of HNO_3 (0.00156 m) according to the reaction $8H_2S(aq) + 3.2HNO_3 \rightarrow S_8°(aq) + 1.6N_2(aq) + 9.6H_2O$. The resulting value of the initial pH appeared to be 2.8. No evidence of H_2S oxidation up to S°(el.) has been observed at ordinary temperature. The cooled solutions released gas (N_2) and thin suspension of elementary sulfur S(el.) was formed. H_2S (by iodometry), SO_4^{2-} (through $BaSO_4$), $S_2O_3^{2-}$ and other unsaturated sulfur compounds (by iodometry in the filtrate after $BaSO_4$ precipitation) were determined in the solutions. Elementary sulfur was dissolved in CCl_4 extractant and measured with the use of spectrophotometry. Gold was determined from the loss in foil weight and chemical analysis of the solution (atomic adsorption in the flame). Fig.2 demonstrates the kinetics of Au dissolution and S°(aq) formation. The data on the composition of the solutions, the calculated values m_{H2}(aq) and
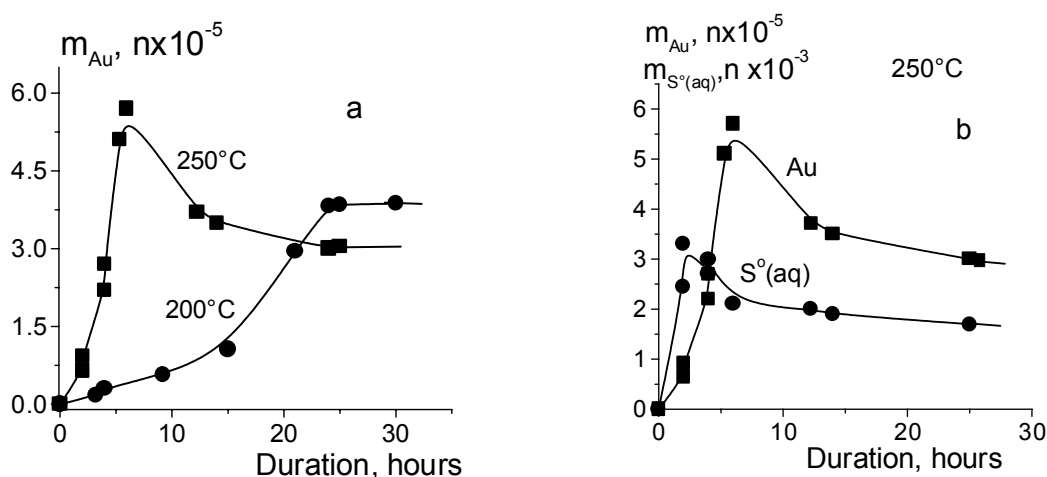
Fig.2. Kinetic dependencies according to the concentrations of the dissolved Au at t=200and 250°C (a) and Au and S°(aq) concentrations at t=250°C (b). High value of activation energy of the gold dissolution process (E_a=83 KJ/mol) points to the kinetic regime of its limiting stage.

t,°C	H_2S(aq), n•10^{-2}m	$S_8°$(aq), n•10^{-4}m	Au, n•10^{-5}m			H_2(aq), n•10^{-7}m	f_{H2}, n•10^{-6} bar	pH (±0.1)
			1	2	3			
200	9.2(±1)	2.5(±0.2)	3.7(±0.1)	3.5(±0.2)	*3.6(±0.3)*	*1.27(±0.02)*	5.4(±0.3)	5.0
	9.6	4.7	-	-	*5.7*	*1.21*	5.1	3.9
250	9.6(±1)	2.3(±0.2)	2.9(±0.1)	3.0(±0.2)	*2.95(±0.3)*	*2.58(±0.02)*	2.7(±0.3)	3.3
	9.8	1.4	-	-	*6.5*	*2.82*	2.9	3.8

1. – Au concentrations after the loss in weight; 2 – Au concentrations according to the solution analysis; 3 – Au mean value

f_{H2}(gas) are given for the longest experiments (24-30 hours) in the upper line of the Table. The results of the calculated modeling (see the lower line of the Table) are obtained using G° values for Au(HS)°(aq), Au(HS)$_2^-$(aq) according to [5] and for $S_8°$(aq) according to [6]. Good correlation of the experimental and calculated values m_{H2}(aq) and f_{H2}(gas) is evident. At the same time the calculated Au concentrations are higher than the experimental concentrations by 2.1•10^{-5} and 3.55•10^{-5} at 200 and 250°C, respectively. It is distinctly higher the experimental error. Closer investigations with the use of the elaborated method are required to refine the thermodynamic constants of the gold dissolution reactions.

References

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