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Physico-Chemical Modeling of the Sulfo-Arsenide System of Gold Bearing Ore Deposits

N.V. VILOR* AND L.A. KAZMIN**

Institute of Geochemistry, Siberian Division of the Russian Academy of Sciences, Irkutsk, 664033, Russia* (vilor@igc.irk.ru)
Research Center for Geotechnology, Russian Academy of Sciences, Petropavlovsk-Kamchatsky, 683002, Russia. **

Abstract. The existence of gold-arsenic mineralization, the presence of enhanced concentrations of gold in arsenopyrite, especially in its fine grain varieties showing positive gold-arsenic ratios in gold-quartz and gold-pyritic ores indicate the important role of As in hydrothermal gold transport. The most accessible approach to the investigation of these complicated systems is provided by physico-chemical modeling. In the present work the isobaric isothermal potentials (ΔG°_{f298}) of thioarsenides, the most important group of arsenic compounds in the solution, have been determined and refined on the basis of the creation of physico-chemical models using the data on the As sulfide solubility in the As – S – O – H system. The data obtained were reconciled with the thermodynamic data available by solving the reverse thermodynamic problem. Numerical physico-chemical modeling has been carried out for a series of tests in both pure water and hydrogen sulfide solutions (0.0032 - 0.011m) with the initial pH values from 1.14 to 8.4 in the 25-250°C temperature range under saturated water steam pressure. The computer-calculated constants are included in the modeling of tests on orpiment dissolution in sulfide-sodium solutions. The As_2S_{3ryst} solubility in the 25-250°C temperature range has first been obtained. A specific feature of the process is a sharp increase in dissolved arsenic total concentration as the pH value of the hydrothermal phase rises from 4 to 6-7. Concentration increases and gradient decreases with temperature rise. The predominant forms are represented by thioarsenites. Just as in acidic, so in weakly and moderately alkaline solutions the orpiment solubility is caused by the concentration combination of thioarsenous acid H_3AsS_3 and its oligomers $H_4As_2S_5^0$ and $H_2As_2S_4^0$. At a temperature of over 200-250°C these concentrations can be compared only with that of the $AsOH(HS)_2^0$ complex of mixed composition.

Introduction

The existence of mineralization of gold-arsenic type, the presence of enhanced concentrations of gold in arsenopyrite, especially in its fine-grain varieties showing positive gold-arsenic ratios in gold-quartz and gold-pyritic ores indicate the important role of As in the hydrothermal gold transport and its active part in the process of ore-formation. In the experimental studies Nekrasov (1991) has shown a non-linear dependence of gold solubility on the arsenic content in the solution and suggested the composition of the forming gold-arsenic complexes. The arsenic participation in gold hydrothermal transport seems to be beyond any doubt. However, it should be taken into account that the mutual transport medium is a complex multi component solution involving mineral buffers in thermodynamically open systems. The most accessible approach to the investigation of these complicated systems is provided by physical-chemical modeling, which opens up wide vistas for the elucidation of fine details of the gold and arsenic geochemistry depending on the combination of main physico-chemical parameters. But the development of various important numerical physico-chemical ore-formation models involving the process of gold dissolution deposition in the presence of As is hindered by the absence of very important thermodynamic constants such as isobaric-isothermal potentials of ions, complexes and compounds containing Au and As in complex sulfide chloride solutions like natural ore-bearing hydrothermal ones.

Material and Methods

In the present work the isobaric isothermal potentials (ΔG°_{f298}) of thioarsenides, the most important group of arsenic compounds in the solution, have been determined and refined on the basis of the creation of physico-chemical models using the literature data on the As sulfide solubility in the As – S – O – H system. The data obtained were reconciled with the thermodynamic database available by solving the reverse thermodynamic problem. The macro component composition of the system is complicated by the obligatory presence of NaOH and HCl, which regulate pH value and ionic force. The results were calculated using the "Selector" program complex (PC) with an algorithm proposed by the present authors. Numerical physico-chemical modeling has been carried out for a series of tests in both pure water and hydrogen sulfide solutions (0.0032 - 0.011 m) with the initial pH values from 1.14 to 8.4 (Weissberg et al. 1966; Mironova et al. 1983; Mironova and Zotov, 1988; Mironova et al.

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1990), in the 25-250°C temperature range under saturated water steam pressure. The computer calculated constants are included in the modeling of tests on orpiment dissolution in sulfide sodium solutions.

The compositions of arsenic containing particles in the solution with allowance for the data from (Mironova and Zotov, 1988; Webster, 1990; Weissberg et al. 1966) and those in the As – S – Na – Cl –H – O system under modelling.

The solution phase contains 166 particles as dependent components. In the gas phase there are 43 individual gases including volatile compounds of arsenic, chlorine, sulfur and sodium. Among the solid phases there are crystalline orpiment, red arsenic, arsenolite, claudite, arsenic and sodium salts. Complete physico-chemical model of the system involves 305 dependent components.

potentials of arsenic containing components of aqueous solution were primarily evaluated by the multi-step regression method. In present compositions of solutions the concentrations of arsenic particles and compounds satisfying the accuracy of numerically reproducible experiments have been calculated to reveal, as a result, the only solution corresponding to a minimum free energy of the system in the n-dimensional space of all its components and thermodynamic conditions (Fig.1, Table 1).

The As_2S_3 cryst solubility in the 25-250°C temperature range has first been obtained (Fig. 2). A specific feature of the dissolution process is a sharp increase in arsenic total concentration as the pH value of the hydrothermal phase rises from 4 to 6-7. Concentration increases gradient decreases with temperature rise. The plot slope becomes gentler in the area of alkaline solutions (Figs 3, 4). The

Table.1. Thermodynamic constants of hydrosulfide, sulfoarsenite and some mixed arsenic species.

N	Формула	ΔG°_{F298}	$\Delta H_F^{\circ}{}_{298}$	S°_{298}	$C^{\circ}p$	V°	$a_1 10$	$a_2 10^{-4}$	a_3	$a_4 10^{-4}$	c_1	$c_2 10^{-4}$	$\omega 10^{-5}$
1	$HAsS_2^{*}$	-12275	-10826	44.2	62.065	23.56	4.9762	4.3814	3.9969	-2.9599	42.0626	9.6082	-0.038
2	As_2^{-}	-6618	-17060	4.305	-57.785	7.49	3.3023	0.2955	5.6013	-2.791	-13.901	-14.8053	1.516
3	$H_3AsS_3^{*}$	-25810	-27561	71.623	280.719	74.53	11.9509	21.4246	-2.7326	-3.6643	170.5605	54.148	-0.038
4	$H_2AsS_3^{-}$	-20100	-26948	55.253	143.079	58.47	10.2359	17.2377	-1.0877	-3.4912	102.97	26.1107	1.3901
5	$HAsS_3^{-2}$	-11300	-21083	45.394	64.595	42.4	8.7159	13.5291	0.3651	-3.3378	75.5567	10.1235	3.3995
6	AsS_3^{-3}	-525	-11743	40.568	14.62	26.34	6.6827	8.562	2.3236	-3.1325	50.7156	-0.0564	3.8858
7	$H_2As_2S_4^{*}$	-33279	-28906	93.345	169.739	82.66	13.0634	24.143	-3.8061	-3.7766	105.3401	31.5414	-0.038
8	$HAs_2S_4^{-}$	-27218	-35166	52.008	30.948	66.59	11.1615	19.4981	-1.9771	-3.5846	31.9633	3.2696	0.8413
9	$As_2S_4^{-2}$	-16235	-23280	53.012	-28.154	50.53	9.4954	15.4311	-0.3802	-3.4164	11.8737	-8.7694	2.414
10	$H_4As_2S_5^{*}$	48624	-43764	133.858	163.36	133.63	20.0381	41.1862	-10.5356	-4.481	101.5913	30.242	-0.038
11	$H_3As_2S_5^{-}$	-39150	-38438	118.947	117.883	117.57	17.6075	35.2449	-8.1857	-4.2354	68.4464	20.9783	-0.7274
12	$H_2As_2S_5^{-2}$	-29680	-32950	105.857	72.827	101.51	16.1996	31.811	-6.8433	-4.0934	63.7274	11.8004	1.6095
13	$HAs_2S_5^{-3}$	-20210	-26784	95.485	45.14	85.44	14.5941	27.8928	-5.3063	-3.9314	63.8097	6.1605	3.3658
14	$HAs_3S_5^{*}$	-23680	-22473	83.17	131.816	90.79	14.1759	26.8615	-4.8795	-3.8889	83.0537	23.8164	-0.038
15	$As_3S_5^{-}$	-14250	-19837	60.37	57.858	74.72	12.2313	22.1118	-3.0083	-3.6926	46.5998	8.7512	0.7148
16	$H_3As_3S_6^{*}$	-46417	-39640	140.747	405.354	141.76	21.1506	43.9047	-11.609	-4.5933	243.8056	79.5361	-0.038
17	$H_2As_3S_6^{-}$	-36684	-33967	127.115	192.002	125.7	18.8645	38.3177	-9.4015	-4.3624	115.9859	36.0763	-0.2998
18	$HAs_3S_6^{-2}$	-27950	-34383	96.415	81.86	109.63	17.8194	35.7731	-8.4164	-4.2571	83.0493	13.6404	3.1145
19	$As_3S_6^{-3}$	-16400	-28888	81.425	20.841	93.57	15.7712	30.7694	-6.4432	-4.0503	51.3072	1.2108	3.5567
20	$H_2As_4S_7^{*}$	-39860	-45994	97.885	213.556	149.89	22.2631	46.6231	-12.6824	-4.7056	131.0904	40.4669	-0.038
21	$HAs_4S_7^{-}$	-31800	-36924	101.202	130.741	133.83	20.334	41.9114	-10.8266	-4.5109	89.8206	23.5975	0.7566
22	$As_4S_7^{-2}$	-24537	-28544	104.995	12.145	117.76	18.4278	37.2557	-8.9932	-4.3184	28.1903	-0.5605	1.6229
23	$As(OH)S^{*}$	-47126	-63836	0.135	10.263	6.19	2.5993	-1.4267	6.2903	-2.7199	11.6198	-0.9439	-0.038
24	$As(OH)_2S^{-}$	-96968	-121541	29.584	8.482	31.14	6.4258	7.927	2.5899	-3.1064	21.9347	-1.3067	1.1822
25	$As(OH)_2HS^{*}$	-106438	-122647	57.5	80.117	54.6	9.2237	14.7604	-0.1013	-3.3888	52.6714	13.2854	-0.038
26	$As(OH)HS^{+}$	-56413	-59427	46.083	40.518	29.65	6.3004	7.6213	2.7093	-3.0937	42.9254	5.219	1.4146
27	$AsOH(HS)_2^{*}$	-56546	-51987	110.531	179.696	64.56	10.5866	18.0908	-1.4163	-3.5265	111.1916	33.5696	-0.038
28	$AsS(OH)HS^{-}$	-58413	-74869	39.869	23.21	48.5	9.3294	15.0265	-0.2224	-3.3997	45.1406	1.6934	2.7449
29	$As(HS)_2^{+}$	-14200	-11340	48.943	99.465	39.62	7.657	10.9361	1.4005	-3.2307	77.3549	17.2265	1.3918
30	$AsHS^{+2}$	-4100	-5786	-5.187	23.543	4.71	3.0848	-0.2349	5.8079	-2.769	38.3799	1.761?	1.9978

As^{+5}	H_3AsO_4	$H_2AsO_4^{-}$	$HAsO_4^{2-}$	AsO_4^{3-}
As^{3+}	AsO^{+}	$As(OH)_2^{+}$	$As(OH)^{2+}$	$AsCl_3$
$AsCl_2^{+}$	$AsCl^{2+}$	$AsCl_4^{-}$	$As(OH)_2Cl$	$As(OH)Cl_2$
H_3AsO_3	$H_2AsO_3^{-}$	$HAsO_3^{2-}$	AsO_3^{3-}	$HAsO_2$
AsO^{2-}	$H_4As_2O_5$	$H_3As_2O_5^{-}$	$H_2As_2O_5^{2-}$	$HAs_2O_5^{3-}$
$As_2O_5^{4-}$	As_2S_3	$HAsS_2$	AsS_2^{-}	H_3AsS_3
$H_2AsS_3^{-}$	$HAsS_3^{2-}$	AsS_3^{3-}	$H_2As_2S_4$	$HAs_2S_4^{-}$
$As_2S_4^{2-}$	$H_4As_2S_5$	$H_3AsS_5^{-}$	$H_2As_2S_5^{2-}$	$HAs_2S_5^{3-}$
$As_2S_5^{-4}$	$H_3As_3S_6$	$H_2As_3S_6^{-}$	$HAs_3S_6^{-2}$	$As_3S_6^{-3}$
$H_2As_4S_7$	$HAs_4S_7^{-}$	$As_4S_7^{2-}$	HAs_3S_5	$As_3S_5^{-}$
$H_6As_4S_9$	$H_5As_4S_9^{-}$	$H_4As_4S_9^{2-}$	$H_3As_4S_9^{3-}$	$H_2As_4S_9^{4-}$
$HAs_4S_9^{5-}$	$As_4S_9^{6-}$	$H_2As_8S_{13}$	$HAs_8S_{13}^{-}$	$As_8S_{13}^{2-}$
HAs_9S_{14}	$As_9S_{14}^{-}$	$H_2As_{12}S_{19}$	$HAs_{12}S_{19}^{-}$	$As_{12}S_{19}^{2-}$
$As(HS)_2^{+}$	$As(HS)^{2+}$	$As(OH)S$	$As(OH)_2S^{-}$	$As(OH)_2HS$
$As(OH)(HS)_2$	$As(OH)(HS)^{+}$	$AsS(OH)(HS)^{-}$	H_3As, H_2As^{-}	HAs^{2-}, As^{3-}

Results and Discussion

In the presented versions of solving the above reverse thermodynamic problem using the "Selector" PC the orpiment solubility has been calculated with accuracy achieved in particular experiments (Mironova and Zotov, 1988; Mironova et al., 1990; Webster, 1990). The suggested composition of particles is in agreement with the database in a series of numerical experiments where the starting values of unknown isobaric isothermal

predominate forms are represented by thioarsenides, the contents of arsenous acids being one order lower under the given conditions of oxygen deficiency. Just as in acidic, so in weakly and moderately alkaline solutions the orpiment solubility is caused by the concentration combination of thioarsenous acid H_3AsS_3 and its dimeric versions $H_4As_2S_5$ and $H_2As_2S_4$. At temperatures of over 200-250°C these concentrations can be compared only with that of the AsOH $(HS)_2$ complex of mixed composition (Fig. 5).

In the acidic range of hydrothermal composition the arsenic sulfide solubility is explained by prevailing formation of this combination of uncharged particles stable to a temperature of 250°C. A higher concentration of arsenous acid is assumed only at further elevation of temperature. The role of thioarsinite dissociates H_3AsS_3 is insignificant at concentrations from $1x10^{-8}$ to $1x10^{-7}$ mole/kg. In a weakly alkaline solution of hydrogen sulfide and sodium sulfide the leading position is still occupied

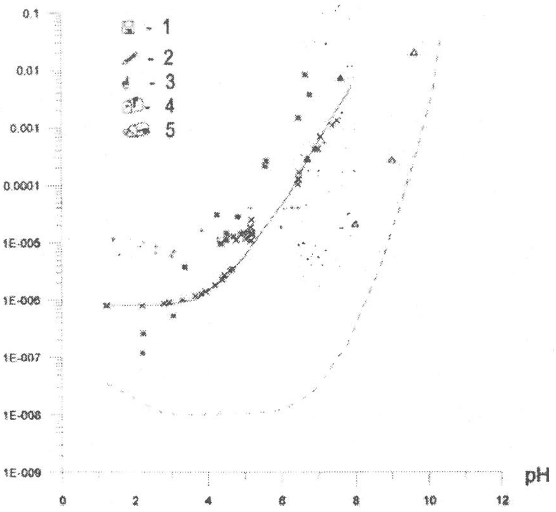


Fig.1. The orpiment solubility was calculated as the pH and temperature (25°C) function for the water saturated vapor pressure, according to experimental accuracy [5,7]. 2,4 – H_2O, 1,3,5 – 0,011m H_2S.

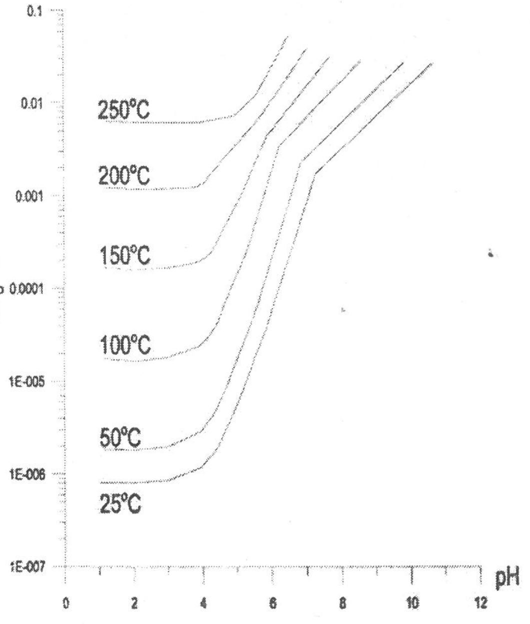


Fig. 2. The orpiment solubility was calculated as the pH and temperature function for the water saturated vapor pressure.

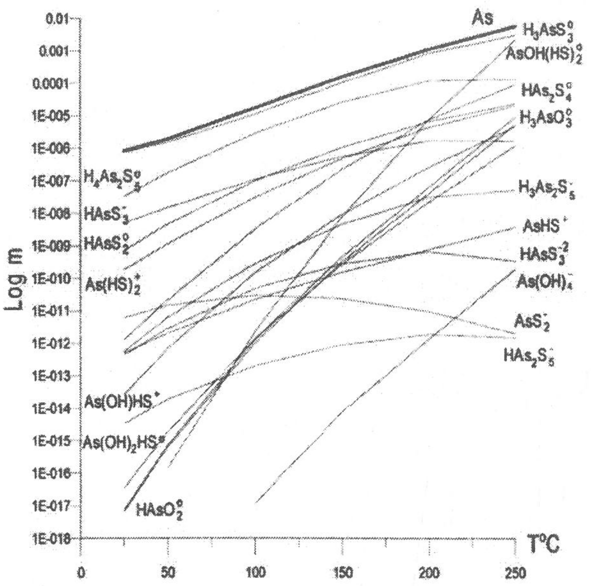


Fig. 3. Compound and complex arsenic concentrations were calculated for orpiment -0,011 m H_2S solution interaction (pH = 1,1-1,3) as temperature function.

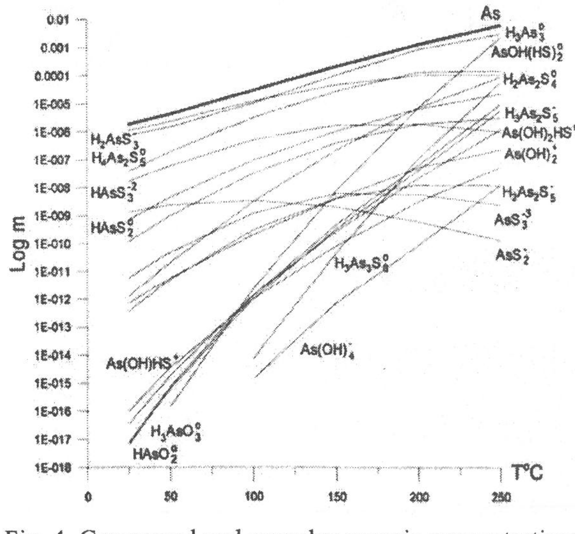


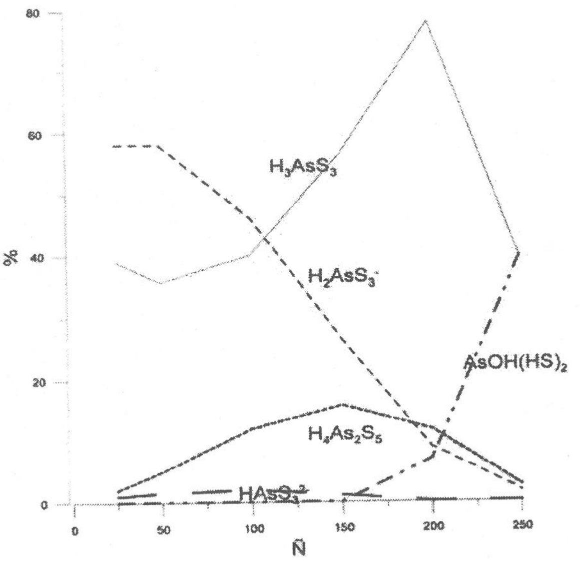
Fig. 4. Compound and complex arsenic concentrations were calculated for orpiment - 0,011 m H_2S solution interaction as temperature function.

by thioarsenous acid and neutral complexes, alternative hydrosulfide isomers as well as oligomers and hydroxo hydrosulfides is retained. However, at 150-200°C they co-exist in comparable amounts with thioarsenites dissociate $H_2AsS_3^-$. Fuller dissociation of thioarsenous acid is of no importance. The observed pH-dependent variations of isotherm inclination of orpiment solubility are due to step-wise expansion of the association of particles responsible for arsenic going to the solution (Fig. 5).

Thus, at temperatures below 100°C thioarsenous acid and single charged thioarsenite ion prevail in the solution. Then the ion concentration decreases whereas the role of neutral acidic $H_4As_2S_5$ complex becomes more prominent. Starting from 200°C, it is the complexes of mixed type, possibly co-existing with arsenous acid in a higher temperature range, that acquire paramount importance.

Conclusion

Thus, the geochemical result of the undertaken physical-chemical modeling is that the process of orpiment dissolution in sulfurous hydrothermal phase depends on the temperature and the acidity-alkalinity ratio. In the area of acidic solutions the temperature is the main factor determining arsenic sulfide sedimentation. A temperature decrease in the hydrothermal system in the presence of caolinite-sericite buffer leads to the formation of colloidal



orpiment-realgar (in the case of excess sulfur) ore sediments. In the alkaline range of the hydrothermal system compositions, it is the alkalinity conditions that are responsible for ore deposition. These involve quick changes of pH values in hydrothermal sedimentation process when deep thermal springs reach the level of increased oxygen potential and fast hydrogen sulfide oxidation. The joint action of pH and temperature decrease causes the formation of arsenic-sulfide sediment, which is transformed into massive ore deposit at the epigenesis stage. A set of thermodynamic constants of arsenic compounds and complexes, which provides the basis for further modeling of gold-bearing sulfoarsenoide systems enclosing arsenopyrite has been obtained. The leading role of thioarsenites and sulfurous oligomers in the hydrothermal arsenic transport at low and moderate temperatures of ore formation has been demonstrated.

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