Effect of Selenium on Silver Transport and Precipitation by Hydrothermal Solutions: Thermodynamic Description of the Ag–Se–S–Cl–O–H System

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Abstract—An internally consistent thermodynamic database has been compiled for the Ag–Se (–II, 0, +IV)–S (–II, +VI)–Cl–O–H system on the basis of published experimental data. This database is fit for predicting the chemical properties of species over a broad interval of temperatures (0–600°C) and pressures (1–3000 bar). The stability constant of the hydroselenide silver complexes $[AgHSe_{aq}]$ and $[Ag(HSe)_2^-]$ has been estimated. A thermodynamic model of the effect of Se on the transport properties of Ag-bearing hydrothermal fluid has been developed. Selenium has been found to be a good precipitant even if its concentration in the fluid is five orders lower than the sulfur concentration. When the temperature falls, the role of selenium as a precipitant becomes increasingly important. It has also been shown that the effect of hydroselenide complexes on Ag behavior in natural hydrothermal fluids may be ignored.

INTRODUCTION

At many epithermal and massive sulfide deposits, gold and silver are contained in the form of tellurides and selenides (Lindgren, 1933; White and Hedenquist, 1995; Richards, 1995; Kovalenker, 2004). Thereby, gold correlates more closely with Te, and silver, with Se (Lindgren, 1933; Heald et al., 1987). The physical and chemical causes of these relationships are not clear, primarily because of insufficient thermodynamic information on Se and Te aqueous species and their complexes with noble metals under hydrothermal conditions. Meanwhile, it is known that sulfide sulfur, a close chemical analogue of these elements, to a great extent controls Au and Ag solubility and transport in hydrothermal fluids, owing to the formation of fairly stable hydrosulfide complexes of those metals (Barnes, 1979; Gammons and Barnes, 1989; Zotov and Baranova, 1995; Benning and Seward, 1996).

This paper is a first step in the attempt to find a quantitative explanation of the processes that lead to Au–Ag–Te–Se mineralization by considering the Ag–Se subsystem. The objective of this study is to compile, on the basis of available experimental information, an internally consistent thermodynamic database for the Ag–Se (–II, 0, +IV)–S (–II, +VI)–Cl–O–H system that would be fit for predicting the chemical properties of species within a broad range of temperatures (0–600°C) and pressures (1–3000 bar). The only summary on the Se–O–H subsystem (D'yachkova and Khodakovsky, 1968) available to date in the literature was prepared

without consideration of modern precision methods for describing aqueous species. Therefore, its use is restricted to a narrow range of temperatures and pressures, which does not embrace the entire hydrothermal region. The summary of thermodynamic data published by Xiong (2003) is also based on estimates reported by D'yachkova and Khodakovsky (1968) and does not take into consideration the possible existence of Ag hydroselenide complexes.

Our database may be used for development of various models that simulate silver transfer and precipitation by S–Se–Cl-bearing hydrothermal fluids.

EXPERIMENTAL

At present, the Helgeson–Kirkham–Flowers (HKF) equation of state is widely used to predict the behavior of aqueous solution species at high temperatures and pressures (Helgeson et al., 1981; Tanger and Helgeson, 1988). The use of this equation allows one to describe the thermodynamic properties of aqueous electrolytes at an infinite dilution with a sufficient accuracy within a broad range of temperatures (25–1000°C) and pressures (1–5000 bar). Later on, the application of the HKF equation was extended to nonelectrolyte (Shock et al., 1989) and complex (Shock et al., 1997; Sverjensky et al., 1997) species of aqueous solutions.

In terms of the HKF model, any thermodynamic property of an aqueous species is represented as a sum

$$\Xi = \Xi_n + \Xi_s, \tag{1}$$

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where Ξ_s is a solvation term, which reflects the contribution of the electrostatic interaction between ion and solvent (H_2O), and Ξ_n is a structural term, which reflects the contribution of the remaining, mostly covalent, interactions in the species–solvent system.

In describing the solvation part of the chemical potential, the authors of the HKF model used the Born equation (Born, 1920); i.e., the Gibbs function of hydration of an ion with charge Q and radius r_e is the difference between the energies of its charging in a medium with dielectric permeability ε and in vacuum ($\varepsilon = 1$):

$$\mu_s = \omega\left(\frac{1}{\varepsilon} - 1\right), \qquad (2)$$

where ω is the Born parameter of the ion. For a free ion, ω is determined unequivocally by its crystallochemical radius. For complex aqueous species, this approach is inapplicable because the notion of crystallochemical radius loses its meaning. In such a case, the authors of the model involved empirical correlative relations between the entropy of the species and its Born parameter (Shock and Helgeson, 1988). However, these relations do not provide a reliable predictive potential because they have been mainly established for free ions.

Differentiation (2) by temperature and pressure in combination with the equation for the dielectric properties of pure H_2O allows one to obtain relationships of type (1) for the partial entropy S_{298}, heat capacity $C_{p,298}$, and volume V_{298} of an aqueous species under standard conditions ($T_r = 298.15$ K, $P_r = 1$ bar) (Johnson et al., 1992):

$$S_{298} \text{ (cal·mol}^{-1}\text{·K}^{-1}) = S_n - 5.7987 \times 10^{-5}\omega, \qquad (3a)$$

$$C_{p,298} \text{ (cal·mol}^{-1}\text{·K}^{-1}) = C_{pn} - 9.1102 \times 10^{-5}\omega, \qquad (3b)$$

$$V_{298} \text{ (cm}^3\text{·mol}^{-1}) = V_n - 2.7757 \times 10^{-5}\omega. \qquad (3c)$$

Here, the index n marks the structural components of the corresponding thermodynamic properties. In this paper, the value of the Born parameter is accepted to be zero ($Q = 0$) for all uncharged complexes.

To describe the structural terms of heat capacity and volume, six individual empirical parameters are used according to the HKF model. Parameters $a_1–a_4$ are intended for describing the temperature- and pressure-dependent partial volume of the species, whereas parameters c_1 and c_2 are intended for describing the temperature-dependent heat capacity. Empirical relationships proposed by Shock and Helgeson (1988) allow the set of HKF parameters to be "restored" at known $C_{p,298}$, V_{298}, and ω values of a species. Further, we will call these relationships *internal correlations*.

Our objective was to describe the thermodynamic properties of aqueous species on the basis of the HKF model. If not explicitly specified, the thermodynamic properties of pure phases (native silver; chlorargyrite ($AgCl_{cr}$); acanthite/argentite (Ag_2S); the gases H_2, O_2, and H_2S), simple ions (Na^+, Cl^-, HS^-, OH^-), and ion couples ($NaCl^0$, $NaOH^0$) were taken from the

SUPCRT92 thermodynamic database (Johnson et al., 1992) and its supplements (Shock et al., 1997; Sverjensky et al., 1997) without any revision or refinement. The HKF parameters for HCl^0 were taken according to Tagirov et al. (1997). The thermodynamic properties of dissolved hydrogen sulfide H_2S^0 were calculated on the basis of a new equation of state for nonelectrolyte aqueous species (Akinfiev and Diamond, 2003). The use of this equation allows one to avoid errors inherent in the HKF model when describing dissolved gases in the supercritical region of H_2O (Plyasunov and Shock, 2001). This statement is illustrated by Fig. 1, where experimental values of the partial molar volume of dissolved H_2S are compared with the values calculated from the HKF model and the equation derived by Akinfiev and Diamond (2003). It is evident that the use of this equation of state appreciably increases the accuracy of H_2S^0 description in the near-critical region.

The HKF parameters of aqueous species were calculated and refined using the UT–HEL program (Yu.V. Shvarov, 1995). The UT–HEL program minimizes differences between experimental and calculated values of the Gibbs function for species by optimizing their standard chemical potential μ_{298} and entropy S_{298} and all seven coefficients of the HKF equation of state: $a_1–a_4$, c_1, c_2, and ω.

However, as a rule, a mere optimization is either impossible or yields improbable HKF model coefficients. Therefore, the *method of isocoulombic reactions* is widely used (Jackson and Helgeson, 1985). It was established that, if in the equation of reaction each charged reagent corresponds to the same amount of equally charged product, then the logarithm of the equilibrium constant of the reaction linearly depends on the inverse temperature over a wide temperature range. For example, in the exchange reaction of the type

$$AX_n^{m-} + BY_k^{l-} \Leftrightarrow BX_n^{m-} + AY_k^{l-} \qquad (4)$$
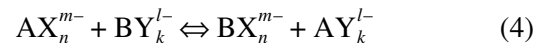
with participation of the complexes AX_n^{m-}, BY_k^{l-}, BX_n^{m-}, and AY_k^{l-}, the presence of equally charged species on both sides of the reaction reduces the contribution of the electrostatic term of the Gibbs function. It turned out that, in most cases, the variation of heat capacity may be ignored ($\Delta_r C_p \approx 0$) (Mesmer et al., 1988; Ruaya, 1988), as well as the variation of reaction entropy ($\Delta_r S \approx 0$) (Gu et al., 1994). In this paper, we assume, as a first approximation of isocoulombic reaction (4), that the changes in the corresponding electrostatic and structural terms equal zero:

$$\Delta_r\omega = 0; \quad \Delta_r S_n = 0; \quad \Delta_r C_{pn} = 0; \quad \Delta_r V_n = 0. \quad (5)$$

These conditions will be used to calculate the thermodynamic properties of aqueous species in the absence of reliable experimental data or will be taken as a criterion to determine the plausibility of these properties obtained as a result of optimization by the UT–HEL program.
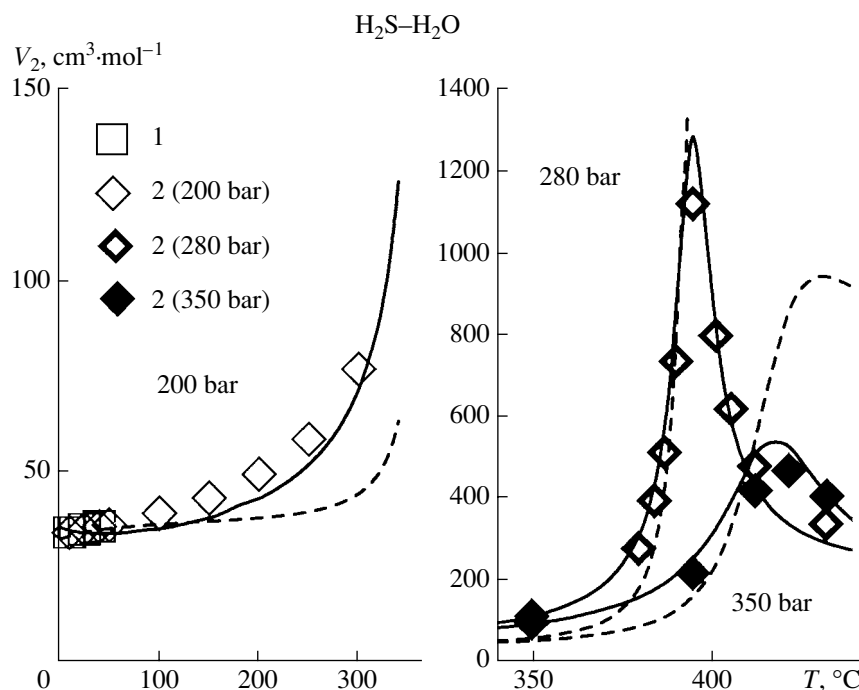
H$_2$S–H$_2$O

Fig. 1. Temperature dependence of the partial molar volume of dissolved H$_2$S at 1, 200, 280, and 350 bar. (1) Barbero et al. (1982); (2) Hnědkovsky et al. (1996). The dashed line designates calculation by the HKF model; the solid line, calculation by the equation of state (Akinfiev and Diamond, 2003).

This work is based on the well-known fact that the chemical properties of sulfur and selenium are similar, though not identical (Huheey, 1983). In particular, the stoichiometry of Ag selenide complexes [AgSe$_{aq}$ and Ag(HSe)$_2^-$] was selected by analogy with reliably defined hydrosulfide complexes [AgHS$_{aq}$, Ag(HS)$_2^-$] (Stefánsson and Seward, 2003).

THERMODYNAMIC PARAMETERS OF SPECIES

As was already mentioned, the Ag–S–O–H subsystem served as a basic system in our study. We also used a recently revised thermodynamic database (Akinfiev and Zotov, 2001). However, recently (2001–2004), an inconsistency was revealed in the experimental data on the stability constants of *the first Ag hydrosulfide complex* (AgHS$_{aq}$) at low temperatures (Fig. 2).[1] Test experiments (Tagirov et al., 2006) suggested that the solubility of crystalline Ag sulfide at room temperature reported by Stefánsson and Seward (2003) and Sugaki et al. (1987) was erroneously overestimated. Probably, in the experiments carried out by Stefánsson and Seward (2003) and Sugaki et al. (1987), and to a lesser degree in those of Tagirov et al. (2006), the H$_2$S oxidation was not eliminated completely and Ag thiosulfate

complexes probably occurred. The results obtained by Schwarzenbach et al. (1958) and Schwarzenbach and Widmer (1966) with radioisotope marker are devoid of such an uncertainty. This is the reason why low-temperature ($T < 100$°C) data obtained with the solubility method (Ol'shansky et al., 1959; Sugaki et al., 1987; Stefánsson and Seward, 2003; Tagirov et al., 2006) were omitted from further consideration.

The thermodynamic parameters of AgHS$_{aq}$ were calculated in the following way. A set of chemical potential values of the complex under different *PT* conditions (μ_{PT}) was used as initial information. The respective μ_{PT} values were obtained by processing primary experimental data on the solubility of solid phases. The solubility was estimated with a modified version of the BALANCE program (Akinfiev, 1986), which was designed for calculating equilibria in multisystems. Afterwards, the obtained set of μ_{PT} values was used for estimating the HKF parameters of the (AgHS$_{aq}$) complex with the UT–HEL program (Yu.V. Shvarov, 1995). The calculation results are summarized in Table 1 and shown in Fig. 2. The calculated entropy of (AgHS$_{aq}$) (34.772 cal·mol^{-1}·K^{-1}) is close to the value obtained from the ionic association model (33–39 cal·mol^{-1}·K^{-1}) (Akinfiev, 1995). Furthermore, the accepted value of the structural term of entropy for (AgHS$_{aq}$) is close to a linear relationship of the thermodynamic parameter versus the number of ligands (Fig. 3). Such a linear correlation is characteristic of various metal complexes (Hovey, 1988; Sverjensky et al., 1997; Zotov et al., 2002),

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[1] The experimental data (Stefánsson and Seward, 2003) on the stability constants of [Ag(HS)$_2^-$] are in good agreement with previously estimated values. Therefore, the description presented by Akinfiev and Zotov (2001) did not require any revision.
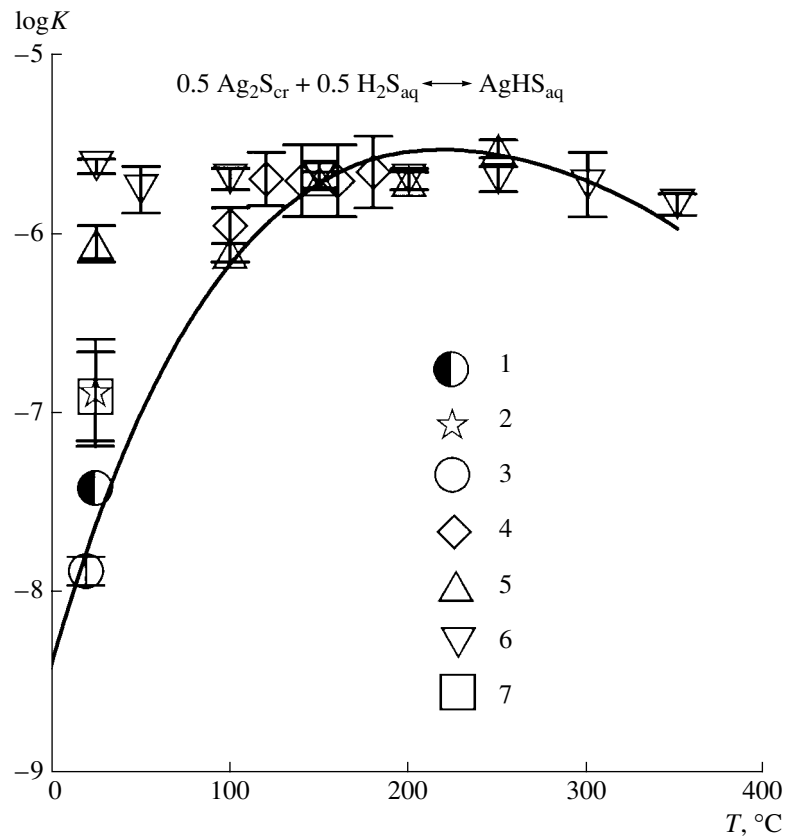
Fig. 2. Temperature-dependent $\log K$ of reaction of argentite dissolution under the pressure of saturated H_2O vapor. (1) Schwarzenbach et al. (1958); (2) Ol'shansky et al. (1959); (3) Schwarzenbach and Widmer (1966); (4) Melent'ev et al. (1969); (5) Sugaki et al. (1987); (6) Stefánsson and Seward (2003); (7) Tagirov et al. (2006). The curve was calculated using parameters from Table 1.

and its observance will facilitate correct choice of the thermodynamic parameter value. If low-temperature data are regarded as basic (Sugaki et al., 1987; Stefánsson and Seward, 2003), the corresponding entropy of $(AgHS_{aq})$ under standard conditions ($S_n = 16.07$ cal·mol^{-1}·K^{-1}) will markedly differ from the model prediction (Fig. 3).

The equation of state was used to predict the thermodynamic properties of *dissolved hydrogen selenide* (H_2Se_{aq}) (Akinfiev and Diamond, 2003). Experimental data (McAmis and Felsing, 1925; Dubeau et al., 1971) on the solubility of gaseous (H_2Se_{gas}) within the temperature interval 14–71°C were recalculated taking into account the dissociation of (H_2Se_{aq}):

$$H_2Se_{aq} \Leftrightarrow HSe^- + H^+ \qquad (6)$$
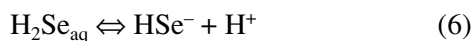
(see below) to obtain the Henry's law constant (k_H) for H_2Se. Then the temperature relationship of k_H was processed in order to obtain the parameters of the equation of state (Akinfiev and Diamond, 2003). The calculation results are presented in Table 2, and a comparison of the experimental and theoretical descriptions is given in Fig. 4.

The thermodynamic properties of *hydroselenide ion* (HSe^-) were calculated on the basis of the isocoulombic reaction:

$$H_2Se_{aq} + HS^- \Leftrightarrow H_2S_{aq} + HSe^-. \qquad (7)$$
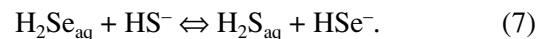
The use of such a simplified approach is dictated by the absence of experimental data on a temperature dependence of (HSe^-) properties. At present, only the dissociation constant of hydrogen selenide (6) has been reliably defined under standard conditions: $pK^0_{298,\,1\,bar} = 3.85 \pm 0.05$ (Séby et al., 2001; Olin et al., 2004). Accepting this value of the constant and the Gibbs function value from Table 1,[2] $\Delta_f G^0_{298,\,1}$ $(HSe^-) = 10395\ (\pm70)$ cal·mol^{-1}. The Born parameter of (HSe^-) was assumed to be equal to the Born parameter of hydrosulfide ion: $\omega(HSe^-) = \omega(HS^-) = 1.441 \times 10^5$ cal·mol^{-1} (Johnson et al., 1992) because the crystallochemical radii of these ions are alike: $r_x(HSe^-) = 191$ pm and $r_x(HS^-) = 193$ pm (Huheey, 1983). The use of relations (5)

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[2] As inferred from reactions (6), (7), the parameters of (H_2Se_{aq}) and (HSe^-) are interrelated and therefore they were calculated using the iteration method. The effect of (HSe^-) on the Henry's law constant obtained from the experiment on solubility (H_2Se) is insignificant and thus iterations converge rapidly.

Table 1. Standard thermodynamic properties (298.15 K, 1 bar) and the HKF parameters of aqueous solution species

Species	$\Delta_f G^{0a}_{298}$	$\Delta_f H^{0a}_{298}$	S^{0b}_{298}	$C^b_{p,298}$	V^c_{298}	$a_1 \times 10^d$	$a_2 \times 10^{-2a}$	a_3^e	$a_4 \times 10^{-4f}$	c_1^b	$c_2 \times 10^{-4f}$	$\omega \times 10^{-5a}$	Source
Ag^+	18427	25281	17.54	7.90	−0.8	1.7285	−3.5608	7.1496	−2.6318	18.8783	−4.4327	0.2160	Akinfiev and Zotov, 2001
$AgCl_2^-$	−51350	−60092	49.78	−16.60	37.1	7.1327	9.8065	1.8947	−3.1844	4.8953	−6.7789	0.6667	″
$Ag(HS)_2^-$	287	−6636	49.00	3.35	42.82	7.8651	11.4225	1.2604	−3.2512	13.9576	−2.3624	0.6367	″
$Ag(OH)_2^-$	−61901	−88893	15.518	−23.3	−6.84	1.2839	−4.6464	7.5763	−2.5869	3.4950	−7.7808	1.2039	″
$AgCl_{aq}$	−17399	−18810	32.067	−5.33	21.631	4.2750	3.7555	4.2739	−2.9343	3.0441	−4.1199	0.0	″
$AgHS_{aq}$	2314[i]	2722	34.772[i]	1.81[i]	24.46	5.7821[h]	4.7007[h]	3.9024[h]	−2.9733[h]	−36.0117[h]	18.6121[h]	0.0[g]	″
$AgOH_{aq}$	−22019	−31173	19.600	−6.42	0.365	1.8149	−3.3498	7.0667	−2.6405	2.4041	−4.3424	0.0	″
$AgHSe_{aq}$	9849[g]	11374	40.989[g]	3.42[g]	24.46[g]	5.1121[g]	4.7007[h]	3.9024[h]	−2.9733[h]	8.1692[h]	−2.3386[h]	0.0[g]	This paper
$Ag(HSe)_2^-$	153577[g]	10671	61.434[g]	6.56[g]	42.82[g]	7.8651[h]	11.4225[h]	1.2604[h]	−3.2512[h]	15.8212[h]	−1.6979[h]	0.6367[h]	″
HSe^-	10395[g]	4797	22.517[g]	−20.56[g]	20.65[g]	5.1353[h]	4.7572[h]	3.8802[h]	−2.9757[h]	7.2622[h]	−7.2233[h]	1.4410[g]	″
HS^-	2860	−3850	16.3	−22.45	20.20	5.0119	4.9799	3.4765	−2.9849	3.42	−6.27	1.4410	Johnson et al., 1992
Cl^-	−31379	−39933	13.56	−29.28	17.33	4.0320	4.8010	5.5630	−2.847	−4.40	−5.714	1.4560	″
OH^-	−37595	−54977	−2.56	−32.59	−4.71	1.2527	0.0738	1.8423	−2.7821	4.15	−10.346	1.7246	″

Notes: [a] cal·mol⁻¹; [b] cal·mol⁻¹·K⁻¹; [c] cm³·mol⁻¹; [d] cal·mol⁻¹·bar⁻¹; [e] cal·K·mol⁻¹; [f] cal·K·mol⁻¹; [g] method of isocoulombic reactions (4); [h] internal correlations of the HKF equation (Shock and Helgeson, 1988); [i] least-squares method, UT–HEL program (Yu. V. Shvarov, 1995).
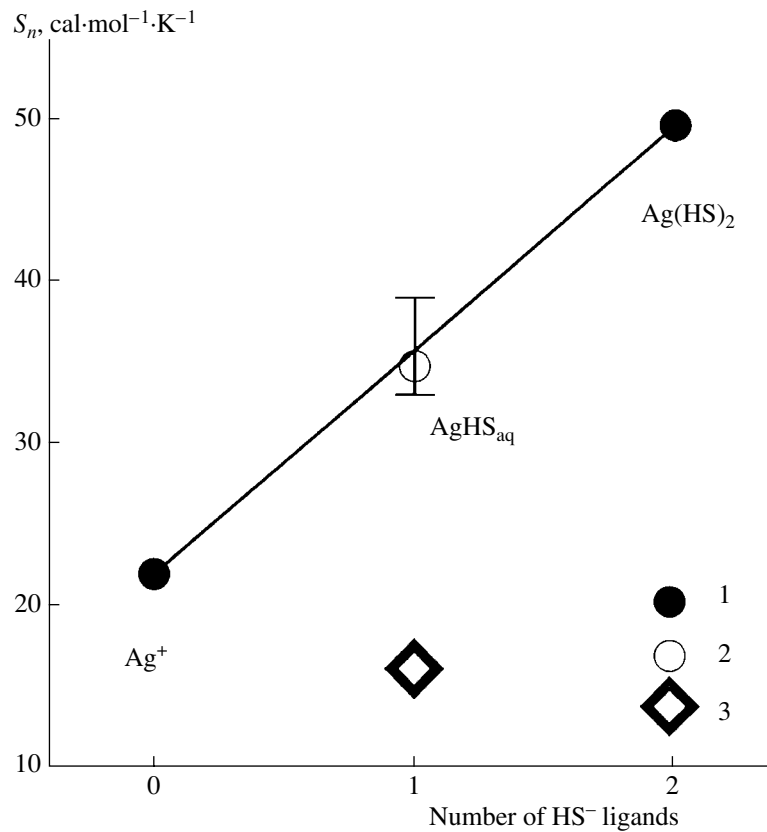
Fig. 3. Structural terms of entropy of Ag-bearing species under standard conditions versus the number of HS^- ligands. (1) Entropy values for $[Ag^+]$ and $[Ag(HS)_2^-]$ (Akinfiev and Zotov, 2001); (2) entropy value for $[AgHS_{aq}]$ accepted in this paper; (3) entropy value based on low-temperature experimental data (Sugaki et al., 1987; Stefánsson and Seward, 2003). The vertical bar is an uncertainty of the ion association model (Akinfiev, 1995).

for reaction (7) yields the following values of the partial molal thermodynamic properties (HSe^-) under standard conditions: $S^0_{298}(HSe^-) = 22.517$ cal·mol^{-1}·K^{-1}, $C_{p, 298}(HSe^-) = -20.53$ cal·mol^{-1}·K^{-1}, and $V_{298}(HSe^-) = 20.65$ cm^3·mol^{-1}. The HKF parameters (a_1–a_4, c_1, and c_2) were calculated on the basis of internal correlations (Shock and Helgeson, 1988) (Table 1).

The enthalpy of (HSe^-) formation under standard conditions estimated from the accepted $\Delta_f G^0_{298, 1}(HSe^-)$ and $S^0_{298}(HSe^-)$ values yields $\Delta_f H^0_{298, 1}(HSe^-) = 4797$ cal·mol^{-1}, which is close to the estimation of

$\Delta_f H^0_{298, 1} = 4200 \pm 2000$ cal·mol^{-1} reported by Latimer (1938).

To describe the thermodynamic properties of *Ag hydroselenide complexes*, we had to apply simplified techniques on the basis of isocoulombic reactions. Only one experimental paper on the solubility of crystalline (Ag_2Se) in aqueous solutions of selenides under standard conditions (Mehra and Gubeli, 1970) is available in the literature. The results of this experiment are shown in Fig. 5.

The constant solubility (Ag_2Se) over a wide pH range (from 2 to 10), most likely, testifies to an experimental error. An expert estimation given by Olin et al. (2004) confirms this opinion: the techniques used by

Table 2. Thermodynamic parameters of the equation of state (Akinfiev and Diamond, 2003) for dissolved gases

Gases	$\Delta_f G^{0a}_{298}$	$\Delta_f H^{0a}_{298}$	S^{0b}_{298}	$C^b_{p, 298}$	V^c_{298}	ξ	a^d	b^e	Source
H_2S_{aq}	−6682	−10095	27.362	51.87	34.9	−0.2020	−11.4803	12.7158	Akinfiev and Diamond, 2003
H_2Se_{aq}	5143	2851	33.579	53.48	34.9	−0.1928	−14.3279	14.4459	This paper

Note: ^{a} cal·mol^{-1}; ^{b} cal·mol^{-1}·K^{-1}; ^{c} cm^3·mol^{-1}; ^{d} cm^3·g^{-1}; ^{e} cm^3·K$^{0.5}$·g^{-1}.
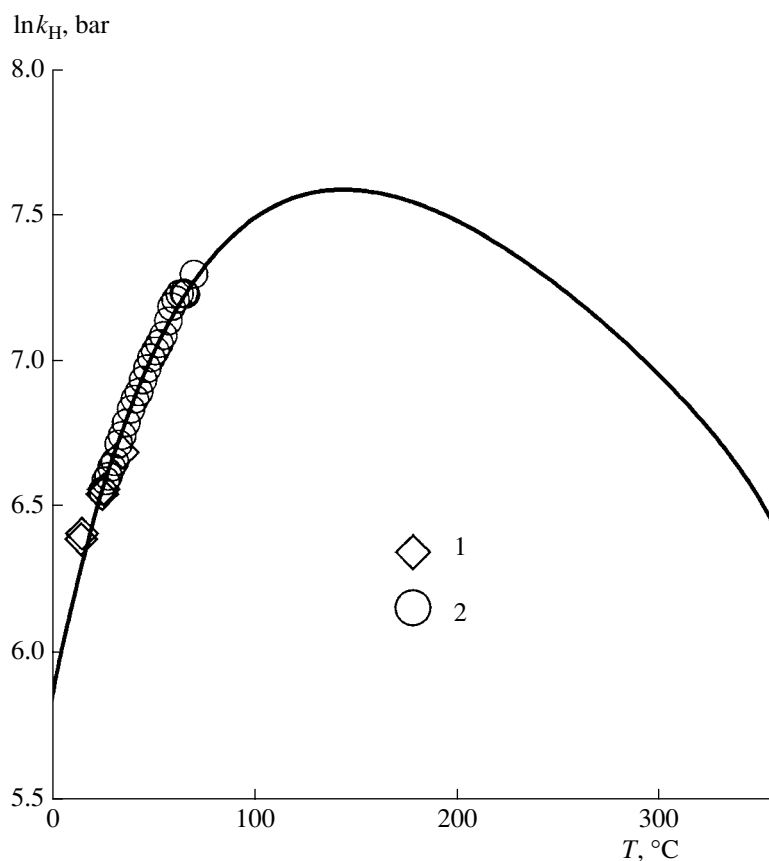
Fig. 4. Temperature dependence of Henry's law constant (H_2Se). Pressure at $T < 100°C$ corresponds to a total pressure of 1 bar, and pressure at $T > 100°C$ corresponds to the pressure of saturated H_2O vapor. (1) McAmis and Felsing (1925); (2) Dubeau et al. (1971), recalculated taking into account H_2Se_{aq} dissociation (see the text for explanation). The curve was calculated using the equation derived by Akinfiev and Diamond (2003) and with the parameters from Table 2.

Mehra and Gubeli (1970) did not eliminate the occurrence of colloidal species (Ag_2Se) in the analyzed solution because of an insufficiently reliable filtration technique (Rai et al., 1995). Therefore, further it will be assumed that the solubility $\Sigma Ag = 10^{-7.89}$ mol·kg^{-1} reported by Mehra and Gubeli (1970) (Fig. 5) corresponds to the upper limit of the true Ag selenide solubility. Hence, all our subsequent estimations will correspond to the upper stability limit of hydroselenide complexes.

Writing the reaction of (Ag_2Se) dissolution as

$$0.5Ag_2Se_{cr} + HSe^- + 0.5H_2Se_{aq} \Leftrightarrow Ag(HSe)_2^- \quad (8)$$

and accepting that the maximum concentration of $[Ag(HSe)_2^-]$ is $[m(Ag(HSe)_2^-)] = 10^{-7.89}$ mol·kg^{-1} at a constant total Se concentration in the experiment equal to $\Sigma Se^{-2} = m(H_2Se_{aq}) + m(HSe^-) = 0.06545$ mol·kg^{-1}, the Gibbs function of $[Ag(HSe)_2^-]$ formation under standard conditions will be obtained as $\Delta_f G_{298,1}^0 [Ag(HSe)_2^-] \geq 14995$ cal·mol^{-1}. The data for the remaining species of the reaction were taken from Tables 1–3.

Now we will use this value for comparing the relative stability of hydroselenide and hydrosulfide silver complexes:

$$Ag(HS)_2^- + 2HSe^- \Leftrightarrow Ag(HSe)_2^- + 2HS^-. \quad (9)$$

As a result, $\Delta_r G_{298,1}(9) = -362$ cal, a value that is very close to zero. It means that the stability constants of the $[Ag(HSe)_2^-]$ and $[Ag(HS)_2^-]$ complexes are close to each other. Therefore, it is assumed further that the stability of Ag hydroselenide complexes is the same as that of hydrosulfide, and for all isocoulombic reactions

$$Ag(HS)_n^{n-1} + nHSe^- \Leftrightarrow Ag(HSe)_n^{n-1} + nHS^- \quad (10)$$

$\Delta_r G = 0$.

The application of this assumption to reaction (9) gave $\Delta_f G_{298,1}^0 [Ag(HSe)_2^-] = 15357$ cal·mol^{-1}. By analogy, the isocoulombic reaction involving the first hydroselenide complex

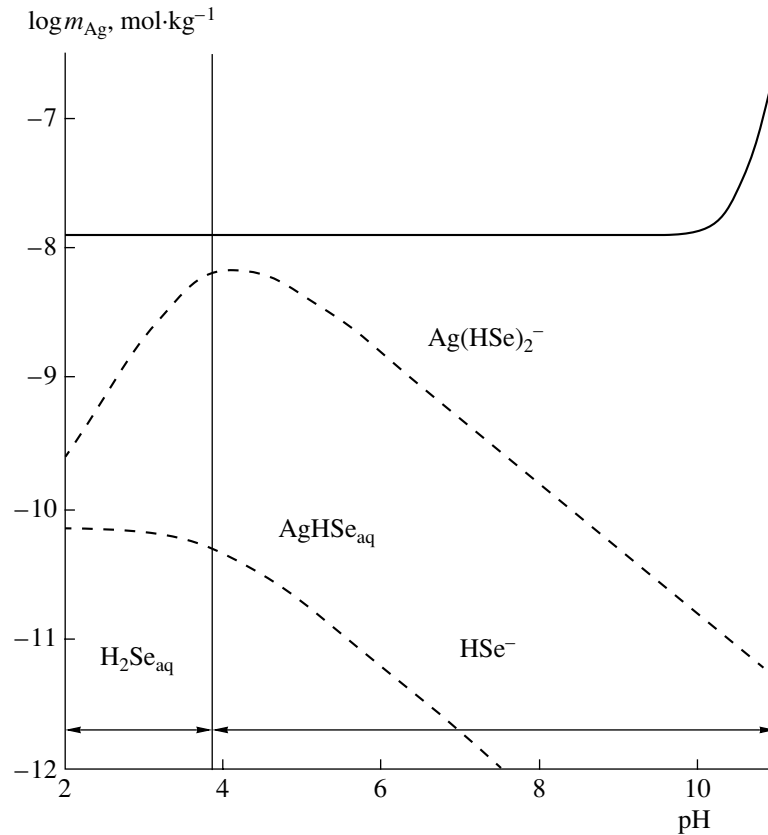$$AgHS_{aq} + HSe^- \Leftrightarrow AgHSe_{aq} + HS^- \quad (11)$$

Fig. 5. Solubility of crystalline (Ag_2Se) versus pH at 25°C and 1 bar in selenide aqueous solution at constant total concentration $\Sigma Se^{-II} = 0.06545$ mol·kg^{-1}. The solid curve corresponds to experimental data (Mehra and Gubeli, 1970); the dashed curves are our estimates of concentrations of Ag hydroselenide complexes [AgHSe$_{aq}$] and [Ag(HSe)$_2^-$]. The vertical line separates the fields with dominating (H$_2$Se$_{aq}$) and (HSe$^-$), respectively.

at $\Delta_r G$ (11) $= 0$ yields $\Delta_f G^0_{298,1}$ (AgHSe$_{aq}$) $= 9849$ cal·mol^{-1}.

The solubility of (Ag$_2$Se$_{cr}$) calculated under standard conditions as a function of pH, taking into account the formation of Ag hydroselenide complexes, is shown in Fig. 5 with dashed curves. It is evident that the Ag concentration is no higher than 10^{-8} mol·kg^{-1} and thus

is consistent with the accepted assumption on the upper stability limit of the complexes.

The thermodynamic parameters of the [AgHSe$_{aq}$] and [Ag(HSe)$_2^-$] complexes, which are necessary for predicting their properties at elevated temperatures and pressures, were calculated on the basis of relationship (5) and internal correlations (Shock and Helgeson, 1988) (Table 1).

Table 3. Thermodynamic parameters of minerals and gases

Formula	Phase	$\Delta_f H^{0a}_{298.1}$	$\Delta_f G^{0a}_{298.1}$	S^{0b}_{298}	$V^c_{298.1}$	$C_p^b = a + bT + cT^{-2}$			T^d_{limit}	Source
						a	$b \times 10^3$	$c \times 10^{-5}$		
Ag$_2$Se$_{cr}$	Naumannite	−9591	−11 209	35.827	37.50	6.6048	30.0270	3.4783	406	Olin et al., 2004
Ag$_2$Sel$_{cr}$	β-phase	1836^e				19.7029	1.6738	0.0000	1170	"
H$_2$Se$_{gas}$	Gas	6938	3637	52.342		7.5900	3.4900	−0.3110	1500	"
Se$_{cr}$	Crystal	0	0	10.060	16.42	5.9277	0.3001	−0.2082	494	"
Se$_{liq}$	Liquid	1600^e				8.4000	0.0000	0.0000	900	"

Note: ^{a} cal·mol^{-1}; ^{b} cal·mol^{-1}·K^{-1}; ^{c} cm^3·mol^{-1}; ^{d} K; ^{e} enthalpy of phase transition.
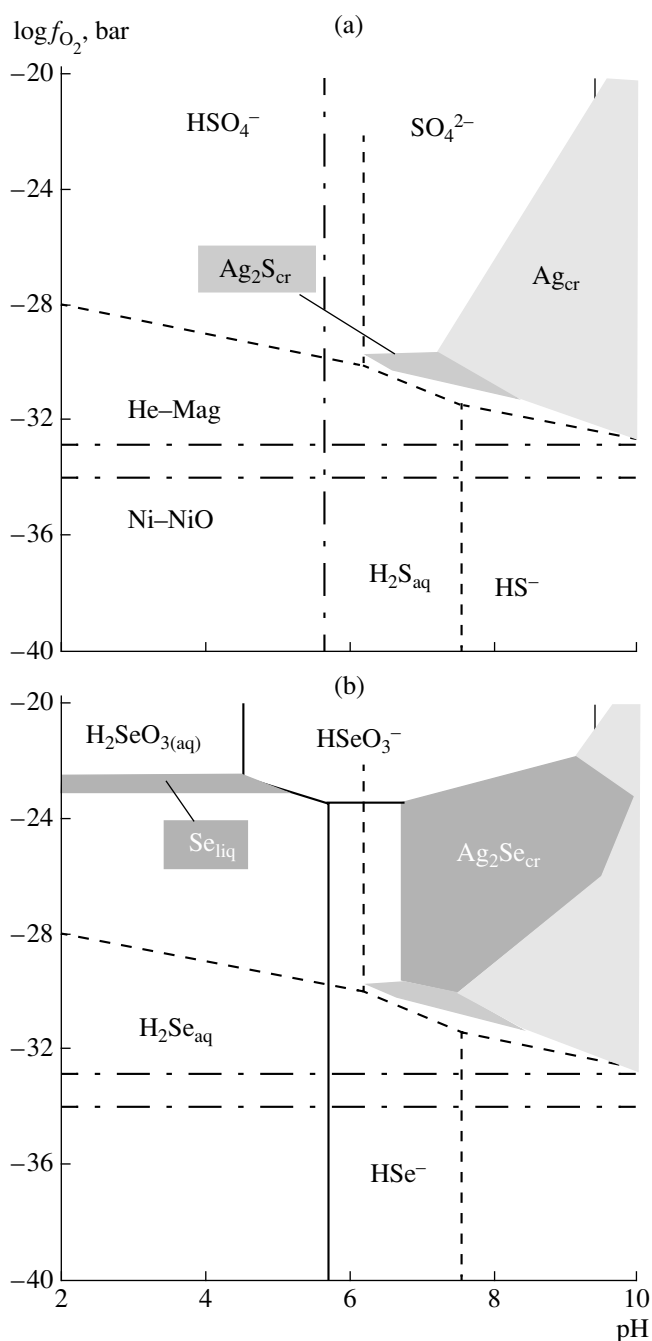
Fig. 6. Fields with dominating species in the Ag–Se–S–Na–Cl–O–H system depending on acidity of fluid at 300°C and the pressure of saturated H_2O vapor. (a) Ag–S–Na–Cl–O–H system; (b) overall system including Se. Total molal concentrations of elements are $\Sigma Ag = 10^{-7}$, $\Sigma S = 0.01$, $\Sigma Se = 10^{-8}$. The NaCl concentration is accepted to be equal to $m_{NaCl} = 0.3$ mol·kg^{-1}. Dashed lines separate fields with dominating S aqueous species, and solid lines separate fields with dominating Se aqueous species. The vertical dot-and-dash line indicates the fluid's neutral point at the given pressure and temperature; horizontal dot-and-dash lines indicate the oxygen fugacity for the HM buffer (upper line) and the NNO buffer (lower line). Gray areas are stability zones of solid phases and liquid native selenium.

It should be emphasized once again that the thermodynamic description of hydroselenide complexes accepted in this paper is an estimate from above for the stability constants of these complexes.

DISCUSSION

The thermodynamic parameters of the species belonging to the Ag–Se–S–Na–Cl–O–H system described in this paper provide a good opportunity for developing various models of Ag migration and precipitation in Se-bearing hydrothermal fluids. The equilibrium calculations were performed using a modified version of the BALANCE program (Akinfiev, 1986). The thermodynamic properties of pure solid phases (native silver, acanthite/argentite (Ag_2S_{cr}), pyrite (FeS_2), pyrrhotite (FeS), magnetite (Fe_3O_4), potassium feldspar ($KAlSi_3O_8$), muscovite [$KAl_3Si_3O_{10}(OH)_2$], and quartz (SiO_2)); gases ($O_{2,gas}$, $H_{2,gas}$, H_2S_{gas}); and species of the aqueous solution ($SO_{2,aq}$, HSO_3^-, SO_3^{2-}, HSO_4^-, SO_4^{2-}, $H_2SeO_{3,aq}$, $HSeO_3^-$, SeO_3^{2-}, $HSeO_4^-$, SeO_4^{2-}, Na^+, $NaCl_{aq}$, $NaOH_{aq}$, HS^-, Cl^-, and OH^-) were taken from the thermodynamic database SUPCRT92 (Johnson et al., 1992) and its supplements (Shock et al., 1997; Sverjensky et al., 1997) without any revision or refinement.[3] The thermodynamic properties of Se-bearing phases (naumannite Ag_2Se_{cr}, native selenium $Se_{cr, liq}$, and H_2Se_{gas}) were taken from (Olin et al., 2004) and are summarized in Table 3. Dissolved gases (H_2S_{aq}) and (H_2Se_{aq}) were described on the basis of the equation of state (Akinfiev and Diamond, 2003) (Table 2). The HKF parameters of HCl_{aq} were taken from (Tagirov et al., 1997) and those of chloride, hydrosulfide, hydroselenide, and hydroxo complexes of silver were taken from (Akinfiev and Zotov, 2001) and from this paper (Table 1).

To illustrate the capabilities of the database, the calculated diagrams of pH-dependent redox equilibria in the Ag–Se–S–Na–Cl–O–H system at 300°C and saturated H_2O vapor pressure are shown in Fig. 6.

The very small field of argentite Ag_2S_{cr} stability (Fig. 6a) attracts attention. The upper limit of its stability field is determined by the oxidation of sulfide sulfur and the dissolution of the solid phase according to the reaction

$$Ag_2S_{cr} + 4Cl^- + 2O_{2,gas} \Rightarrow 2AgCl_2^- + SO_4^{2-}. \quad (12)$$

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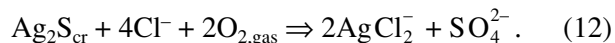
[3] It should be noted that the data for $H_2SeO_{3,aq}$, $HSeO_3^-$, SeO_3^{2-}, $HSeO_4^-$, and SeO_4^{2-} reported by Johnson et al. (1992) are not very reliable. However, as will be shown hereafter, the effect of these species on silver behavior in fluids typical of epithermal deposits is insignificant.
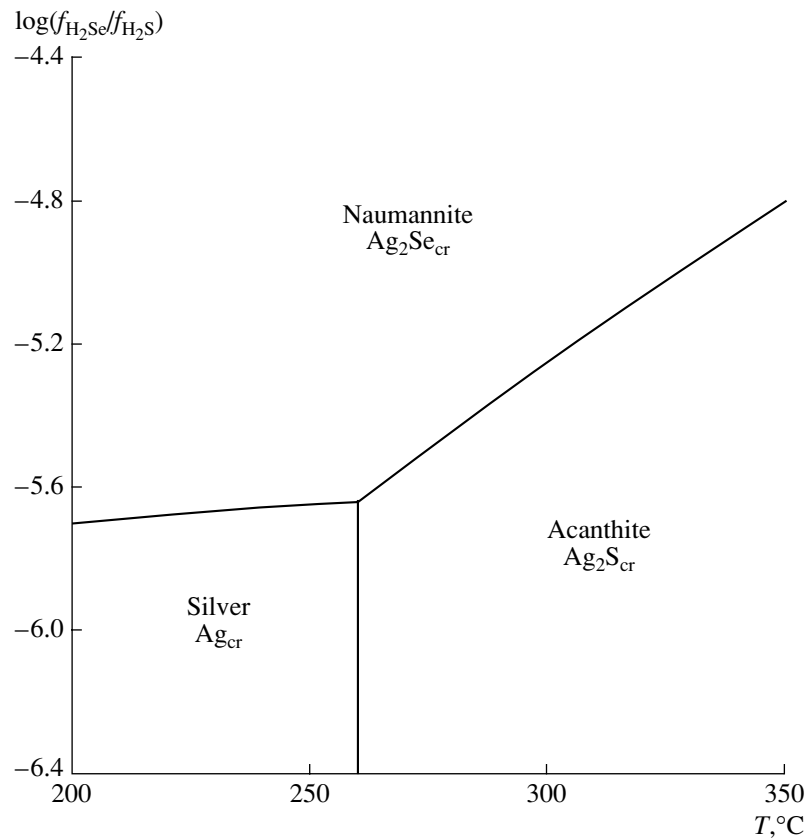
Fig. 7. Stability fields of Ag-bearing solid phases as a function of temperature at the pressure of saturated H_2O vapor. The redox potential and H_2S concentration correspond to the pyrite–pyrrhotite–magnetite buffer, and the acidity of the fluid is controlled by the potassium feldspar–muscovite–quartz buffer at molality K^+ ($m_{K^+} = 0.01$). The electrolyte's background $m_{NaCl} = 0.3$ mol·kg^{-1}.

The position of the lower stability limit is controlled by (Ag_2S_{cr}) dissolution in sulfide-bearing fluid due to the formation of highly stable hydrosulfide Ag complexes:

$$Ag_2S_{cr} + 2HS^- \Rightarrow 2Ag(HS)_2^-. \qquad (13)$$
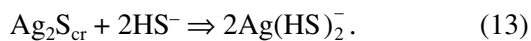
Reaction (13) is a leading one in natural hydrothermal fluids, the redox potential of which is found in the interval between the HM and NNO buffers.

A significant feature of selenium in the hydrothermal process is that fields with dominating selenide species (Se^{-II}) are much wider than those of sulfide sulfur and even in oxidized fluids sulfate sulfur can coexist with reduced selenium (Se^{-II}) ($f_{O_2} \leq 10^{-24}$ bar) (Fig. 6b).[4] The appearance of even traces (10^{-8} mol·kg^{-1}) of selenium in the solution is sufficient for it to become oversaturated with Se-bearing phases. A stability field of native selenium appears in the acid zone, while in the alkaline zone the solution becomes oversaturated with naumannite (Ag_2Se_{cr}) according to the reaction

$$2AgCl_2^- + HSe^- + OH^- \Leftrightarrow Ag_2Se_{cr} + 4Cl^- + H_2O.$$
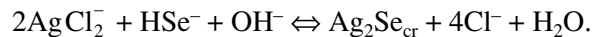
As can be seen, the stability field of naumannite is much greater than that of argentite. This implies that selenium may be an effective precipitant even under the conditions characteristic of epithermal deposits, where the concentration of metal in fluid is high because of high solubility of sulfosalts.

The temperature-dependent stability fields of Ag selenide and sulfide phases with different fugacity ratios of hydrogen selenide (H_2Se) and hydrogen sulfide (H_2S) in the system are illustrated in Fig. 7. Even in the case where the Se content is five orders lower than the S content, the Se-bearing solid phase (naumannite) is found to be less soluble. At the same time, its stability field expands as temperature falls. Thus, the role of selenium as a precipitant increases with a decrease in temperature.

The performed modeling calculations show that, due to a low concentration of selenium typical of natural fluids at massive sulfide deposits (Huston et al., 1995), the effect of hydroselenide complexes on the sil-

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[4] According to the data reported by Olin et al. (2004), the uncertainty of the thermodynamic properties of selenide species at 300°C may shift their stability limits within half an order of oxygen fugacity, which does not influence the conclusion on the relative stability of selenide species in solution.

ver behavior in fluid may be ignored. We emphasize once again that the accepted estimates of stability constants of Ag hydroselenide complexes were estimated from above; therefore, in reality their effect is still lesser.

From the geochemical point of view, the low solubility of metal selenides is the most important. The calculations indicated that the appearance of even minor amounts of selenium in the fluid (1–10 mg/kg) is sufficient for oversaturation of the solution and, thus, for the mass precipitation of ore element, the more so as the selenide ion remains stable within the wide range of oxygen fugacity (Fig. 6b) typical of epithermal deposits (Kovalenker, 2004).

REFERENCES

1. N. N. Akinfiev, "Algorithm of Calculation of Heterogeneity Equilibria for Microcomputers," Geokhimiya **24** (6), 882–890 (1986).

2. N. N. Akinfiev, " A Model for Calculating ab Initio Calculations on Ionic Association in Supercritical Aqueous Fluids: 1 : 1 Electrolytes," Geokhimiya **33** (3), 426–440 (1995) [Geochem. Intern. **32** (11), 116–131 (1995)].

3. N. N. Akinfiev and L. W. Diamond, "Thermodynamic Description of Aqueous Nonelectrolytes at Infinite Dilution over a Wide Range of State Parameters," Geochim. Cosmochim. Acta **67**, 613–627 (2003).

4. N. N. Akinfiev and A. V. Zotov, "Thermodynamic Description of Chloride, Hydrosulfide, and Hydroxocomplexes of Ag(I), Cu(I), and Au(I) at Temperatures of 25–500°C and 1–2000 Bars Pressures," Geokhimiya **39** (10), 1–17 (2001) [Geochem. Intern. **39** (10), 990–1006 (2001)].

5. J. A. Barbero, K. G. McCurdy, and P. R. Tremaine, "Apparent Molal Heat Capacities and Volumes of Aqueous Hydrogen Sulfide and Sodium Hydrogen Sulfide near 25°C: The Temperature Dependence of H_2S Ionisation," Can. J. Chem. **60**, 1872–1880 (1982).

6. H. L. Barnes, "Ore Minerals Solubility," in *Geochemistry of Hydrothermal Ore Deposits* (Wiley, New York, 1979; Mir, Moscow, 1982).

7. L. G. Benning and T. M. Seward, "Hydrosulphide Complexing of Au(I) in Hydrothermal Solutions from 150–400°C and 500–1500 bar," Geochim. Cosmochim. Acta **60**, 1849–1871 (1996).

8. Von M. Born, "Volumen und Hydratationswarme der Ionen," Zeitschr. Physik **1**, 45–48 (1920).

9. C. Dubeau, J.-C. Sisi, and N. Ozanne, "Solubility of Hydrogen Selenide Gas in Water," J. Chem. Eng. Data **16**, 78–79 (1971).

10. I. B. D'yachkova and I. L. Khodakovsky, "Thermodynamic Equilibria in $S–H_2O$, $Se–H_2O$, and $Te–H_2O$ Systems in the Temperature Range of 25–300°C and Their Geochemical Interpretation," Geokhimiya **6** (11), 1358–1375 (1968).

11. C. H. Gammons and H. L. Barnes, "The Solubility of Ag_2S in near Neutral Sulfide Solutions at 25 to 300°C," Geochim. Cosmochim. Acta **53**, 279–290 (1989).

12. Y. Gu, C. H. Gammons, and M. S. Bloom, "A One-Term Extrapolation Method for Estimating Equilibrium Constants of Aqueous Reactions at Elevated Temperatures," Geochim. Cosmochim. Acta **58**, 3545–3560 (1994).

13. P. Heald, N. K. Foley, and D. O. Hayba, "Comparative Anatomy of Volcanic-Hosted Epithermal Deposits: Acid-Sulfate and Adularia-Sericite Types," Econ. Geol. **82** (1), 1–26 (1987).

14. H. C. Helgeson, D. H. Kirkham, and G. C. Flowers, "Theoretical Prediction of the Thermodynamic Behaviour of Aqueous Electrolytes at High Pressures and Temperatures: IV. Calculation of Activity Coefficients, Osmotic Coefficients, and Apparent Molal and Standard and Relative Partial Molal Properties to 600°C and 5 Kb," Am. J. Sci. **291**, 1249–1516 (1981).

15. L. Hnědkovsky, R. H. Wood, and V. Majer, "Volumes of Aqueous Solutions of CH_4, CO_2, H_2S, and NH_3 at Temperatures from 298.15 to 705 K and Pressures to 35 MPa," J. Chem. Thermodyn. **28**, 125–142 (1996).

16. J. K. Hovey, "Thermodynamics of Aqueous Solutions," PhD. Thesis (Univ. Alberta, Edmonton (Canada), 1988).

17. J. E. Huheey, *Inorganic Chemistry. Principles of Structure and Reactivity*, 3rd Ed. (Harper and Row, New York, 1983; Khimiya, Moscow, 1987).

18. D. L. Huston, S. H. Sie, and G. F. Suter, "Selenium and Its Importance to the Study of Ore Genesis: The Theoretical Basis and Its Application to the Volcanic-Hosted Massive Sulfide Deposits Using Pixeprobe Analysis," in *Nulclear Instruments and Methods in Phys. Research B.*, Vol. 104, pp. 476–480.

19. K. J. Jackson and H. C. Helgeson, "Chemical and Thermodynamic Constraints on the Hydrothermal Transport and Deposition of Tin: I. Calculation of the Solubility of Cassiterite at High Pressures and Temperatures," Geochim. Cosmochim. Acta **49**, 1–22 (1985).

20. J. W. Johnson, E. H. Oelkers, and H. C. Helgeson, "SUPCRT92: A Software Package for Calculating the Standard Molal Thermodynamic Properties of Minerals, Gases, Aqueous Species, and Reactions from 1 to 5000 bars and 0 to 1000°C," Comp. Geosci. **18**, 899–947 (1992).

21. V. A. Kovalenker, "Metallic Mineralization Systems of Epithermal Au–Ag Deposits: Concepts, Reality, and Models," in *Problems of Ore Geology, Petrology, and Geochemistry* (IGEM RAS, Moscow, 2004), pp. 160–183 [in Russian].

22. W. M. Latimer, *The Oxidation States of Elements and Their Potentials in Aqueous Solutions* (Prentice Hall, New York, 1938).

23. W. Lindgren, *Mineral Deposits*, 4th ed. (McGraw-Hill, New York, 1933).

24. A. J. McAmis and W. A. Felsing, "The Solubility of Hydrogen Selenide," J. Am. Chem. Soc. **47**, 2633–2637 (1925).

25. M. C. Mehra and A. O. Gubeli, "The Complexing Characteristics of Insoluble Selenides: 1. Silver Selenide," Can. J. Chem. **48**, 3491–3497 (1970).

26. B. N. Melent'ev, V. V. Ivanenko, and L. A. Pamfilova, *Solubility of Some Ore Sulfides under Hydrothermal Conditions* (Nauka, Moscow, 1968) [in Russian].

27. R. E. Mesmer, W. L. Marshall, D. A. Palmer, et al., "Thermodynamic of Aqueous Association and Ionization Reactions at High Temperatures and Pressures," J. Solution Chem. **17**, 699–718 (1988).

28. A. Olin, B. Nolang, E. G. Osadchy, et al., *Chemical Thermodynamics of Selenium* (OECD Nuclear Energy Agency, Issy-les-Moulineaux, 2004).

29. Ya. I. Ol'shansky, V. V. Ivanenko, and A. V. Khromov, "Solubility of Silver Sulfide in Aqueous Solutions Saturated with Hydrogen Sulfide," Dokl. Akad. Nauk SSSR **124** (2), 410–413 (1959).

30. A. V. Plyasunov and E. L. Shock, "Correlation Strategy for Determining the Parameters of the Revised Helgeson-Kirkham-Flowers Model for Aqueous Nonelectrolytes," Geochim. Cosmochim. Acta **65**, 3879–3900 (2001).

31. D. Rai, A. R. Felmy, and D. A. Moore, "The Solubility Product of Crystalline Ferric Selenite Hexahydrate and the Complexation Constant of $FeSeO_3^+$," J. Solution Chem. **24**, 735–752 (1995).

32. J. P. Richards, "Alcalic-Type Epithermal Gold Deposits—A Review," in *Magmas, Fluid, and Ore Deposits* (Mineral. Assoc. Canada, Short Course Ser., 1995), Vol. 23, pp. 367–400.

33. J. R. Ruaya, "Estimation of Instability Constants of Metal Chloride Complexes in Hydrothermal Solutions up to 300°C," Geochim. Cosmochim. Acta **52**, 1983–1996 (1988).

34. G. Schwarzenbach and G. Widmer, "Die Loslichkeit von Metalsulfiden. II. Silbersulfid," Helv. Chim. Acta **49**, 111–123 (1966).

35. G. Schwarzenbach, O. Gubeli, and H. Zust, "Thiokomplexe des Silbers und die Loslichkeit von Silbersulfid," Chimia **12**, 84–86 (1958).

36. F. Séby, M. Potin-Gautier, E. Giffaut, et al., "A Critical Review of Thermodynamic Data for Selenium Species at 25°C," Chem. Geol. **171**, 173–194 (2001).

37. E. L. Shock and H. C. Helgeson, "Calculation of the Thermodynamic and Transport Properties of Aqueous Species at High Pressures and Temperatures: Correlation Algorithms for Ionic Species and Equation of State Predictions to 5 kb and 1000°C," Geochim. Cosmochim. Acta **52**, 2009–2036 (1988).

38. E. L. Shock, H. C. Helgeson, and D. A. Sverjensky, "Calculation of the Thermodynamic Properties of Aqueous Species at High Pressures and Temperatures: Standard Partial Molal Properties of Inorganic Neutral Species," Geochim. Cosmochim. Acta **53**, 2157–2183 (1989).

39. E. L. Shock, D. C. Sassani, M. Willis, and D. A. Sverjensky, "Inorganic Species in Geologic Fluids: Correlation Among Standard Molal Thermodynamic Properties of Aqueous Ions and Hydroxide Complexes," Geochim. Cosmochim. Acta **61**, 907–950 (1997).

40. A. Stefánsson and T. M. Seward, "Experimental Determination of the Stability and Stoichiometry of Sulphide Complexes of Silver(I) in Hydrothermal Solutions to 400°C," Geochim. Cosmochim. Acta **67**, 1395–1413 (2003).

41. A. Sugaki, S. D. Scott, K. Hayashi, and A. Kitakaze, "Ag_2S Solubility in Sulfide Solutions up to 250°C," Geochem. J. **21**, 291–305 (1987).

42. D. A. Sverjensky, E. L. Shock, and H. C. Helgeson, "Prediction of Thermodynamic Properties of Aqueous Metal Complexes to 1000°C and 5 kb," Geochim. Cosmochim. Acta **61**, 1359–1412 (1997).

43. B. R. Tagirov, N. N. Baranova, A. V. Zotov, et al., "Experimental Determination of the Stabilities of $Au_2S(cr)$ at 25°C and $Au(HS)_2^-$ at 25–250°C," Geochim. Cosmochim. Acta., 2006 (in press).

44. B. Tagirov, A. V. Zotov, and N. N. Akinfiev, "Experimental Study of Dissociation of HCl from to 500°C and from 500 to 2500 bars: Thermodynamic Properties of HCl(aq)," Geochim. Cosmochim. Acta **61**, 4267–4280 (1997).

45. J. C. Tanger IV and H. C. Helgeson, "Calculation of the Thermodynamic and Transport Properties of Aqueous Species at High Pressures and Temperatures: Revised Equations of State for Standard Partial Molal Properties of Ions and Electrolytes," Am. J. Sci. **288**, 19–98 (1988).

46. N. C. White and J. W. Hedenquist, "Epithermal Gold Deposits: Styles, Characteristics, and Exploration," SEG Newsletter, No. 23, 9–13 (1995).

47. Y. Xiong, "Predicted Equilibrium Constants for Solid and Aqueous Selenium Species to 300°C: Applications to Selenium-Reach Mineral Deposits," Ore Geol. Reviews **23**, 259–276 (2003).

48. A. V. Zotov and N. N. Baranova, "The Solubility of Au_2S and AuAgS in Near Neutral Sulphide Solutions at Temperatures of 25 and 80°C and Pressures of 1 to 500 bars," in *Proceedings of WRI-8* (Vladivostok, 1995), pp. 773–776.

49. A. V. Zotov, B. R. Tagirov, I. I. Diakonov, and K. V. Ragnarsdottir, "A Potentiometric Study of Eu^{3+} Complexation with Acetate Ligand from 25 to 170°C at P_{sat}," Geochim. Cosmochim. Acta **66**, 3599–3613 (2002).