Thermodynamic description of chloride, hydrosulfide, and hydroxo complexes of Ag(I), Cu(I), and Au(I) at temperatures of 25-500 degrees C and pressures of 1-2000 bar

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Thermodynamic Description of Aqueous Species in the System Cu−Ag−Au−S−O−H at Temperatures of 0−600°C and Pressures of 1−3000 Bar

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Received October 22, 2008

INTRODUCTION

Understanding the processes responsible for the mobilization, transport, and deposition of the ore-forming Ag−Au−Au triad is largely underlain by the availability of reliable thermodynamic information on the components of this system. Experimental data accumulated so far on the behavior of these elements in hydrothermal solutions are unsystematic and often inconsistent. The thermodynamic reviews [1, 2] published in the late 1990s have not eliminated this problem, because the parameters of complex species reported therein were based mostly on empirical correlations based on the "free" Cu^+ and Au^+ ions, whose properties were determined unreliably. This was the reason why we attempted, in 2001, to generalize and process experimental information accumulated by that time on the stability constants of chloride, hydrosulfide, and hydro-complexes of Ag(I), Cu(I), and Au(I) in hydrothermal conditions. The thermodynamic summary on this basis for the system Ag(I)−Cu(I)−Au(I)−S(II)−Cl−O−H was published in [3]. Experimental data were recently published on the stability of Cu and Au hydrosulfide complexes at low temperatures [4, 5], and new data were obtained on Au and Ag behavior in hydrothermal sulfide solutions [6−8]. Our research was focused on the correction of thermodynamic constants for Cu, Ag, and Au hydrosulfide complexes with regard to lately obtained experimental data.

METHODS

The behavior of solute components at high temperatures and pressures can be predicted with the use of the Helgeson−Kirkham−Flowers (HKF) equation of state [9−11], which is currently widely applied for this purpose. This equation makes it possible to accurately enough describe the limiting thermodynamic properties of aqueous solutions within broad ranges of temperatures (25−1000°C) and pressures (1−6000 bar). In order to comprehensively describe the thermodynamic properties of a component of aqueous solution, one should know its standard thermodynamic properties ($\Delta_f G^\circ_{298}$ and S°_{298}), Born parameter (ω), and six parameters determining the temperature and pressure dependences for the partial volume ($a_1, ..., a_4$) and heat capacity (c_1, c_2). Empirical relations suggested in [12], and referred here to as *inner correlations* between HKF parameters, make it possible to "reproduce" the set of HKF parameters of a species if its $C_{p,298}$, V_{298}, and ω are known.

In the absence of reliable experimental data, the method of *isocoulombic reactions* [13] can be applied. It was demonstrated [14, 15] that, for exchange reactions with the participation of solute components

$$AX^{m-}_n + BY^{l-}_k \longleftrightarrow BX^{m-}_n + AY^{l-}_k, \qquad (1)$$
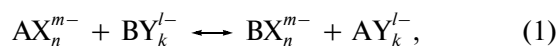
the temperature and pressure dependences of the equilibrium constant can be estimated ignoring the changes in the heat capacity ($\Delta_r C_p \approx 0$) and molar volume ($\Delta_r V \approx 0$) of the reaction.

Where not specified otherwise below, the values of thermodynamic properties of pure phases (*native silver*, *acanthite/argentite* (Ag_2S), and H_2, O_2, and H_2S gases), "simple" ions (Na^+, Cl^-, HS^-, and OH^-), and ion pairs ($NaCl_{aq}$ and $NaOH_{aq}$) were borrowed from the SUPCRT92 thermodynamic database [16] and its extensions [1, 2] without any revisions and amendments, and HKF parameters of HCl_{aq} were compiled from [17].

The thermodynamic properties of aqueous hydrogen sulfide H_2S_{aq} were calculated by a newly obtained equation of state for neutral aqueous species [18]. The application of this equation makes it possible to eliminate errors inherent to the HKF model when applied to dissolved gases in near- and supercritical regions of H_2O [19]. As an illustration of this, in Fig. 1, we compare experimental values for the partial molar volume of aqueous hydrogen sulfide with the analogous values calculated by the HKF model (dashed lines) and equation from [18] (solid lines).
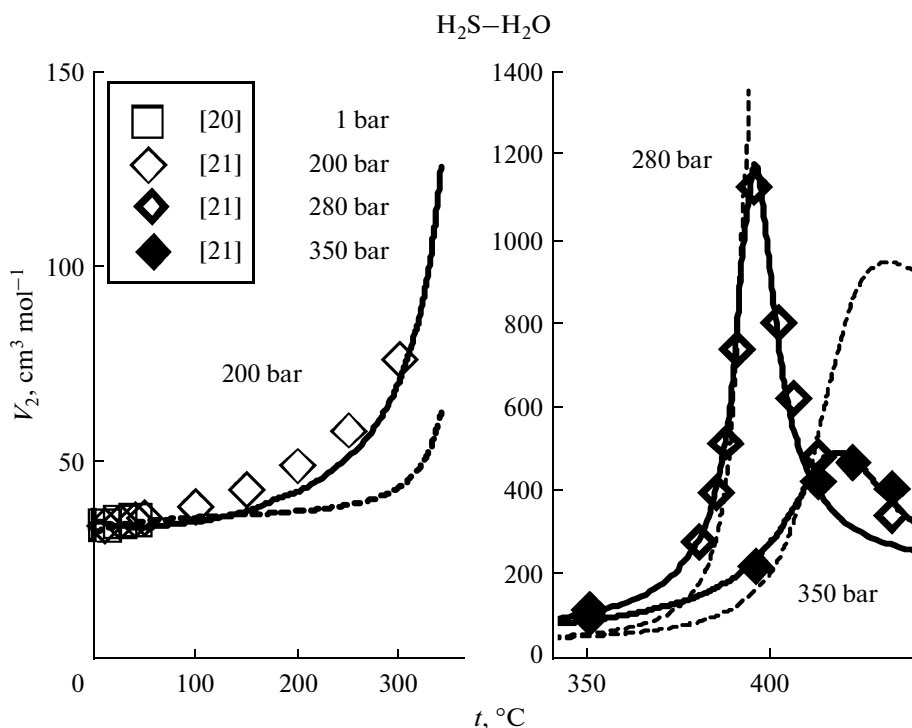
H$_2$S–H$_2$O

Fig. 1. Temperature dependence of the partial volume of dissolved H$_2$S at pressures of 1, 200, 280, and 350 bar. Lines represent calculation results: dashed lines—HKF model and solid line—equation of state [18].

It can be readily seen that the application of the newly obtained equation of state significantly improves the accuracy of the description for H$_2$S$_{aq}$ in the near- and supercritical regions. At the same time, when a temperature dependence is derived for Henry constant of aqueous H$_2$S$_{aq}$ can be reproduced by use of the proposed equation of state within the experimental error in subcritical (0–360°C, water saturation pressure) region and enables oneself reasonable description of the H$_2$S$_{aq}$ in the supercritical region [22] as well (Fig. 2).

The parameters of the equation of state for solute H$_2$S$_{aq}$ assumed herein are listed in Table 1. They are somewhat different from those reported in [18] due to other optimization conditions: we took into account the statistical weight of the data [26] at 250–350°C. The values of the standard chemical potential of H$_2$S$_{aq}$ calculated with the assumed values of the empirical parameters of the equation of state (Table 1, ξ, *a*, and *b*) are presented in Table 2.

The HKF parameters for solute components were fitted with the use of the UT-HEL computer program [27], which enables one to minimize discrepancies between experimentally determined and calculated values for the Gibbs function of a component by optimizing the values of its standard chemical potential μ_{298}, entropy S_{298}, and all seven coefficients of the HKF equation: a_1, ..., a_4, c_1, c_2, and ω.

OPTIMIZATION RESULTS

As was mentioned above, the internally consistent thermodynamic database for the system Cu–Ag–Au–S–O–H presented herein (Tables 1–2) is based on the recently published thermodynamic database [3], with certain corrections introduced into it with regard to experimental results published in 2001–2006 [4–8]. We
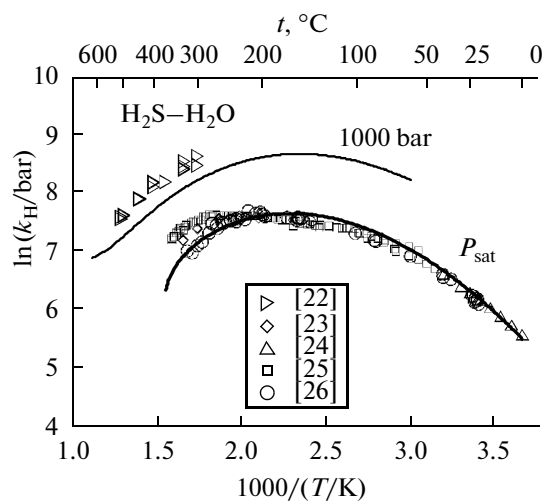

Fig. 2. Temperature dependence of the Henry constant of H$_2$S at various pressures. Symbols—experimental results and lines—calculation using equation of state [18] with parameters form Table 1.

Table 1. Thermodynamic parameters of the equation of state [18] assumed herein for solute hydrogen sulfide H_2S_{aq}

$\Delta_f G^{\circ a}_{298}$	$\Delta_f H^{\circ a}_{298}$	$S^{\circ b}_{298}$	V^c_{298}	$C^b_{p, 298}$	ξ	a^d	b^e
−6652	−9402	28.916	34.9	52.64	−0.2017	−12.8031	13.5396

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}.

Table 2. Chemical potentials of aqueous H_2S_{aq} at various pressures and temperatures μ^0_{PT} (cal mol^{-1}) standardized according to the HKF equation of state ; P_s corresponds to the H_2O vapor saturation pressure

Temperature, °C	Pressure, bar					
	P_s	500	1000	1500	2000	3000
0	−5991	−5567	−5167	−4787	−4423	−3735
25	−6652	−6246	−5859	−5488	−5130	−4450
50	−7426	−7024	−6640	−6271	−5915	−5236
100	−9231	−8816	−8423	−8047	−7685	−6995
150	−11312	−10868	−10452	−10059	−9683	−8971
200	−13618	−13133	−12681	−12262	−11867	−11125
250	−16125	−15579	−15077	−14624	−14203	−13426
300	−18831	−18192	−17613	−17117	−16666	−15849
350	−21831	−20972	−20270	−19718	−19232	−18371
400		−23952	−23030	−22406	−21881	−20975
450		−27186	−25869	−25161	−24595	−23644
500		−30258	−28756	−27961	−27355	−26364
550		−33060	−31638	−30784	−30147	−29123
600		−35815	−34481	−33612	−32956	−31912

have revised and recalculated the thermodynamic properties of four hydrosulfide complexes: $Cu(HS)_2^-$, $Ag(HS)_{aq}$, $Au(HS)_{aq}$, and $Au(HS)_2^-$.

$Cu(HS)_2^-$. In the absence of reliable experimental data, the thermodynamic properties of this complex were evaluated in our earlier paper [3] for the reaction

$$1/2Cu_2S + 1/2\ H^+ + 3/2HS^- \longleftrightarrow Cu(HS)_2^- \qquad (2)$$

on the basis of data in [28] for a temperature of 22°C and using the isocoulombic approach for the reaction of the participation of another chloride complex of Cu(I). The experimental data [4] recently obtained for the temperature interval of 35–95°C led to the revision of the entropy value of this complex. The optimization results obtained with the UT-HEL program are shown in Table 3, and the accuracy of the description is illustrated in Fig. 3a. Data in [34] on the solubility of Cu-bearing mineral associations at temperatures of 200–350°C recalculated to the $Cu(HS)_2^-$, complex

exhibit systematic deviations (1.5–2 kcal mol^{-1}) and were rejected from the optimization procedure. It should be mentioned that the values of the entropy of the complex was significantly changed (by 10 cal mol^{-1} K^{-1}) in comparison to the estimation [3] based on the isocoulombic reaction retaining the same value for $C_{p,298}$.

$AgHS_{aq}$. Ad hoc key [5] led us to suggest that the data [6, 35] on the solubility of crystalline silver sulfide at room temperature are overestimates. These researchers likely failed to completely preclude the oxidation of hydrogen sulfide and the possible occurrence of silver thiosulfate complexes. The Ag_2S solubility determined with the application of a radioactive tracer in [36, 37] is significantly lower than the values measured by other researchers and is likely devoid of this error. Because of this, the low-temperature data in [5, 6, 35, 38, 39] for temperatures lower than 100°C were rejected from the optimization procedure.

Table 3. Standard thermodynamic properties (298.15 K, 1 bar) and HKF parameters of aqueous species assumed herein

Component	$\Delta_f G^{\circ a}_{298}$	$\Delta_f H^{\circ a}_{298}$	$S^{\circ b}_{298}$	$C^b_{p,298}$	V^c_{298}	$a_1 \times 10^d$	$a_2 \times 10^{-2 a}$	$a_3{}^e$	$a_4 \times 10^{-4f}$	c^b_1	$c_2 \times 10^{-4f}$	$w \times 10^{-5 a}$	Reference
HS^-	2860	−3859	16.30	−22.5	20.2	5.0119	4.9799	3.4765	−2.9849	3.4200	−6.2700	1.4410	[16]
$AgCl_2^-$	−51350	−60092	49.78	−16.6	37.1	7.1327	9.8065	1.8947	−3.1844	4.8953	−6.7789	0.6667	[3]
$AgHS_{aq}$	2314^i	2722	34.77^i	1.8^i	24.5	5.1121^h	4.7007^h	3.9024^h	$−2.9733^h$	$−36.0117^h$	18.6121^h	0.0	
$Ag(HS)_2^-$	287	−6636	49.00	3.4	42.8	7.8651	11.4225	1.2604	−3.2512	13.9576	−2.3624	0.6367	[3]
$CuHS_{aq}$	−3401	883	45.56	−8.7	38.3	4.7896	3.9132	4.2119	−2.9408	5.3754	−3.3096	0.0	[3]
$Cu(HS)_2^-$	−5902	−12725	47.09^i	−1.2	70.1	11.6490	20.6614	−2.3710	−3.6331	12.6022	−3.2693	0.7794	
$AuCl_2^-$	−36795	−46⬚	47.16	−26.4	68.6	11.4774	20.2425	−2.2063	−3.6158	27.0677	−22.440	0.8623	[3]
$AuHS_{aq}$	8344^i	11032	50.86^i	1.8	56.5	9.4965	15.4057	−0.3052	−3.1459	$−38.1356^i$	19.6524^i	0.0	
$Au(HS)_2^-$	3487^i	4703	77.46	3.3	75.1	12.3373	22.3421	3.0317	−3.7026	−53.6010	31.4030	0.7673	

Note: ^{a} cal mol^{-1}; ^{b} cal mol^{-1} K^{-1}; ^{c} cm^3 mol^{-1}; ^{d} cal mol^{-1} bar^{-1}; ^{e} cal K mol^{-1} bar^{-1}; ^{f} cal K mol^{-1}. Methods used to determine the thermodynamic parameters of the complexes: ^{h} correlations between parameters of the HKF equation [12]; ^{i} least-squares method, UT-HEL program [27].

The thermodynamic parameters of $AgHS_{aq}$ were calculated as follows. The input information included the values of the chemical potential of the complex at various $P–T$ conditions (μ_{PT}). The corresponding μ_{PT} values were obtained by processing "raw" experimental data on the solubility values of the solid phases. The solubility was calculated by a modified version of the BALANCE computer program [40], which was designed to simulate equilibria in multicomponent systems. The set of the μ_{PT} values thus obtained was then utilized to calculate the HKF parameters of the $AgHS_{aq}$ complex by the $AgHS_{aq}$ program [27]. The calculation results are summarized in Table 4. The calculated value of the entropy of $AgHS_{aq}$(34.77 cal mol^{-1} K^{-1}) is close to the estimate obtained with the use of the ion association model [41] (33−39 cal mol^{-1} K^{-1}). Moreover, the value assumed for the structural entropy component of $AgHS_{aq}$ is close to the linear dependence of the thermodynamic parameter on the number of ligands (Fig. 5). Linear correlations of this type are typical of various complexes of metals [1, 42], and the occurrence of such a correlation also justifies our choice of the thermodynamic parameter value. It should be mentioned that the adoption of the low-temperature data in [6, 35] leads to a significant deviation of the entropy value for $AgHS_{aq}$ from the model predictions ($S = 16.07$ cal mol^{-1} K^{-1}) at standard state conditions (Fig. 5).

Ag(HS)$_2^-$. The thermodynamic properties and HKF parameters of this complex were assumed according to [3] without any changes, although these authors employed other thermodynamic properties for H_2S_{aq}. Inasmuch as the predominance region of the $Ag(HS)_2^-$ complex lies within the field dominated by the HS^- species and its thermodynamic properties were calculated using the reaction

$$1/2 Ag_2S + 1/2 H^+ + 3/2\ HS^- \longleftrightarrow Ag(HS)_2^-, \quad (3)$$
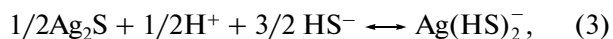
the new parameters of the equation of state for H_2S_{aq} do not affect the thermodynamic properties and HKF parameters of $Ag(HS)_2^-$.

Au(HS)$_2^-$. Analogously we have processed experimental data on the stability constants of another hydrosulfide complex of Au(I), with regard to newly obtained data on its stability, including that at low temperatures (25−150°C) and the thermodynamic properties of Au_2S [5]. The calculation results are presented in Table 3, and the calculated and experimental data for the whole range of temperature (20−500°C) and pressure (1−1000 bar) are compared in Fig. 3b.

Experimental data [43] on the solubility of Au for broad temperature and pressure ranges were not involved in the optimization procedure because these data were later revised in [7]. The value of the volume of the complex under standard conditions $V_{298} = 75.1$ cm^3/mol was assumed as the average of the experimental values of $V_{298} = 60 \pm 20$ cm^3/mol [43] and $V_{298} = 85.1 \pm 15$ cm^3/mol [31].

AuHS$_{aq}$. In our earlier publication [3], the thermodynamic properties of the first hydrosulfide complex were predicted using experimental data [31, 32] and data of [33] on the solubility of Au_{cr} in sulfide-bearing solutions at
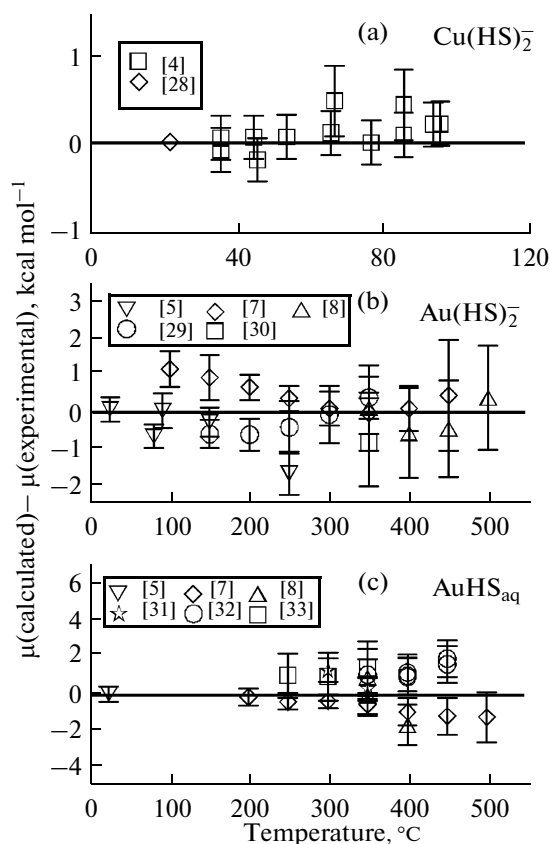
Fig. 3. Temperature dependence of deviations of calculated values of chemical potential μ_{PT} from experimental values for (a) $Cu(HS)_2^-$, (b) $Au(HS)_2^-$, and (c) $AuHS_{aq}$.
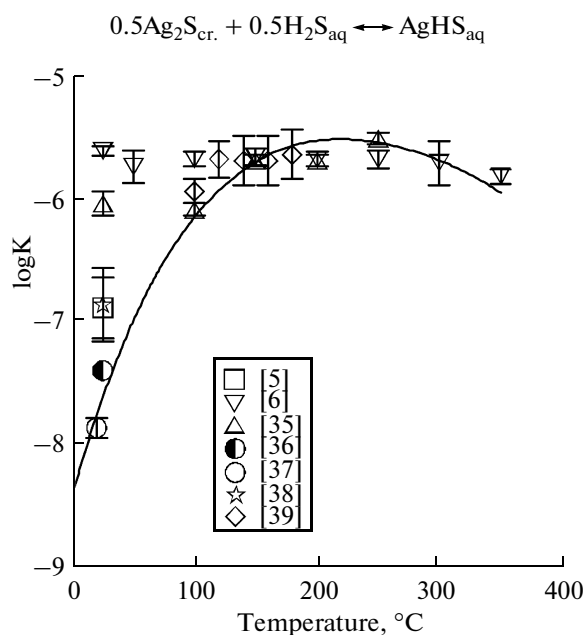

Fig. 4. Temperature dependence of the common logarithm of the constant of the argentite dissolution reaction at water saturation pressure. Symbols—experimental data and line—calculation with the use of parameters for aqueous species of the reaction from Table 3.

temperatures of 250–350°C and water saturation pressure recalculated according to the stoichiometry of the $AuHS_{aq}$ complex. Recently published data [7, 8] cover the ranges of temperature of 200–500°C and pressure of 500–1000 bar, and the Gibbs function for $AuHS_{aq}$ was reliably determined under standard conditions in [5]. All of these experimental data were optimized by the UT-HEL program, to obtain values for $\Delta_f G^\circ_{298}$, S°_{298}, and parameters c_1 and c_2 in the equation for the heat capacity of the complex. The standard values of the heat capacity and volume of $AuHS_{aq}$ were calculated ignoring their changes in the isocoulombic reaction

$$AuCl_2^- + AgHS_{aq} \longleftrightarrow AuHS_{aq} + AgCl_2^- \qquad (4)$$

and using data on $AgCl_2^-$ and $AuCl_2^-$ from [3] and our data on $AgHS_{aq}$ (this publication). Figure 3c illustrates the deviations of the calculated values of the chemical potentials of $AuHS_{aq}$ from the experimental values throughout the whole temperature range. It can be seen that the trends of data [7, 32] with increasing temperature are different. The reasons for this are uncertain.

The internally consistent thermodynamic database presented in this publication for aqueous species in the system Cu–Ag–Au–S–O–H, which involves experimental data published in 2001–2006, makes it possible to simulate geochemical processes in hydrothermal solutions within broad ranges of temperatures (up to 600°C) and pressures (up to 3000 bar).
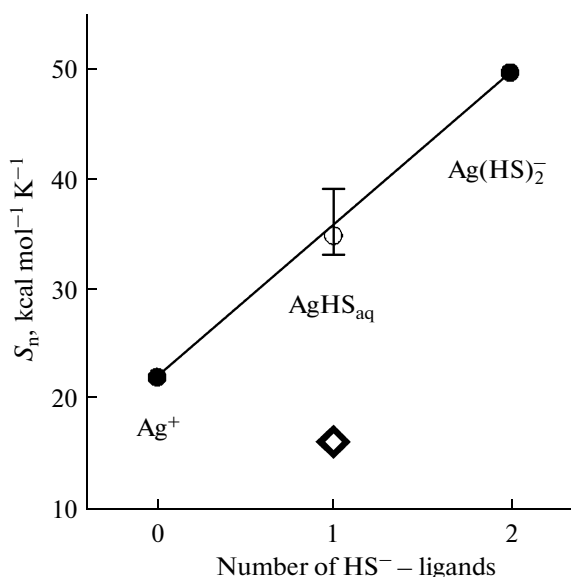

Fig. 5. Dependence of the nonelectrolyte contribution of the entropy of Ag-bearing aqueous species on the number of HS^- ligands under standard conditions. Solid symbols represent reliably determined values of entropy for Ag^+ and $Ag(HS)_2^-$, from [3], and open circle symbol corresponds to values assumed herein for $AgHS_{aq}$. Vertical error bars display the prediction by the model of ion association [41], and diamond represents calculations with regard for data in [6, 35].

REFERENCES

1. 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).

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

3. N. N. Akinfiev and A. V. Zotov, "Thermodynamic Description of Chloride, Hydrosulfide, and Hydroxo Complexes of Ag(I), Cu(I), and Au(I) at Temperatures of 25–500°C and Pressures of 1–2000 Bar," Geokhimiya, No. 10, 1–17 (2001) [Geochem. Int. **39**, 990–1006 (2001)].

4. B. W. Mountain and T. M. Seward, "Hydrosulfide/Sulfide Complexes of Copper(I): Experimental Confirmation of the Stoichiometry and Stability of $Cu(HS)_2^-$ to Elevated Temperatures," Geochim. Cosmochim. Acta **67**, 3005–3014 (2003).

5. 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 **70**, 3689–3701 (2006).

6. 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).

7. A. Stefánsson and T. M. Seward, "Gold(I) Complexing in Aqueous Sulphide Solutions to 500°C at 500 Bar," Geochim. Cosmochim. Acta **68**, 4121–4143 (2004).

8. B. R. Tagirov, S. Salvi, J. Schott, and N. N. Baranova, "Experimental Study of Gold–Hydrosulphide Complexing in Aqueous Solutions at 350–500°C, 500 and 1000 Bars Using Mineral Buffers," Geochim. Cosmochim. Acta **69**, 2119–2132 (2005).

9. H. C. Helgeson, D. H. Kirkham, and G. C. Flowers, "Theoretical Prediction of the Thermodynamic Behavior 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).

10. 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," Amer. J. Sci. **288**, 19–98 (1988).

11. 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).

12. 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).

13. 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).

14. 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).

15. 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).

16. 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).

17. B. Tagirov, A. V. Zotov, and N. N. Akinfiev, "Experimental Study of Dissociation of HCl from 350 to 500°C and from 500 to 2500 Bars: Thermodynamic Properties of HCl(Aq)," Geochim. Cosmochim. Acta **61**, 4267–4280 (1997).

18. 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).

19. 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).

20. 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 Ionization," Can. J. Chem. **60**, 1872–1880 (1982).

21. L. Hnédkovsky, 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).

22. N. Kishima, "A Thermodynamic Study on the Pyrite–Pyrrhotite–Magnetite–Water System at 300–500°C with Relevance to the Fugacity/Concentration Quotient of Aqueous H_2S," Geochim. Cosmochim. Acta **53**, 2143–2155 (1989).

23. T. N. Kozintseva, "Study of H_2S Solubility in Water at Elevated Temperatures," Geokhimiya, No. 6, 758–765 (1964).

24. E. C. W. Clarke and D. N. Glew, "Aqueous Nonelectrolyte Solutions. Part VIII. Deuterium and Hydrogen Sulfides Solubilities in Deuterium Oxide and Water," Can. J. Chem. **49**, 691–698 (1971).

25. S. E. Drummond, *Boiling and Mixing of Hydrothermal Fluids: Chemical Effects of Mineral Precipitation*, Ph. D. Thesis. (Pennsylvania State Univ. 1981).

26. O. M. Suleimenov and R. E. Krupp, "Solubility of Hydrogen Sulfide in Pure Water and in NaCl Solutions, from 20 to 320°C and at Saturation Pressures," Geochim. Cosmochim. Acta **58**, 2433–2444 (1994).

27. Yu. V. Shvarov, *UT-HEL: A Program for the Calculation of HKF Parameters of Aqueous Species (Version 2.0)* (Geol. Fac. MGU, Moscow, 1995) [in Russian] (unpublished).

28. B. W. Mountain and T. M. Seward, "The Hydrosulphide/Sulphide Complexes of Copper (I): Experimental Determination of Stoichiometry and Stability at 22°C and Reassessment of High Temperature Data," Geochim. Cosmochim. Acta **63**, 11–30 (1999).

29. D. M. Shenberger and H. L. Barnes, "Solubility of Gold in Aqueous Sulfide Solutions from 150 to 350°C," Geochim. Cosmochim. Acta **53**, 269–278 (1989).

30. M. E. Berndt, T. Buttram, D. Earley, and W. E. Seyfried, Jr., "The Stability of Gold Polysulfide Complexes in Aqueous Solutions: 100 to 150°C and 100 Bars," Geochim. Cosmochim. Acta **58**, 587–594 (1994).

31. N. N. Baranova and A. V. Zotov, "Stability of Gold Sulphide Species (AuHS$^{\circ}_{aq}$ and Au(HS)$^{-}_{2}$) at 300, 350°C and 500 Bar: Experimental Study," Mineral. Mag. **62A**, 116–117 (1998).

32. F. Gibert, M.-L. Pascal, and M. Pichavant, "Gold Solubility in Hydrothermal Solutions: Experimental Study of Stability of Hydrosulphide Complex of Gold (AuHS°) at 350 to 450°C and 500 Bars," Geochim. Cosmochim. Acta **62**, 2931–2947 (1998).

33. K. Hayashi and H. Ohmoto, "Solubility of Gold in NaCl- and H$_2$S-Bearing Aqueous Solutions at 250–350°C," Geochim. Cosmochim. Acta **55**, 2111–2126 (1991).

34. D. Crerar and H. Barnes, "Ore Solution Chemistry V. Solubilities of Chalcopyrite and Chalcocite in Hydrothermal Solutions at 200°C to 350°C," Econ. Geol. **71**, 772–794 (1976).

35. A. Sugaki, S. D. Scott, K. Hayashi, and A. Kitakaze, "Ag$_2$S Solubility in Sulfide Solutions Up to 250°C," Geochem. J. **21**, 291–305 (1987).

36. G. Schwarzenbach, O. Gübeli, and H. Züst, "Thiokomplexe des Silbers und die Loeslichkeit von Silbersulfid," Chimia **12**, 84–86 (1958).

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

38. Ya. I. Ol'shanskii, V. V. Ivanenko, and A. V. Khromov, "On the Solubility of Sulfurous Silver in Aqueous Solutions Saturated in H$_2$S," Dokl. Akad. Nauk SSSR **124** (2), 410–413 (1959).

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

40. N. N. Akinfiev, "Algorithm of Calculations of Heterogeneous Equilibria for Electronic Microcomputers," Geokhimiya, No. 6, 882–890 (1986).

41. N. N. Akinfiev, "Model for Calculation *ab initio* Ionic Association in Supercritical Aqueous Fluids: 1 : 1 Electrolytes," Geokhimiya, No. 3, 426–440 (1995).

42. J. K. Hovey, *Thermodynamics of Aqueous Solutions*, PhD. Thesis. (University of Alberta, Edmonton, 1988).

43. 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).