Au-Ag-Te-Se deposits
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Pyrrhotite-pyrite equilibria in the Ag-Fe-S system at 245 to 310°C and standard pressure

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Abstract. The reaction $FeS_2(cr) + 2Ag(cr) = 'FeS'(cr) + Ag_2S(cr)$ was studied by measuring the temperature dependence of the electromotive force (EMF) of the all-solid-state galvanic cell with common gas space: (-) Pt | Ag | AgI | Ag_2S, 'FeS', FeS_2 | Pt (+). The measurements were carried out in the flow of argon at atmospheric pressure, and AgI was used as a solid electrolyte. As a result of the measurements of EMF as a function of temperature, two linear ($\Delta_r C_p = 0$) trends were obtained, which characterize the equilibrium β-pyrrhotite + pyrite (po + py), and the metastable equilibrium of presumably monoclinic pyrrhotite, $Fe_{0.875}S$, with pyrite (mpo + py). The lower temperature limit (518 K) corresponds to the equilibrium pyrite + metallic silver ($E = 0$). From experimental results of this study and literature data for Ag_2S, the temperature dependence of the gaseous sulfur activity was determined pyrite + hexagonal pyrrhotite (β + py), pyrite+monoclinic pyrrhotite (mpo + py), and monoclinic pyrrhotite + β-pyrrhotite (β + mpo):

$\log aS_2(\beta + py) = (14.95 \pm 0.05) - (15040 \pm 28) \cdot T^{-1}$, (518<*T*/K<601)

$\log aS_2(mpo + py) = (11.66 \pm 0.09) - (13152 \pm 50) \cdot T^{-1}$, (518<*T*/K<565)

$\log aS_2(\beta + mpo) = (39.8 \pm 0.2) - (29305 \pm 120) \cdot T^{-1}$ (298.15<*T*/K<565)

Thermodynamic functions at standard temperature and pressure were determined for monoclinic pyrrhotite, $Fe_{0.875}S$, as follows: $\Delta_f G_m(mpo, 298.15 \text{ K}) = -(140100 \pm 3000)$ J·mol^{-1}, $S^o_m(mpo, 298.15 \text{ K}) = (49.2 \pm 0.3)$ J·mol^{-1}·K^{-1}, $\Delta_f H_m(mpo, 298.15 \text{ K}) = -(166500 \pm 3000)$ J·mol^{-1}, where the standard state of sulfur was assumed to be S_2 ideal gas at 1 bar (10^5 Pa).

Key words: thermodynamic equilibrium, pyrrhotite, pyrite, galvanic cell

Introduction

Among binary sulfide systems, the system Fe-S is most interesting for geologists and metallurgists. Most ore deposits contain one or several forms of iron sulfide, and the same minerals are also the most abundant rock-forming sulfides. In magmatic ore deposits, the iron sulfides are the dominant minerals in ore groundmass. Pyrrhotite (po, $Fe_{1-x}S$) and pyrite (py, FeS_2) are the only sulfides that can be identified as rock-forming minerals. In most studies of sulfide assemblages, Fe-S is used as a bounding system.

The thermodynamics of the γ-pyrrhotite-pyrite equilibrium was extensively studied in the past (Kullerud and Yoder, 1959; Arnold, 1962; Toulmin and Barton, 1964; and references within). The most complete and extensively used experimental study of this system was published by Toulmin and Barton (1964), who used the electrum tarnishing method (Barton and Toulmin, 1964) to determine the fugacity of gaseous sulfur.

The high-temperature galvanic cell technique (*aka* EMF technique) used in this study is the most precise and direct method to determine the free energy of reactions *in-situ* (Kiukkola and Wagner, 1957a, b). Fully solid-state cells with common gas space have been proved to be highly efficient for measuring the volume effects of reactions at elevated gas pressures (Osadchii et al., 1998) and for determining the standard thermodynamic properties of silver and gold sulfides (Osadchii and Rappo, 2004).

Thermodynamic background

The phase relations in the Ag-Fe-S system were studied by Taylor (1970). At temperatures below (521±8) K and the component ratio Ag:Fe:S = 1:1:2, the stable assemblage is represented by metallic silver and pyrite. At higher temperatures, these phases give way to the assemblage argentite + pyrrhotite + pyrite, and then the phase relations undergo no significant changes up to 805 K. Above 805 K, a ternary eutectics occurs. All phases in the system are almost pure compounds. The contents of silver in iron sulfides and iron in argentite do not exceed 0.1 atom.% (Taylor, 1970), and it was also confirmed that the composition of $Fe_{1-x}S$ in the Ag_2S + po + py assemblage above (521±8) K are identical by measurement with the po in the binary assemblage po + py, as determined by Arnold (1962) and Toulmin and Barton, (1964).
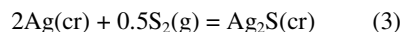
The phase relations are described by the solid-phase reaction:

$$FeS_2(cr) + 2Ag(cr) = `FeS'(cr) + Ag_2S(cr) \quad (1)$$
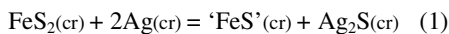
where all phases, except pyrrhotite, are in standard states (activities are equal to unity). Reaction (1) can be also presented as a sum of two reactions involving gaseous sulfur:

$$FeS_2(cr) = `FeS'(cr) + 0.5S_2(g) \quad (2)$$

and

$$2Ag(cr) + 0.5S_2(g) = Ag_2S(cr) \quad (3)$$
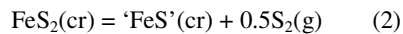
Under thermodynamic equilibrium conditions, the sulfur activities in Reactions (2) and (3) are equal, and in Reaction (1), the sulfur activity is eliminated.

The studied Ag-Fe-S system is considered condensed, i.e., all reactions are fully solid-phase, and the pressure of gaseous sulfur is not used as a thermodynamic parameter. The total pressure (imposed on solid phases) is 1 atm. Ar. Nevertheless, this approach does not exclude the possibility of presenting data in terms of gaseous sulfur activity, such as in Reactions (2) and (3). Such experimental conditions correspond to the definition of a "condensed" system (Kulerud and Yoder, 1959).

Reaction (1) was realized in the flow of argon in the all solid-state galvanic cell with a common gas space:

$$(-)Pt|Ag|AgI|Ag_2S, `FeS', FeS_2|Pt(+) \quad (A)$$

The vertical lines in Cell (A) denote the phase boundaries or electric contacts with electrodes. The phases separated by commas represent the mechanical mixture of the sample system (or working electrode). The reference system (or reference electrode) is represented by pure crystalline silver. The cell polarity (shown in parentheses) on the inert platinum electrodes is dictated by the fact that the chemical potential of silver on the reference electrode is always higher than that on the working electrode. Thus, the flow of Ag^+ ions through the solid electrolyte in the cell and the flow of electrons in the external circuit are both directed from the left to the right. The EMF of Cell (A) measured by a voltmeter is always positive, E(A)>0 by definition (spontaneous process).

The EMF of Cell (A) is related to the free energy and the equilibrium constant of Reaction (1) via the fundamental thermodynamic equation:

$$\Delta_r G_m = -nFE = - R\ln10 T\log K_r \quad (4)$$

where $\Delta_r G_m$ is the molar Gibbs free energy change for a reaction; n is the number of electrons in the electrochemical process ($n = 2$ in Cell A); F is the Fraraday constant (96,484.56 C·mol^{-1}); E is the EMF of the galvanic cell in volts; R is the gas constant

(8.31441 J·K^{-1}·mol^{-1}); T is the absolute temperature; and K_r is the equilibrium constant.

If the temperature dependence $E(A) = f(T)$ is known, Equation (4) can be used to determine the temperature dependence of the molar Gibbs energy for Reactions (1) and (3), which are equal in equilibrium, $\Delta_r G_m(1) = \Delta_r G_m(3)$:

$$\Delta_r G_m(3) = -2FE(A) \qquad (5)$$

Combining Equations (4) and (5) and the free energy data for the formation of argentite from silver and $S_2(g)$, one can determine a_{S2} in Reaction (3) from $E(A) = f(T)$ measurements, as follows:

$$\log a S_2(3) = [\Delta_f G_m(Ag_2S,cr) + 2FE(A)]/0.5R\ln 10 T$$
$$(6)$$

Under the equilibrium conditions, $a S_2(3) = a S_2(2)$, and Equation (6) determines the temperature dependence of the gaseous sulfur activity above the po + py couple, according to Reaction (2). In this case, the pyrrhotite compositions in equilibrium with pyrite need not be known. It is obvious that at $E(A) = 0$, the $\log a S_2(3)$ value is determined by the Ag + Ag$_2$S equilibrium at a given temperature. The EMF of Cell (A) should have a maximum value at the line of condensation of gaseous sulfur ($\log a S_2 = 0$) at the standard pressure.

Equation (6) written for a particular reaction can be used for calculating a_{S2} in all the equilibria considered in this paper.

After substitution of the molar free energies of formation of Ag$_2$S (Richardson and Jeffes, 1952),

$$\Delta_f G_m(Ag_2S,cr) = -87,82 + 34.56 \cdot T, \ J \cdot mol^{-1} \ (7)$$

and re-arrangement, Equation (6) becomes:

$$\log a S_2 = (-9174.5 + 20.159 E/mV) \cdot T^{-1} + 3.61 \ (8)$$

Equation (8) can be applied to any solid-state reactions involving the potential-forming Reaction (3).

Experimental

All iron sulfides were obtained by dry synthesis in evacuated (10^{-4} bar) silica glass capsules in the temperature range 673-823 K.

The sealed capsules were annealed in horizontal resistance furnaces at a particular temperature (± 5 K) for 5-10 days. The capsules were cooled in air. Troilite was synthesized from pure elements, with slight excess of sulfur (about 3-5 mg.g^{-1} of sample). The equilibrium assemblage (po + py) with the molar ratio 1:1 was synthesized from troilite and sulfur in three steps with grinding in between. All synthesized substances were examined under the microscope in reflected light and analyzed by X-ray powder diffraction (XRD, CoK$_\alpha$ radiation, Fe filter).

The sample system (working electrode) was prepared from the mixture (po + py) + Ag$_2$S, in which components were taken in a molar ratio of 1:1:1. The powder mixture (400 mg) was pressed to tablets 6 mm in diameter under the load of 1-1.2 tons. The reference system (reference electrode) was prepared from silver (99.9%) in the form of a cylinder 6 mm in diameter and 4 mm in thickness.

The working surfaces of the electrodes were polished to a mirror luster to improve electric contacts.

For the EMF experiments, we employed the method of 'temperature titration', i.e., stepwise heating with waiting for a constant (equilibrium) EMF value at each given temperature.

Equlibrium in Cell (A) was attained both quickly and reproducibly over the whole temperature range studied. This fact can be partially explained by the presence of silver sulfide in the system. Ag$_{2\pm\delta}$S is an ion conductor and also shows some semiconductor properties (Miyatani, 1968). The relatively high mobility of silver ions and electronic conductivity resulted in the establishment of local equilibrium between the phases of the sample system, i.e., at the three-phase contact po + py + Ag$_2$S. The role of Ag$_2$S in the fast equilibration in the system Ag-Fe-S is also illustrated by the comparison of the annealing times of the systems Fe-S (Toulmin and Barton, 1964) and Ag-Fe-S (Taylor, 1970).

The equilibrium among pyrrhotite, pyrite, and the gas phase (in the Fe-S system) and the equilibrium between the gaseous sulfur and the

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sulfide electrode is attained for a longer period of time, like in cell with separate gas space (87 days at 597 K) (Schneeberg, 1973).

Experimental results and calculations

Data obtained from the EMF measurements in Cell (A) are described by linear ($\Delta_r C_p = 0$) equation, which refers to the field of equilibrium of pyrite with (β) pyrrhotite:

$$E(A)\beta/py, mV = -290.9 + 0.562 \cdot T,$$
$$(518 < T/K < 601) \quad (9)$$

The temperature dependence of the gaseous sulfur activity above the pyrrhotite-pyrite equilibrium can be determined by substitution of equation (9) into equation (8):

$$\log aS_2(\beta/py) = (14.95 \pm 0.05) - (15040 \pm 28) \cdot T^{-1}$$
$$(10)$$

The errors were determined by the least-squares method for the confidence interval of 2δ.

At 518±3 K, metallic silver is formed in the right half-cell of Cell (A), and hence $E(A) = 0$. At any temperature below this point, the processes occurring in the sample system are inaccessible for investigation by the EMF method. According to Taylor (1970), a stable assemblage, $Ag + FeS_2 \pm Ag_2S$ is formed in the system.

In several experimental runs, the freshly prepared cells were held at a temperature below 518 K for several days to two months. When the temperature was subsequently raised to (518 ±3) K, different EMF trends were observed (Fig. 1). Trend H was obtained after two-month exposition of the system at T = 449 K. Trend M was obtained with the 10-day exposition. Trend L was obtained for the sample system that was originally composed of the mixture if fine silver powder, pyrite, and argentite with stepwise (5 K) increase of temperature from 449 K to readable EMF values over four weeks.

Given that the highest trend 'H' corresponds to the equilibrium of monoclinic pyrrhotite of constant composition ($Fe_{0.875}S$, i.e., Fe_7S_8) with pyrite, we can determine the sulfur vapor pressure above the mpo + py equilibrium and standard thermodynamic functions for mpo using the following reaction and experimental data:
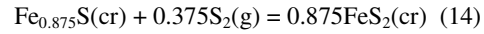
$$FeS_2(cr) + 2Ag(cr) = \text{'FeS'}(mpo) + Ag_2S(cr)$$
$$(11)$$
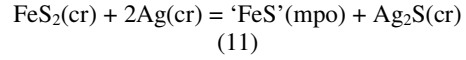
$$E(A)mpo + py, mV = -(197.3 \pm 3.7) + (0.399 \pm 0.007) \cdot T, (518 < T/K < 574), \ R^2 = 0.9999 \ (12).$$

After substitution of equation (12) to Equation (8), we derive the expression for $\log aS_2$

$$\log aS_2(mpo+py) = 11.66 - 13152 \cdot T^{-1} \ (13)$$

in the reaction of pyrite formation from monoclinic pyrrhotite (phase of constant composition) and gaseous sulfur:

$$Fe_{0.875}S(cr) + 0.375S_2(g) = 0.875FeS_2(cr) \ (14)$$

Then, simultaneously solving Equations (9) and (12), one can find the temperature of transition of the monoclinic pyrrhotite to hexagonal pyrrhotite:
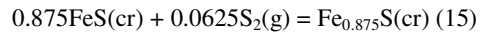
$$T_{trs}(mpo-po) = (574 \pm 5) \ K$$

The enthalpy of this transition:

$$\Delta_{trs}H(mpo-\beta) = -(9400 \pm 1000) \ J \cdot mol^{-1}$$

The temperature dependence of the molar Gibbs energy for Reaction (14) can be determined using Equation (13):

$$\Delta_r G_m (14) = 0.375R\ln10 T \log aS_2(mpo + py) = -94421 + 83.818 \cdot T$$

The equilibrium β-pyrrhotite + monoclinic pyrrhotite (β + mpo) curve (Reaction 15) is also shown in Fig. 1 (Equation 16).

$$0.875FeS(cr) + 0.0625S_2(g) = Fe_{0.875}S(cr) \ (15)$$

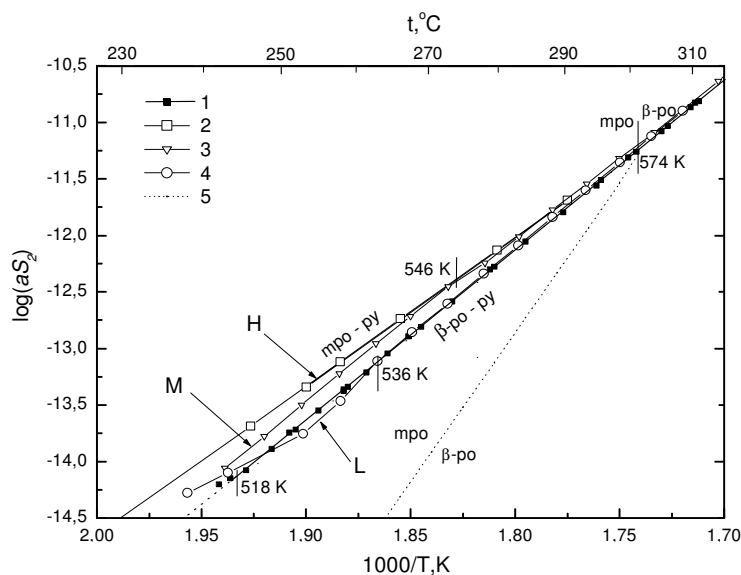$$\log aS_2(\beta + mpo) = 39.76 - 29305 \cdot T^{-1} \ (16)$$

Fig. 1. Temperature trends of the reactions involving py, β-po, and mpo plotted as functions of temperature and gaseous sulfur activity. 1- Reaction 1, Equation 9; 2- Reaction 11, Equation 13; 2, 3, and 4- Trends H, M and L, respectively; 5- Reaction 15, Equation 16

Conclusions

The use of the pyrite + pyrrhotite and, presumably, also pyrrhotite + pyrrhotite equilibria as geological thermometers is not possible. However, if the temperature of a sulfide + sulfide paragenesis (e.g. hexagonal pyrrhotite + pyrite) was independently determined, the corresponding sulfur activity can be determined with high precision using the experimentally-obtained equations. Similar information can be obtained from the assemblages: monoclinic pyrrhotite + pyrite and hexagonal pyrrhotite + monoclinic pyrrhotite, but the accuracy of these estimates remains open to discussion.

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