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Determination of standard thermodynamic properties of sulfides in the Ag-Au-S system by means of a solid-state galvanic cell

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ABSTRACT

Thermodynamic properties of the following phase reactions in the Ag-Au-S system have been investigated via electromotive force (EMF) measurements in solid-state galvanic cells with Ag_4RbI_5 as a solid electrolyte:

$$Ag(cr) + Ag_3AuS_2(cr) = 2Ag_2S(cr) + Au(cr)$$
$$Ag(cr) + 2AgAuS(cr) = Ag_3AuS_2(cr) + Au(cr)$$
$$Ag(cr) + Au_2S(cr) = AgAuS(cr) + Au(cr)$$
$$AgAuS(cr) + Ag_2S(cr) = Ag_3AuS_2(cr)$$

The EMF temperature dependences observed for these reactions, together with auxiliary thermodynamic properties for Ag_2S, acanthite, from Robie and Hemingway (1995), result in the following standard thermodynamic properties at 298.15 K and 1 bar (10^5 Pa): $\Delta_f G^o(Ag_3AuS_2, cr) = -69478(200)$ J/mol and $S^o(Ag_3AuS_2, cr) = 273.37(56)$ J/(mol·K) (uytenbogaardtite), $\Delta_f G^o(AgAuS, cr) = -27621(210)$ J/mol and $S^o(AgAuS, cr) = 128.11(60)$ J/(mol·K) (petrovskaite), and $\Delta_f G^o(Au_2S, cr) = 1077(650)$ J/mol and $S^o(Au_2S, cr) = 128.1(2.0)$ J/(mol·K). Au_2S(cr) is a thermodynamically metastable phase, but the values of its thermodynamic functions are open to discussion.

INTRODUCTION

Gold-silver sulfides do not have significant economic importance compared to native gold. However, mineral assemblages in the Ag-Au-S system occur in many gold-silver deposits, and investigation of their thermodynamic properties is important for understanding the geochemistry, transport, and deposition of gold.

At temperatures lower than 386 K, the Ag-Au-S system (Graf 1968) contains three stable stoichiometric sulfides: acanthite (Ag_2S), uytenbogaardtite (Ag_3AuS_2), and petrovskaite (AgAuS). Uytenbogaardtite (Ag_3AuS_2) was discovered by Barton et al. (1978) in specimens from Tambang Sawah (Benkoelen district, Sumatra, Indonesia), the Comstock lode (Storey County, Nevada, U.S.A.), and Smeinogorsk (Schlangenberg, Altai, Russia). At all three localities, uytenbogaardtite occurs as small blebs up to 100 μm across and as rims intimately associated with acanthite, electrum, quartz, and other minerals. Liujinyinite (Ag_3AuS_2) was found in three ore deposits in China (Chen Zhen-jie et al. 1979) and is considered to be uytenbogaardtite (Fleischer et al. 1980). Petrovskaite (AgAuS) was discovered by Nesterenko et al. (1984) in oxidized Au-sulfides of the Maykain "C" ore deposit, Central Kazakhstan. It occurs as small rims around native gold (85–100 mass% Au) up to 20 μm across and is associated with kerargirite (AgCl).

AgAuS was used by Zotov et al. (1996) for determination of aqueous gold hydrosulfide complex stability. Thus, the accuracy of thermodynamic properties for these important aqueous species is directly related to the uncertainty of thermodynamic data for AgAuS.

The phase relations of the $Ag_{2-x}Au_xS$ ($0 < x < 1$) pseudobinary system have been extensively studied (cf. Tavernier et al. 1967; Graf 1968; Llabres and Messien 1968; Smit et al. 1970; Folmer et al. 1976; Barton 1980). However, no experimental data on phase relations for the AgAuS-Au_2S part of the $Ag_{2-x}Au_xS$ system ($x > 1$) have been reported in the literature. Reliable thermodynamic data are only available for acanthite (Ag_2S) [see, for example, reviews by Mills (1974), and Sharma and Chang (1986), and references therein], whereas the thermodynamic properties of uytenbogaardtite and petrovskaite are not well defined. The only calculation of these thermodynamic values was carried out by Barton (1980) via thermodynamic analysis of electrum-sulfide equilibria at 100–850 K. However, Barton (1980) noted that his thermodynamic data contained uncertainties. This is also illustrated by an inconsistency in the standard Gibbs free energy of formation for metastable Au_2S reported by Barton and Skinner (1979) and determined by Barton (1980): 28.7(10.5) kJ/mol and 10.8(8.4) kJ/mol, respectively. According to Ishikawa et al. (1995), Au_2S decomposes at temperatures above 490 K.

The objective of the present study is to determine the standard thermodynamic properties of uytenbogaardtite, petrovskaite, and Au_2S using electromotive force (EMF) measurements in solid-

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state galvanic cells with common inert gas. This method has proved to be direct, effective, and most accurate for determination of standard molar free energies of formation and molar entropy change in solid state reactions (Kiukkola and Wagner 1957a, 1957b).

PHASE REACTIONS AND GALVANIC CELLS

The following reactions were studied to determine the thermodynamic properties of Ag_3AuS_2, AgAuS, and Au_2S:

$$Ag(cr) + Ag_3AuS_2(cr) = 2Ag_2S(cr) + Au(cr) \quad (1)$$
$$Ag(cr) + 2AgAuS(cr) = Ag_3AuS_2(cr) + Au(cr) \quad (2)$$
$$Ag(cr) + Au_2S(cr) = AgAuS(cr) + Au(cr) \quad (3)$$
$$AgAuS(cr) + Ag_2S(cr) = Ag_3AuS_2(cr) \quad (4)$$

These reactions were realized in the form of galvanic cells with an Ag_4RbI_5 superionic compound, which has a specific Ag^+ conduction (Despotuli et al. 1989) as solid electrolyte:

A: Pt | Ag | Ag_4RbI_5 | Ag_3AuS_2, Ag_2S, Au | Pt
B: Pt | Ag | Ag_4RbI_5 | Ag_3AuS_2, AgAuS, Au | Pt
C: Pt | Ag | Ag_4RbI_5 | Au_2S, AgAuS, Au | Pt
D: Pt | Ag_3AuS_2, Ag_2S, Au, | Ag_4RbI_5 | Ag_3AuS_2, AgAuS, Au | Pt

The vertical lines in cell notation indicate the phase boundaries or electrical contacts between different parts (electrodes) of an electrochemical cell. The phases separated by commas represent mechanical mixtures in the sample and reference systems (see below).

Equilibria 1–4 are consistent with the Ag-Au-S phase diagram at temperatures below 386 K (Fig. 1a). All sulfides in this system are stable in the presence of pure gold and sulfur, whereas pure silver and silver-rich electrum react with all phases except Ag_2S. We assume that the Ag_2S-Au_2S cross section is a binary system, and the homogeneity range of uytenbogaardtite and petrovskaite is very narrow (Folmer et al. 1976). All reactions and galvanic cells listed above correspond to the pseudoternary system Ag_2S-Au_2S-Ag_xAu_{1-x}. As the system does not contain pure sulfur, electrum of any fixed composition, as well as pure gold, can exist in Cells A, B, and C. However, to reduce the number of auxiliary data (Au activity in electrum of fixed composition), these cells contained only pure crystalline gold.

Two different reference systems were used in the electrochemical cells: (1) in Cells A-C, pure crystalline silver was used as a reference system. For example, half-cell reactions of Cell A can be written as: $Ag = Ag^+ + e$ (left hand side, reference system, negative electrode) and $Ag^+ + e + Ag_3AuS_2 = 2Ag_2S + Au$ (right hand side, sample system, positive electrode). The overall cell reaction can therefore be described as: $Ag(cr) + Ag_3AuS_2(cr) = 2Ag_2S(cr) + Au(cr)$, which is identical to Reaction 1. Electrochemical processes in Cells B and C are the same as above. (2) In Cell D, both reference and sample systems contain a mixture of sulfides and gold. Half-cell reactions can be written as: $2Ag_2S + Au = Ag^+ + e + Ag_3AuS_2$ (left hand side, reference system, negative electrode) and $Ag^+ + e + 2AgAuS = Ag_3AuS_2 + Au$ (right hand side, sample system, positive electrode). The overall cell reaction can therefore be described as: $2AgAuS(cr) + 2Ag_2S(cr) = 2Ag_3AuS_2(cr)$.

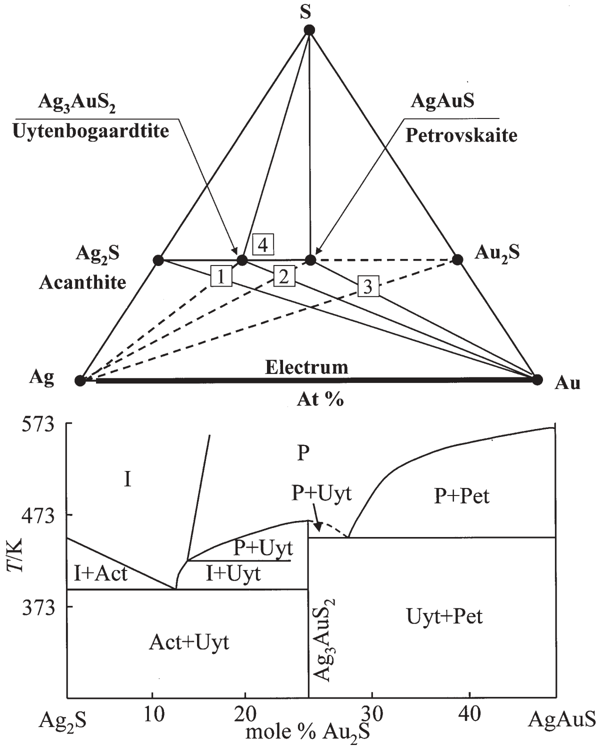

FIGURE 1. (**a**) Phase relations in the Ag-Au-S system at 298–386 K (after Barton 1980). The figures in squares indicate the numbers of phase reactions studied. (**b**) Temperature-composition (mol% Au_2S) diagram for the binary Ag_2S-AgAuS system (after Graf 1968; Folmer et al. 1976; and Barton 1980). Act = acanthite, Uyt = uytenbogaardtite, Pet = petrovskaite, I = body-centered cubic solid solution, P = primitive cubic solid solution.

The polarity of the galvanic cells is determined by the difference in the chemical potential of silver between the left and right half-cells. In Cells A, B, and C, the left half-cells contain pure silver, and hence, the chemical potential of silver in the left half-cells is always higher than that in the right half-cells. The polarity of Cell D can be determined as follows. The chemical potentials of the phases present in both left and right half-cells are cancelled. Thus, the left half-cell is represented by the chemical potential of Ag_2S, whereas the right half-cell is represented by the chemical potential of petrovskaite (AgAuS), the composition of which can also be described as $Ag_{2-x}Au_xS$ at $x = 1$. Thus, the chemical potential of Ag_2S, and therefore the chemical potential of Ag as well, is higher in the left half-cell than in the right half-cell.

Cells A through D are written in such a way that the chemical potential of silver in the left half-cell is higher than that in the right half-cell. Accordingly, the fluxes of silver ions through the solid electrolyte and the fluxes of electrons in the external circuit are both directed from the left to the right. This implies that the left-hand Pt electrode acquires a negative charge, and the right-side Pt electrode acquires a positive charge. The positive EMF values measured in Cells A-D indicate a spontaneous process ($\Delta_r G^o_T < 0$) in the corresponding Reactions 1–4.

A temperature-composition projection of the Ag_2S-Au_2S system (Fig. 1b) shows that there are eutectoids between Ag_2S and

Ag_3AuS_2 at 386 K, and between Ag_3AuS_2 and AgAuS at 454 K. Accordingly, the upper temperature limit for studying Reactions 1 and 4, including the stoichiometric phases, is 386 K. Thus, the upper temperature limit in the measurements performed in this study was 386 K. The lower temperature limit was chosen for each cell to enable stable and reproducible EMF readings.

EXPERIMENTAL METHODS

Synthesis and characterization of the solid phases

99.95 and 99.99% Au and Ag foil, 99.99% S, Au powder (Aldrich Chem. Co. –20 mesh, 99.999+%), and Ag_2S (Aldrich Chem. Co. 99.9%) were used for the synthesis experiments. Ag_2S was also synthesized from elemental Ag and S in a sealed evacuated silica glass tube at 393–413 K. The XRD patterns for both commercially available and synthesized Ag_2S corresponded to acanthite (JCPDS card 14-0072).

To characterize the solid phases and to prepare the electrodes (sample and reference systems), uytenbogaardtite, petrovskaite, their mixture, and mixtures of $Ag_2S + Ag_3AuS_2$ were prepared in batches of 1–1.2 g by reacting Ag-Au alloys (electrum) and sulfur. Several compositions of electrum were synthesized by fusing a mixture of small pieces of gold and silver in a silica glass ampoule in the hot oxy-gas flame. The alloy obtained was flattened to ~0.2 mm thickness and then cut into small pieces ~0.5 × 2 mm in size. A weighed amount of these pieces of electrum was loaded together with a stoichiometric amount of sulfur into a silica-glass tube. To eliminate most of the vapor space, a tightly fitting silica glass rod was inserted into the tube, which was subsequently evacuated and sealed. The synthesis was performed in horizontal tube furnaces. For the first 2–3 days of synthesis, the charged tube was annealed at 673 K to allow the sulfur to react with the electrum, after which it was heated to ~793 K and annealed for other 1–2 days. Then the tube was cooled together with the furnace and opened. XRD analysis of the synthesized samples indicated pure phases or mixtures of desired compositions. To eliminate possible heterogeneities, the synthesized sulfide material was ground, loaded again into a silica glass tube together with an additional 1–5 mg of sulfur, and the same annealing procedure was repeated. The excess sulfur crystallized at the free end of the tube while cooling. The resulting products were examined by XRD analysis. The powder patterns corresponded to JCPDS cards 19-1146 for petrovskaite, 20-461 for uytenbogaardtite, and 14-0072 for acanthite.

Au_2S was prepared as described by Renders and Seward (1989). Briefly, this method involved reaction of metallic gold with hot aqua regia with subsequent evaporation and addition of H_2O plus a concentrated NH_4OH mixture to form fulminating gold $[Au(NH_3)_3(OH)_3]$. The product was filtered and repeatedly washed with hot distilled water. The resulting wet product was dissolved in a KCN solution and then bubbled with H_2S gas for 1 h. Finally, Au_2S was deposited from this solution by adding concentrated HCl with subsequent heating to a temperature slightly below the boiling point. After cooling, the precipitate was washed with bidistilled H_2O, ethanol, diethyl ether, and CS_2 to remove S_2, and then was washed again with diethyl ether, ethanol, and water to remove organic solvents. The product was dried over P_2O_5 in the dark for several days. A small amount (less than 1 vol%) of fine well-crystallized (2–5 μm) gold was found with a light microscope. XRD patterns of this product corresponded to pure crystalline Au_2S (Ishikawa et al. 1995), JCPDS card no. 18-1997.

Preparation of electrodes and cell arrangement

Sulfides for the electrodes (sample systems) of Cells A, B, and D were prepared by direct synthesis from mixtures (mole ratio 1:1) of sulfur and electrum $Ag_{0.875}Au_{0.125}$ and $Ag_{0.625}Au_{0.375}$, respectively. Sample systems for these cells were prepared by grinding gold powder together with the sulfide mixture (mole ratio sulfide:sulfide:gold is equal to 2:2:1). Sample systems for Cell C were prepared from mixtures of AgAuS + Au_2S + Au in molar ratio 2:2:1. Electrode tablets (2 mm in thickness and 6 mm in diameter, ~0.4 g mass) were pressed under ~2 tons load and then mirror polished.

A schematic cell arrangement is shown in Figure 2. The cell consists of a silver disc (reference system), a tablet of a solid electrolyte, and a tablet of a sample system. The solid electrolyte tablet (2 mm thick and 5–6 mm in diameter) was cut from a block of crystalline transparent yellow-green Ag_4RbI_5, and then mirror polished. The cell in the form of a tablet stack was placed into a silica glass tube (6.5 mm ID) between Pt disks, which were connected with Cu leads and adjusted by spring to improve the electrical contact. The small distance between the electrodes (less than 1 cm) allowed for minimization of temperature gradients within the cell. Finally, the whole cell assembly was placed into another silica glass tube (11 mm ID) with gas inlet and outlet spouts. Measurements were performed under a dried argon gas flow of 0.5–1 cm^3 per minute.

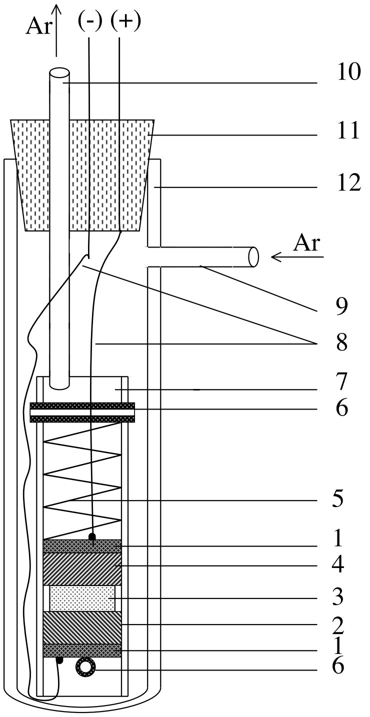

FIGURE 2. Sketch of the solid-state galvanic cell with a common gas space. (1) Pt-electrode, (2) reference system, (3) solid electrolyte (Ag_4RbI_5), (4) sample system, (5) spring, (6) ceramic latch, (7) silica glass tube (cell holder), (8) Cu-lead, (9) inlet gas sprout, (10) outlet gas sprout, (11) rubber plug, (12) silica glass tube.

Furnace, temperature, and EMF measurements

The cells were placed into the isothermal (at least 20 mm high) zone of a vertical resistance (direct current) furnace (18 mm ID and 250 mm high). The temperature was kept constant to within ±0.1 K with a "PROTHERM-100" electronic temperature controller and was measured in the middle of the cell with an accuracy of ±0.1 K using a K-type thermocouple. The thermocouples were calibrated against a standard Pt thermometer in a water ultrathermostat. Both the temperature and the EMF measurements were carried out automatically with an accuracy of 0.010(5) mV with a multi-channel millivoltmeter and recorded using a computerized data-acquisition system. High-input impedance (~10^{13} Ω) channels were used for the EMF measurements.

Cell operations

The measurements were performed as a "temperature titration". The temperature was changed in 5–10 K steps, and at every temperature value the EMF of the cell was monitored until the equilibrium EMF value was reached. The reversibility of the equilibrium was checked by performing upward and downward temperature changes. Equilibrium was assumed when the EMF remained unchanged within ±0.03 mV for at least 12 hours.

Equilibrium EMF values were typically attained in 1–10 days. After a short circuit of 5–10 seconds and/or polarization by direct current of 0.5 V, the equilibrium EMF value recovered within 3–24 hours.

Phase composition of the sample systems was confirmed by XRD analysis after the experiments. All parts of the cells after completion of the experiments were in the same state as before loading. It should be pointed out that the solid electrolyte remained in very good condition after the EMF experiments. Examination with an optical microscope did not reveal any tarnishing or dendrite formation.

RESULTS AND CALCULATIONS

EMF values

The EMF values measured in Cells A-D as a function of temperature are listed in Table 1 and shown in Figure 3. Fitting the linear equation $E = \mathrm{a} + \mathrm{b}\cdot T$, which implies $\Delta_r C_p$ is constant and equal to zero, to these experimental data yielded the following equations:

$$E(\mathrm{A})/\mathrm{mV} = (50.04 \pm 0.70) + (0.180 \pm 2.017\cdot10^{-3})\cdot T/\mathrm{K} \quad (320.8 < T/\mathrm{K} < 386,\ R^2 = 0.99971) \tag{5}$$

$$E(\mathrm{B})/\mathrm{mV} = (79.27 \pm 0.77) + (0.229 \pm 2.273\cdot10^{-3})\cdot T/\mathrm{K} \quad (310 < T/\mathrm{K} < 383,\ R^2 = 0.99955) \tag{6}$$

$$E(\mathrm{C})/\mathrm{mV} = (271.4 \pm 6.6) + (0.09 \pm 0.02)\cdot T/\mathrm{K} \quad (307.6 < T/\mathrm{K} < 341.4,\ R^2 = 0.935) \tag{7}$$

$$E(\mathrm{D})/\mathrm{mV} = (32.40 \pm 1.31) + (0.047 \pm 0.093)\cdot T/\mathrm{K} \quad (333 < T/\mathrm{K} < 377,\ R^2 = 0.9954) \tag{8}$$

The precision of the experimental data was calculated by the least-squares method (± 2σ).

Calculation of thermodynamic properties

The Gibbs free energy and entropy change of the reaction can be calculated from the EMF values of a galvanic cell using the following equations:

$$\Delta_r G\ (\mathrm{J/mol}) = -n\cdot10^{-3}\cdot\mathrm{F}\cdot E$$
$$\Delta_r S\ (\mathrm{J/K\cdot mol}) = n\cdot10^{-3}\cdot\mathrm{F}\cdot(\mathrm{d}E/\mathrm{d}T)$$
$$\Delta_r H\ (\mathrm{J/mol}) = -n\cdot10^{-3}\cdot\mathrm{F}\cdot[E - (\mathrm{d}E/\mathrm{d}T)\cdot T]$$

where n is the number of electrons participating in the cell reaction, F stands for the Faraday constant 96484.56 C/mol, and E is the cell EMF in millivolts.

The accuracy of the thermodynamic properties for Ag-Au sulfides and Au_2S calculated in the present study relies on the precision of thermodynamic values for Ag_2S, acanthite. Note also that the uncertainty in thermodynamic data for AgAuS includes uncertainty of thermodynamic values for both Ag_2S and Ag_3AuS_2; data for Au_2S are the most uncertain. The thermodynamic properties for Ag_2S(cr) reported by Robie and Hemingway (1995) were used in our calculations. We note that Robie and Hemingway (1995) used data on the heat capacity and entropy of Ag_2S(cr) from Gronvold and Westrum (1986).

Thermodynamic functions of Reactions 1–3 calculated using Equations 5–7 are listed in Table 2.

Temperature functions of the standard Gibbs energy of formation of the sulfides studied are presented in the form of the equation $\Delta_f G^o_T = \mathrm{a} + \mathrm{b}\cdot T$ for the temperature range 298–386 K (Table 3).

The standard Gibbs energy and standard entropy of Ag_2S(cr), Ag_3AuS_2(cr), AgAuS(cr), and Au_2S(cr) at 298.15 K and 1 bar were calculated as follows:

TABLE 1. Measured temperatures and EMF (E_{meas}) of galvanic Cells A-D (reactions 1–4), and values of $\Delta E = E_{\mathrm{meas}} - E_{\mathrm{calc}}$, where E_{calc} is calculated using Equations 5–8

T/K	E_{meas}/mV	ΔE /mV
	Cell A, Reaction 1, Equation 5, experiment A-570	
312.6	106.25	−0.02
318.6	107.51	0.14
322.4	108.11	0.05
324.2	108.37	−0.01
330.6	109.47	−0.06
333.2	110.14	0.14
337.5	110.59	−0.19
344.4	112.11	0.09
349.9	112.92	−0.09
355.2	114.05	0.08
360.1	114.75	−0.10
366.0	115.93	0.01
372.6	117.05	−0.06
376.6	117.81	−0.02
381.4	118.72	0.03
385.8	119.54	0.05
	Cell B, Reaction 2, Equation 6, experiment A-551	
310.8	150.37	0.04
313.2	150.78	0.18
315.2	151.43	−0.01
318.2	152.20	−0.10
318.2	151.90	0.20
320.2	152.66	−0.10
322.6	153.08	0.03
324.0	153.57	−0.14
324.6	153.61	−0.04
327.8	154.35	−0.05
331.2	155.03	0.05
333.6	155.56	0.07
335.8	156.14	−0.01
339.4	157.01	−0.05
342.6	157.76	−0.07
347.4	158.94	−0.15
350.6	159.50	0.02
356.8	160.90	0.04
361.4	162.12	−0.13
367.4	163.42	−0.06
371.8	164.55	−0.18
378.0	165.54	0.25
382.4	166.69	0.11
	Cell C, Reaction 3, Equation 7, experiment A-573	
307.6	298	0.3
312.6	299	−0.3
317.9	299	0.2
323.8	300	−0.03
330.2	300	0.2
335.6	301	−0.3
341.4	301	0.2
	Cell D, Reaction 4, Equation 8, experiment A-574	
333.2	47.95	0.04
344.6	48.54	−0.02
355.8	48.99	0.06
366.2	49.60	−0.06
376.8	49.97	0.06

$$\Delta_f G^o(Ag_3AuS_2,\ \mathrm{cr}) = 2\Delta_f G^o(Ag_2S,\ \mathrm{cr}) - \Delta_r G^o(1)$$
$$S^o(Ag_3AuS_2,\ \mathrm{cr}) = 2S^o(Ag_2S,\ \mathrm{cr}) + S^o(\mathrm{Au},\ \mathrm{cr}) - S^o(\mathrm{Ag},\ \mathrm{cr}) - \Delta_r S^o(1)$$

$$\Delta_f G^o(\mathrm{AgAuS},\ \mathrm{cr}) = 1/2[\Delta_f G^o(Ag_3AuS_2,\ \mathrm{cr}) - \Delta_r G^o(2)]$$
$$S^o(\mathrm{AgAuS},\ \mathrm{cr}) = 1/2[S^o(\mathrm{Au},\ \mathrm{cr}) + S^o(Ag_3AuS_2,\ \mathrm{cr}) - S^o(\mathrm{Ag},\ \mathrm{cr}) - \Delta_r S^o(2)]$$

$$\Delta_f G^o(Au_2S,\ \mathrm{cr}) = \Delta_f G^o(\mathrm{AgAuS},\ \mathrm{cr}) - \Delta_r G^o(3)$$
$$S^o(Au_2S,\ \mathrm{cr}) = S^o(\mathrm{AgAuS},\ \mathrm{cr}) + S^o(\mathrm{Au},\ \mathrm{cr}) - S^o(\mathrm{Ag},\ \mathrm{cr}) - \Delta_r S^o(3)$$

Standard thermodynamic properties of sulfides in the Ag-Au-S system at 298.15 K and 1 bar obtained in the present study are

TABLE 2. Standard thermodynamic functions at 298.15 K and 1 bar for Reactions 1–3 calculated from the experimental data listed in Table 1

Reaction/Equation	$\Delta_r G^o$ (J/mol)	$\Delta_r S^o$ (J/K·mol)	$\Delta_r H^o$ (J/mol)
1/5	−10010 ± 270	17.370 ± 0.700	−4830 ± 270
2/6	−14240 ± 280	22.100 ± 0.750	−7650 ± 280
3/7	−28700 ± 800	8.420 ± 2.000	−26190 ± 800

TABLE 3. Coefficients a and b in equation $\Delta_f G^o_T = a + b \cdot T$ $(298 < T/\mathrm{K} < 386)$

Phase	a (J/mol)	b (J/K·mol)
(Ag_3AuS_2, uytenbogaardtite)	−57287	−40.89
(AgAuS, petrovskaite)	−24819	−9.3975
(Au_2S, cr)	1369	−0.98

TABLE 4. Standard thermodynamic properties for crystalline phases in the Ag-Au-S system at 298.15 K and 1 bar

Phase	$\Delta_f G^\circ$ (J/mol)	$\Delta_f H^\circ$ (J/mol)	S° (J/K·mol)	Source*
Ag(cr)	0	0	42.55 ± 0.21	1
Au(cr)	0	0	47.49 ± 0.21	1
S(rhomb)	0	0	32.05 ± 0.05	1
Ag_2S, acanthite	−39700 ± 1000	−32000 ± 1000	142.9 ± 0.3	1
Ag_3AuS_2, cr, low	−63440 ± 6300			2
(uytenbogaardtite)	−69478 ± 1200	−57280 ± 1200	280.28 ± 0.2	4
AgAuS, cr, low	−22420 ± 4200			2
(petrovskaite)	−27620 ± 1210	−24800 ± 1210	131.56 ± 0.2	4
Au_2S(cr)	10820 ± 8400			2
Au_2S(cr)	28660 ± 10500			3
Au_2S(cr)	1077	1390	128.1	4

* 1 = Robie and Hemingway (1995); 2 and 3 = calculated from Barton (1980) and Barton and Skinner (1979) respectively using data for S_2(g) from Robie and Hemingway (1995); 4 = present study.

compared to literature values in Table 4. This table also contains thermodynamic data for Ag(cr), Au(cr), S(rhomb), and Ag_2S, acanthite which were used in the calculations.

Attempts to determine the thermodynamic properties of Au_2S (Reaction 3, Cell C) cannot be considered satisfactory in comparison with the other cells. Cell C with a freshly prepared sample system displayed an EMF of 320(2) mV at room temperature (23 °C = 296.15 K) for several days. Stepwise heating by 10 K per step up to 338 K resulted in a decreasing EMF of 300(3) mV, and this value remained constant for both upward and downward temperature changes in the same order. Subsequent heating resulted in a small increase in EMF of about 0.010(5) mV/T.

In comparison with other cells, the EMF values of Cell C contained permanent noise, appearing as a signal vibration on the order of ±0.5 mV per several seconds. No changes on the tablet surface were observed under the microscope (reflected light) and in XRD patterns both during and after the experiment. Nevertheless, there is no guarantee that a small amount of undetected sulfur was formed during the run. In this case, the additional phase appears in the sample system, and the EMF value of Cell C cannot be deciphered due to conflict with the Gibbs phase rule. We do not have any evidence of formation of solid phases between petrovskaite and Au_2S.

Equation 7a was found from our results (Table 1, Cell C, Reaction 3), and an additional experimental point was taken at 490 K, the temperature of complete thermal decomposition of Au_2S (Ishikawa et al. 1995). Complete decomposition of Au2S in reaction 3 results in the reaction of formation of AgAuS(cr) from elements. The extrapolated value E = 305 mV at 490 K calculated from $\Delta_f G^o_T$ (AgAuS, cr) is presented in Table 3.

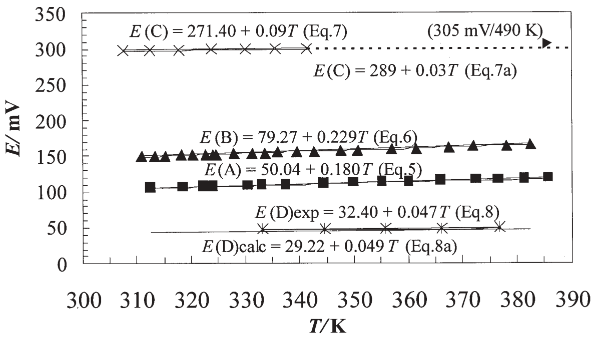

FIGURE 3. EMF (E) of galvanic Cells A-D as a function of temperature (T).

$$E(\mathrm{C})/\mathrm{mV} = (289 \pm 7) - (0.03 \pm 0.01) \cdot T/\mathrm{K}\ (308 < T/\mathrm{K} < 490) \tag{7a}$$

Both results showed that Au_2S(cr) is a thermodynamically metastable phase, but the values of its thermodynamic properties and temperature function are open to discussion.

Cell D is a combination of Cells A and B and $E(\mathrm{D}) = E(\mathrm{B}) - E(\mathrm{A})$. Five $E = f(T)$ points obtained from Cell D (Table 1 and Fig. 3) are described by Equation 4. Comparison of experimentally obtained (Eq. 8) with the calculated (Eq. 8a) value

$$E(\mathrm{D})_{\mathrm{calc}}/\mathrm{mV} = (29.22 \pm 0.80) + (0.049 \pm 2.27 \cdot 10^{-3}) \cdot T/\mathrm{K}\ (320.8 < T/\mathrm{K} < 384.4) \tag{8a}$$

showed good agreement. The difference $\Delta E = E(\mathrm{D})_{\mathrm{calc}} - E(\mathrm{D})_{\mathrm{exp}} = -3.17 + 0.002 \cdot T$ gives discrepancies in $\Delta_r G^o(4)$ at 298.15 and 386 K of 125 and 116 J/mol, respectively [note that $\Delta_r G^o(4) = 1/2 \Delta_r G^o(4a)$], and a small difference in the entropy change. Thus, the results obtained for Cell D confirm that the investigated electrochemical processes reached equilibrium. The temperature dependences of $E(\mathrm{D})_{\mathrm{calc}}$ and $E(\mathrm{D})_{\mathrm{exp}}$ are also plotted in Figure 3.

The results presented here demonstrate the high efficiency of the solid state EMF method for the investigation of sulfide-containing reactions. Silver-bearing phases usually show good kinetic properties. Based on the Ag_4RbI_5 solid electrolyte, this method raises the possibility of studying solid-state reactions in the low-temperature range (298–513 K). A noticeable advantage of this method is the possibility of investigation of all solid-state reactions in many sulfide systems (in this case pressure of S2(g) is not a thermodynamic parameter).

It is necessary to point out that in the case of systems with thermally unstable phases (such as Au_2S in this study), which can slowly decompose during the experiments, the EMF method is able to provide the temperature limit of the phase stability, up to which reproducible (equilibrium) EMF values can be obtained. However, decreasing the temperature of the EMF experiments can substantially reduce the precision of the results. It should also be noted that thermodynamically unstable ($\Delta_f G^o_T > 0$) but thermally stable phases are quite suitable for experimental studies by the EMF method.

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