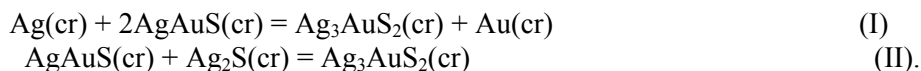


DETERMINATION OF STANDARD THERMODYNAMIC PROPERTIES OF TERNARY SULPHIDES IN THE Ag-Au-S SYSTEM BY SOLID – STATE GALVANIC CELL TECHNIQUE

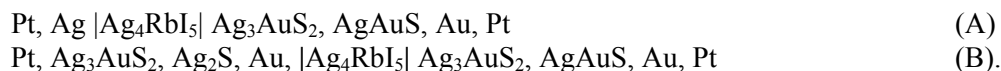
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The Ag-Au-S system contains three stable stoichiometric sulphides at temperatures lower than 386 K: acanthite (Ag_2S), uytenbogaardtite (Ag_3AuS_2) and petrovskaitite (AgAuS). The following reactions were studied to determine the thermodynamic properties of Ag_3AuS_2 and AgAuS according to the phase diagram at temperatures lower than the eutectoid between Ag_2S and Ag_3AuS_2 (386 K) accordingly to [1]:

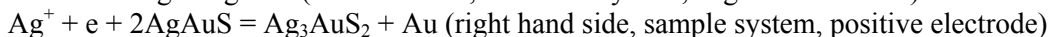
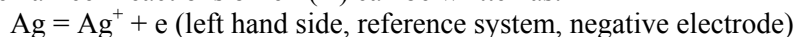


The lower temperature limit was chosen for each reaction to enable stable and reproducible EMF readings. All sulphides are stable with elementary gold and sulphur. While elementary silver reacts with all phases except Ag_2S in the Ag-Au-S system. We assume that the Ag_2S - AgAuS cross section is a practically binary system and the homogeneity range of uytenbogaardtite and petrovskaitite is very small.

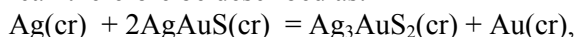
As the reactions do not contain pure sulphur, electrum of any composition, as well as pure gold may present in reactions (I) and (II), and may be used in cells (A) and (B). However, to decrease the number of auxiliary data these cells contained only pure crystalline gold. Reactions (I) and (II) were realised in the form of galvanic cells with a specific Ag^+ conduction superionic Ag_4RbI_5 [2] as a solid electrolyte:



As an example half cell reactions of cell (A) can be written as:



The overall cell reaction can therefore be described as:



which is identical to reaction (I). The electrochemical processes in cell (B) are the same.

Synthesis and characterisation of solid phases

Sample systems for cells (A) and (B) were prepared by direct synthesis of a mixture of sulphides (mole ratio 1:1) from alloys with the composition $\text{Ag}_{0.625}\text{Au}_{0.375}$. Gold powder was added into a thin pulverised sulphide mixture with the mole ratio of sulphide: sulphide: gold equal to 2:2:1. The resulting mixture of ~0.4 g in mass was formed by pressing under ~2 tons load in the form of a tablet 2 mm thickness and 6 mm in diameter, and then mirror polished.

Cell arrangement

A cell was arranged by placing the column of pellets into a silica glass tube. The cell consists of a silver disc, a tablet of a solid electrolyte and a tablet of a sample. The cell was placed between Pt disks connected with Cu leads and adjusted by spring to improve the electrical contact. The small distance between the electrodes (less than 1 cm) enabled minimisation of temperature gradients within the cell. The solid electrolyte was cut as a tablet 2 mm in height and 5-6 mm in average diameter from a block of crystalline yellow green transparent Ag_4RbI_5 , and then mirror polished.

The cell was placed into a silica glass tube with gas inlet and outlet sprouts. Measurements were performed in dried argon permanent gas flow 0.5-1 cm^3 per minute.

Cells operations

The measurements were performed as a “temperature titration”. This method consisted in changing the temperature by 5-20°C and waiting for equilibrium EMF values. The reversibility of equilibria was checked by performing forward and backward temperature changing. Reaching of equilibrium was estimated visually, when EMF remained unchanged (± 0.03 mV) for at least 12 hours.

Phase composition of the sample system was confirmed by XRD after the experiment. All fragments of the cell after running were in the same state as before.

Results and calculations

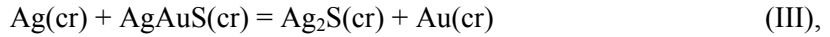
The EMF values measured for cells (A) and (B) as a function of temperature are presented by Equations (1) and (2). The linear equation $E = a + b \cdot T$ in an assumption that $\Delta_r C_p$ is implied constant, but not equal to zero, is fitted to these experimental data to yield

$$E(A)/\text{mV} = (79.267 \pm 0.77) + (0.229 \pm 2.273 \cdot 10^{-3}) \cdot T/K \quad (310 < T/K < 383) \quad (1)$$

$$E(B)/\text{mV} = (32.40 \pm 1.31) + (0.047 \pm 0.093) \cdot T/K \quad (333 < T/K < 377) \quad (2).$$

Precision of experimental data was calculated by the least squares method ($\pm 2\delta$). The Gibbs free energy and entropy change of the reaction can be calculated from EMF of a galvanic cell using the following base thermodynamic equations: $\Delta_r G$ ($\text{J} \cdot \text{mol}^{-1}$) = $-n \cdot 10^{-3} \cdot F \cdot E$ and $\Delta_r S$ ($\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$) = $n \cdot 10^{-3} \cdot F \cdot (dE/dT)$ where n is the number of electrons participating in the cell reaction, F stands for the Faraday constant $96484.56 \text{ C} \cdot \text{mol}^{-1}$ and E is the cell EMF in millivolts.

Subtraction of reaction (II) from reaction (I) gives a metastable reaction:



where $\Delta_r G(\text{III}) = -n \cdot F \cdot \Delta E$

$$\text{and } \Delta E = E(A) - E(B) = 46.9 + 0.18 \cdot T/K \quad (333 < T/K < 377) \quad (3).$$

The standard Gibbs energy and standard entropy at 298.15 K and 1 bar pressure of $\text{AgAuS}(\text{cr})$ and $\text{Ag}_3\text{AuS}_2(\text{cr})$ were calculated as follows:

$$\Delta_r G^\circ(\text{AgAuS}, \text{cr}) = \Delta_r G^\circ(\text{Ag}_2\text{S}, \text{cr}) - \Delta_r G^\circ \quad (\text{III})$$

$$S^\circ(\text{AgAuS}, \text{cr}) = S^\circ(\text{Ag}_2\text{S}, \text{cr}) + S^\circ(\text{Au}, \text{cr}) - S^\circ(\text{Ag}, \text{cr}) - \Delta_r S^\circ \quad (\text{III})$$

$$\Delta_r G^\circ(\text{Ag}_3\text{AuS}_2, \text{cr}) = \Delta_r G^\circ(\text{AgAuS}, \text{cr}) + \Delta_r G^\circ(\text{Ag}_2\text{S}, \text{cr}) + \Delta_r G^\circ \quad (\text{II})$$

$$S^\circ(\text{Ag}_3\text{AuS}_2, \text{cr}) = S^\circ(\text{AgAuS}, \text{cr}) + S^\circ(\text{Ag}_2\text{S}, \text{cr}) + \Delta_r S^\circ \quad (\text{II}).$$

Thermodynamic functions of Reactions (I)-(III) calculated with the aid of Eq. (1)-(3) are listed in Table 1.

Table 1.

Standard thermodynamic functions at 298.15 K and 1 bar pressure for Reactions (I)-(III) calculated from the experimental data.

Reaction/Equation	$\Delta_r G^\circ$ ($\text{J} \cdot \text{mol}^{-1}$)	$\Delta_r S^\circ$ ($\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)	$\Delta_r H^\circ$ ($\text{J} \cdot \text{mol}^{-1}$)
(I)/(1)	-14240 ± 280	22.100 ± 0.750	-7650 ± 280
(II)/(2)	-4480	4.530	-3130
(III)/(3)	-9700	17.370	-4530

Standard thermodynamic properties of sulphides in the Ag-Au-S system derived in the present study for 298.15 K, 1 bar are compared with the literature values in Table 2. This table also contains auxiliary thermodynamic data for $\text{Ag}(\text{cr})$, $\text{Au}(\text{cr})$, $\text{S}(\text{rhomb})$ and Ag_2S acanthite which were used in calculations.

Table 2.

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

Phase	$\Delta_r G^\circ$ ($\text{J} \cdot \text{mol}^{-1}$)	$\Delta_r H^\circ$ ($\text{J} \cdot \text{mol}^{-1}$)	S° ($\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)	Source*
$\text{Ag}(\text{cr})$	0	0	42.55 ± 0.21	1
$\text{Au}(\text{cr})$	0	0	47.49 ± 0.21	1
$\text{S}(\text{rhomb})$	0	0	32.05 ± 0.05	1
Ag_2S , acanthite	-39700 ± 1000	-32000 ± 1000	142.9 ± 0.3	1
Ag_3AuS_2 , cr, low (uytenbogaardtite)	-63440 ± 6280	-40470	316.28	2
	-74180 ± 200	-62600 ± 200	277.91 ± 0.2	3
AgAuS , cr, low (petrovskaitite)	-22250 ± 4190	-1280	192.43	2
	-30000 ± 210	-27480 ± 210	130.47 ± 0.2	3

(*) 1 - [3]; 2 - [4]; 3 - present study.

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