**Au-Ag-Te-Se deposits**
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**Thermodynamic properties of phases in Ag-Au-X system, where X = S, Se, Te**

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**Abstract.** The temperature dependences of standard Gibbs free energy of the following phases were determined by the electromotive force (EMF) measurements in all solid-state galvanic cells with Ag,RbI₅ solid electrolyte and common inert gas space at the atmosphere pressure:

\[
\Delta G^\circ_m (\text{Ag}_3\text{AuS}_2, \text{uytenbogaardtite}) = -57287 -40.89 \times T (320<T/K<386)
\]

\[
\Delta G^\circ_m (\text{AgAuS}, \text{petrovskaite}) = -24819 -9.40 \times T (310<T/K<383)
\]

\[
\Delta G^\circ_m (\text{Au}_2\text{S}) = 1369 – 0.98 \times T (307<T/K<341)
\]

\[
\Delta G^\circ_m (\text{Ag}_2\text{Se}, \text{naumannite low}) = -42730 -22.6 \times T (317<T/K<405)
\]

\[
\Delta G^\circ_m (\text{Ag}_2\text{Se}, \text{naumannite high}) = -35018 -41.6 \times T (405<T/K<457)
\]

\[
\Delta G^\circ_m (\text{Ag}_5\text{Te}_3, \text{stützite}) = -81700 – 66.8 \times T (298<T/K<385)
\]

**Key words:** thermodynamic properties, galvanic cells, gold, silver, chalcogenides, uytenbogaardtite, petrovskaite, Au₂S, naumannite, fischesserite, AuSe, stützite

**Introduction**

Investigation of the Ag-Au-S(Se,Te) system is very significant for the modelling of geochemistry, transport and thermodynamic parameters of gold-sulphide, selenide and telluride mineralization. The deposition of gold connected with selenides and with tellurides, in particular, also has practical significance.

At the present time, the mineralogy and paragenetic associations of these systems are investigated sufficiently well (Barton, 1980). There exist compositional diagrams and data for the pseudobinary systems Ag₂S-Au₂S (Graf, 1968; Folmer et al., 1976) and Ag₂Se-Ag₃AuSe₅ (Wiegers, 1976), and also the physical properties of phases (minerals), which have been investigated for their potential as semiconductors and superionics. The thermodynamic properties of the binary silver and gold chalcogenides are available in the literature (Barin, 1995). There were, however, no published data for the thermodynamic properties of three-component systems until recently (Osadchii and Rappo, 2004), hampering further geochemical modelling.

In the present study, the thermodynamic properties of phases were determined by the electromotive force (EMF) method in solid state galvanic cells. This method has proved to
be direct, effective, and most accurate for determination of molar free energy and molar entropy change in reactions (Kiukkola and Wagner, 1957).

**Synthesis and characterization of the solid phases**

The synthesis of the compositions was performed in sealed silica glass ampoules in horizontal tube furnaces. Starting materials were pure elements, mixtures or compounds, which had been obtained directly from pure elements. To avoid potential heterogeneities, each phase was ground at least once in an agate mill.

The resulting products were examined by XRD analysis, by optical microscope under reflected light and by electron microprobe analysis. The power patterns corresponded to JCPDS 19-1146 for petrovskaite, JCPDS 20-461 for uytenbogaardtite, JCPDS 18-1997 for Au₂S, JCPDS 72-0392 for fischesserite, JCPDS 71-2410 for naumannite, JCPDS 81-2246 for AuSe, and JCPDS 47-1350 for stützite.

Cell arrangements and experimental techniques were described by Osadchii and Rappo (2004).

**Phase relations, reactions and galvanic cells**

All ternary phases in the considered systems are stable in the presence of metallic gold or chalcogenides, whereas metallic silver and Ag-rich electrum will react with all phases except Ag₃X.

**The system Ag-Au-S**

The Ag-Au-S phase diagram at temperature below 386 K is shown in Fig. 1. The following reactions were studied to determine the thermodynamic properties of Ag₃AuS₂, AgAuS and Au₂S:

\[
\begin{align*}
\text{Ag(cr)} + \text{Ag₃AuS₂(cr)} &= 2\text{Ag₂S(cr)} + \text{Au(cr)} \quad (1) \\
\text{Ag(cr)} + 2\text{AgAuS(cr)} &= \text{Ag₃AuS₂(cr)} + \text{Au(cr)} \quad (2)
\end{align*}
\]

**Fig. 1. Phase relations in the Ag-Au-S system below 386 K. Figures in squares indicate the numbers of phase reactions studied**

\[
\begin{align*}
\text{Ag(cr)} + \text{Au₂S(cr)} &= \text{AgAuS(cr)} + \text{Au(cr)} \quad (3)
\end{align*}
\]

The reactions were realized in the form of solid state galvanic cells with an Ag₄RbI₅ superionic compound, which has a specific Ag⁺ conductivity (Despotuli et al., 1989) as solid electrolyte:

\[
\begin{align*}
\text{(-) Pt|Ag|Ag₄RbI₅|Ag₃AuS₂, AgAuS, Au|Pt (+)} & \quad (I) \\
\text{(-) Pt|Ag|Ag₄RbI₅|Au₂S, AgAuS, Au|Pt (+)} & \quad (II) \\
\text{(-) Pt|Ag|Ag₄RbI₅|Au₂S, AgAuS, Au|Pt (+)} & \quad (III)
\end{align*}
\]

**Results and calculations**

The Gibbs free energy and entropy change of the reaction can be calculated from the EMF values \((E/mV)\) of a galvanic cell using the base thermodynamic equations:

\[
\Delta G = nFE \times 10^{-3} \quad (4)
\]

where \(n\) is the number of electrons participating in the cell reaction and \(F\) is the Faraday constant 96484.56 C mol⁻¹.

The results of measurements are presented as a linear equation \(E = a + bT\), which implies \(\Delta C_p\) is constant and equal to zero. The experimental data yielded the following equations:

\[
\begin{align*}
E(I)/mV &= (50.0 \pm 0.70) + (0.180 \pm 2.017 \times 10^{-3}) \cdot T/K \\
&\quad (320.8<T<386, R^2 = 0.99971) \quad (5)
\end{align*}
\]

\[
\begin{align*}
E(II)/mV &= (79.27 \pm 0.77) + (0.229 \pm 2.273 \times 10^{-3}) \cdot T/K \\
&\quad (310<T/K<383, R^2 = 0.99955) \quad (6)
\end{align*}
\]
\[ E(III)/mV = (271.4 \pm 6.6) + (0.09 \pm 0.02) \frac{T}{K} \]

\[ (307.6 < T/K < 341.4, R^2 = 0.935) \quad (7) \]

The calculated temperature dependences of standard molar Gibbs energy changes for the phases \( \text{Ag}_3\text{AuS}_2 \), \( \text{AgAuS} \) and \( \text{Au}_2\text{S} \) are listed in conventional form in Table 1. The standard state of sulphur is orthorhombic sulphur.

Table 1. Coefficients \( a \) and \( b \) in equation \( \Delta G_m = a + b \cdot \frac{T}{K} \) for the phases of system \( \text{Ag-Au-S} \)

<table>
<thead>
<tr>
<th>Phase</th>
<th>( a ) (J mol(^{-1}))</th>
<th>( b ) (J K(^{-1}) mol(^{-1}))</th>
<th>( T ), K</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ag}_3\text{AuS}_2 )</td>
<td>-57287</td>
<td>-40.89</td>
<td>320-386</td>
</tr>
<tr>
<td>( \text{AgAuS} )</td>
<td>-24819</td>
<td>-9.3975</td>
<td>310-383</td>
</tr>
<tr>
<td>( \text{Au}_2\text{S}, \text{(cr)} )</td>
<td>1369</td>
<td>-0.98</td>
<td>307-341</td>
</tr>
</tbody>
</table>

The system \( \text{Ag-Au-Se} \)

The \( \text{Ag-Au-Se} \) phase diagram for temperature in the range 298-403 K is presented in Fig. 2. The compound \( \text{AgAuSe} \), the selenium analogue of petrovskaite \( (\text{AgAuS}) \), does not exist in this system.

The studied reactions, which were used for the determination of the thermodynamic properties of \( \text{Ag}_2\text{Se} \), \( \text{Ag}_3\text{AuSe}_2 \) and \( \text{AuSe} \) are:

\[
\begin{align*}
2\text{Ag(cr)} + \text{Se(s)} &= \text{Ag}_2\text{Se(cr)} \quad (8) \\
\text{Ag(cr)} + \text{Ag}_3\text{AuSe}_2\text{(cr)} &= 2\text{Ag}_2\text{Se(cr)} + \text{Au(cr)} \quad (9) \\
3\text{Ag(cr)} + 2\text{AuSe(s)} &= \text{Ag}_3\text{AuSe}_2\text{(cr)} + \text{Au(cr)} \quad (10)
\end{align*}
\]

The reactions were realized in the cells:

(\(-\) Pt \| \( \text{Ag} | \text{Ag}_{4}\text{RbI}_{5} | \text{Se}, \text{Ag}_2\text{Se} \| \text{Pt}(+) \) (IV)

(\(-\) Pt \| \( \text{Ag} | \text{Ag}_{4}\text{RbI}_{5} | \text{Ag}_2\text{Se}, \text{Ag}_3\text{AuSe}_2, \text{AuSe} \| \text{Pt}(+) \) (V)

(\(-\) Pt \| \( \text{Ag} | \text{Ag}_{4}\text{RbI}_{5} | \text{Ag}_2\text{Se}, \text{AuSe}, \text{Au} \| \text{Pt}(+) \) (VI)

The experimental data are presented as following equations:

\[
\begin{align*}
E(IV) &= (221.44 \pm 0.34) + (0.117 \pm 9.5 \times 10^{-4}) \frac{T}{K}, \\
&\quad (317 < T/K < 407), R = 0.999 \quad (11) \\
E(IV) &= (181.47 \pm 0.73) + (0.216 \pm 0.002) \frac{T}{K}, \\
&\quad (405 < T/K < 457), R = 0.999 \quad (12)
\end{align*}
\]

The system \( \text{Ag-Au-Te} \)

The \( \text{Ag-Au-Te} \) phase diagram up to 510 K is shown in Fig. 3.

Only one reaction was studied in the system \( \text{Ag-Au-Te} \):

\[ 5\text{Ag(cr)} + 3\text{Te(cr)} = \text{Ag}_5\text{Te}_3 \quad (15) \]

It was realized in the following cell:

(\(-\) Pt \| \( \text{Ag} | \text{Ag}_{4}\text{RbI}_{5} | \text{Ag}_5\text{Te}_3, \text{Te} \| \text{Pt}(+) \) (VII)
The experimental data are presented as three intervals of E(T) dependence and are described by the following equations:

\[
E(\text{VII}) = (169.4 \pm 0.8) + (0.139 \pm 0.009) \cdot \frac{T}{K}, \quad (298 < \frac{T}{K} < 385), \quad R = 0.992 \quad (16)
\]

\[
E(\text{VII}) = (155.5 \pm 3.6) + (0.175 \pm 0.017) \cdot \frac{T}{K}, \quad (385 < \frac{T}{K} < 410), \quad R = 0.987 \quad (17)
\]

\[
E(\text{VII}) = (145.7 \pm 1.04) + (0.198 \pm 0.005) \cdot \frac{T}{K}, \quad (410 < \frac{T}{K} < 500), \quad R = 0.998 \quad (18)
\]

The obtained E(T) dependences are shown in the Fig.4.

Table 3. Coefficients \(a\) and \(b\) in equation \(\Delta G^\circ_m = a + bT\) for the phase of system Ag-Au-Te

<table>
<thead>
<tr>
<th>Phase</th>
<th>(a) (J mol(^{-1}))</th>
<th>(b) (J K(^{-1}) mol(^{-1}))</th>
<th>(T), K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag(_5)Te(_3)</td>
<td>-81700</td>
<td>-66.8</td>
<td>298 - 385</td>
</tr>
<tr>
<td>Ag(_5)Te(_3)</td>
<td>-75000</td>
<td>-84.5</td>
<td>385 - 410</td>
</tr>
<tr>
<td>Ag(_5)Te(_3)</td>
<td>-70300</td>
<td>-95.4</td>
<td>410 - 500</td>
</tr>
</tbody>
</table>

Acknowledgements. The investigations of the Ag-Au-Se and Ag-Au-Te systems are continued with financial support of RFBR project 03-05-64380.

References


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