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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_4RbI_5 solid electrolyte and common inert gas space at the atmosphere pressure:
$\Delta_f G^o{}_m(Ag_3AuS_2$, uytenbogaardtite) = -57287 -40.89·T (320<T/K<386)
$\Delta_f G^o{}_m$(AgAuS, petrovskaite) = -24819 -9.40·T (310<T/K<383)
$\Delta_f G^o{}_m(Au_2S)$ = 1369 –0.98·T (307<T/K<341)
$\Delta_f G^o{}_m(Ag_2Se$, naumannite low) = -42730 -22.6·T (317<T/K<405)
$\Delta_f G^o{}_m(Ag_2Se$, naumannite high) = -35018 -41.6·T (405<T/K<457)
$\Delta_f G^o{}_m(Ag_3AuSe_2$, fishesserite) = -77210-31.0·T (310<T/K<402)
$\Delta_f G^o{}_m$(AuSe, cr) = -12219 -27.6·T (320<T/K<405)
$\Delta_f G^o{}_m(Ag_5Te_3$, stützite) = -81700 – 66.8·T (298<T/K<385)

Key words: thermodynamic properties, galvanic cells, gold, silver, chalcogenides, uytenbogaardtite, petrovskaite, Au_2S, 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 Ag_2S-Au_2S (Graf, 1968; Folmer et al., 1976) and Ag_2Se-Ag_3AuSe_2 (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 Au_2S, 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 Ag_2X.

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 Ag_3AuS_2, AgAuS and Au_2S:

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

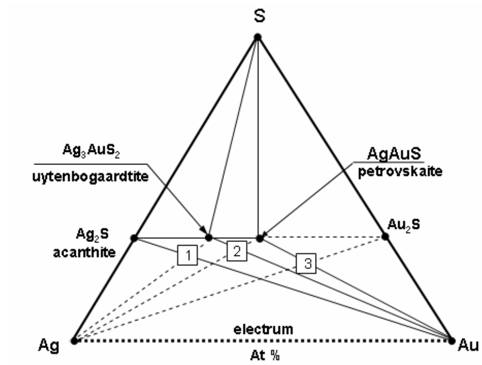

Fig. 1. Phase relations in the Ag-Au-S system below 386 K. Figures in squares indicate the numbers of phase reactions studied

$$Ag(cr) + Au_2S(cr) = AgAuS(cr) + Au(cr) \quad (3)$$

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

(-) Pt|Ag |Ag_4RbI_5|Ag_3AuS_2, Ag_2S, Au |Pt (+) (I)
(-) Pt|Ag|Ag_4RbI_5|Ag_3AuS_2, AgAuS, Au|Pt (+) (II)
(-) Pt|Ag|Ag_4RbI_5|Au_2S, AgAuS, Au|Pt (+) (III)

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:

$$\Delta_r G = -nFE \cdot 10^{-3} \quad (4)$$

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 $E = a + b \cdot T$, which implies $\Delta_r C_p$ is constant and equal to zero. The experi-mental data yielded the following equations:

$$E(I)/mV = (50.0 \pm 0.70) + (0.180 \pm 2.017 \cdot 10^{-3}) \cdot T/K \quad (320.8<T<386, R^2 = 0.99971) \quad (5)$$

$$E(II)/mV = (79.27 \pm 0.77) + (0.229 \pm 2.273 \cdot 10^{-3}) \cdot T/K \quad (310<T/K<383, R^2 = 0.99955) \quad (6)$$

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

The calculated temperature dependences of standard molar Gibbs energy changes for the phases Ag_3AuS_2, AgAuS and Au_2S are listed in conventional form in Table 1. The standard state of sulphur is orthorhombic sulphur.

Table 1. Coefficients a and b in equation $\Delta_f G^o_m = a + b\cdot T$ for the phases of system Ag-Au-S

Phase	a ($J\cdot mol^{-1}$)	b ($J\cdot K^{-1}\cdot mol^{-1}$)	T, K
Ag_3AuS_2	-57287	-40.89	320-386
AgAuS	-24819	-9.3975	310-383
Au_2S, (cr)	1369	-0.98	307-341

The system Ag-Au-Se

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

The studied reactions, which were used for the determination of the thermodynamic properties of Ag_2Se, Ag_3AuSe_2 and AuSe are:

$$2Ag(cr) + Se(s) = Ag_2Se(cr) \quad (8)$$

$$Ag(cr) + Ag_3AuSe_2(cr) = 2Ag_2Se(cr) + Au(cr) \quad (9)$$

$$3Ag(cr) + 2AuSe(s) = Ag_3AuSe_2(cr) + Au(cr) \quad (10)$$

The reactions were realized in the cells:

(-) Pt | Ag |Ag_4RbI_5 |Se, Ag_2Se | Pt (+) (IV)

(-) Pt|Ag|Ag_4RbI_5|Ag_3AuSe_2,Ag_2Se,Au|Pt (+) (V)

(-) Pt|Ag|Ag_4RbI_5|Ag_3AuSe_2,AuSe,Au|Pt (+) (VI)

The experimental data are presented as following equations:

$E(\mathrm{IV}) = (221.44 \pm 0.34) + (0.117 \pm 9.5\cdot 10^{-4})\cdot T/\mathrm{K}$,
$(317<T/\mathrm{K}<407)$, R = 0.999 (11)

$E(\mathrm{IV}) = (181.47 \pm 0.73) + (0.216 \pm 0.002)\cdot T/\mathrm{K}$,
$(405<T/\mathrm{K}<457)$, R = 0.999 (12)

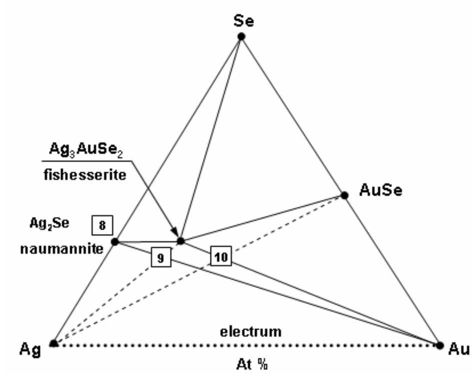

Fig. 2. Phase relations in the Ag-Au-Se system at 298-403 K. The figures in the squares indicate the numbers of phase reactions studied

$E(\mathrm{V}) = (85.51 \pm 0.97) + (0.147 \pm 0.003)\cdot T/\mathrm{K}$,
$(310<T/\mathrm{K}<402)$, R = 0.994 (13)

$E(\mathrm{VI}) = (214.27 \pm 2.04) + (0.191 \pm 5\cdot 10^{-3})\cdot T/\mathrm{K}$,
$(320<T/\mathrm{K}<406)$, R = 0.988 (14)

Table 2. Coefficients a and b in equation $\Delta_f G^o_m = a + b\cdot T$ for the phases of system Ag-Au-Se

Phase	a ($J\cdot mol^{-1}$)	b ($J\cdot K^{-1}\cdot mol^{-1}$)	T, K
Ag_2Se low	-42730	-22.61	317-405
Ag_2Se high	-35020	-41.64	405-457
Ag_3AuSe_2	-77220	-31.03	310-402
AuSe, cr	-7600	12.108	320-405

The system Ag-Au-Te

The Ag-Au-Te phase diagram up to 510 K is shown in Fig. 3.

Only one reaction was studied in the system Ag-Au-Te:

$$5Ag(cr) + 3Te(cr) = Ag_5Te_3 \quad (15)$$

It was realized in the following cell:

(-) Pt | Ag | Ag_4RbI_5 | Ag_5Te_3, Te | Pt (+) (VII)

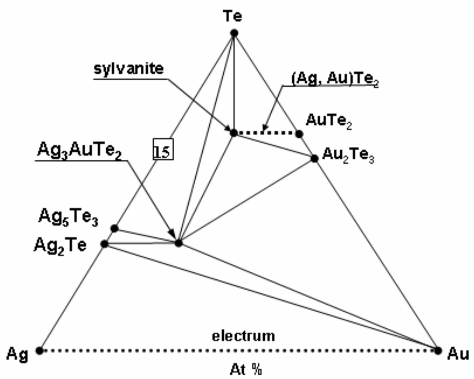

Fig. 3. Phase relations in the Ag-Au-Te system before 510 K. The figures in the squares indicate the numbers of phase reactions studied

The experimental data are presented as three intervals of E(T) dependence and are described by the following equations:

E(VII) = (169.4 ±0.8) + (0.139 ±0.009)·T/K, (298<T/K<385), R = 0.992 (16)

E(VII) = (155.5 ±3.6) + (0.175 ±0.017)·T/K, (385<T/K<410), R = 0.987 (17)

E(VII) = (145.7 ±1.04) + (0.198 ±0.005)·T/K, (410<T/K<500), R = 0.998 (18)

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

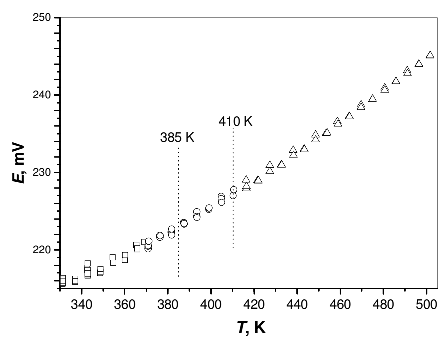

Fig. 4. EMF (E) of galvanic Cell VII as a function of temperature

The existence of three curve sections is connected with concentration changes of Ag in Te (Sitte and Brunner, 1988) and standard thermodynamic properties for Ag_5Te_3 have to be calculated with the low-temperature trend accordingly to reaction (15).

Table 3. Coefficients a and b in equation $\Delta_f G^o{}_m = a + b \cdot T$ for the phase of system Ag-Au-Te

Phase	a (J·mol^{-1})	b (J·K^{-1}·mol^{-1})	T, K
Ag_5Te_3	-81700	-66.8	298 - 385
Ag_5Te_3	-75000	-84.5	385 - 410
Ag_5Te_3	-70300	-95.4	410 - 500

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References

Barin, I., *Thermodynamical Data of Pure Substances*. 1995. VCH Verlagsgesellschaft, Weinheim, p. 15, 16, 101, 103.

Barton, M.D. 1980. The Ag-Au-S system. *Economic Geology*, **75**, 303-316.

Depotuli, A.L., Zagorodnev, V.N., Lichkova, N.V., Minenkova, N.A. 1989. New high conductivity solid state electrolytes: $CsAg_4Br_{3-x}I_{2+x}$ (0.25<x<1). *Solid State Physics*, **37**, 9, 242-244.

Folmer, J.C.W., Hofman, P., Wiegers, G.A. 1976. Order-disorder transitions in the system $Ag_{2-x}Au_xS$ ($0 \le x \le 1$). *Journal of the Less-Common Metals*, **48**, 251-268.

Graf, R.B. 1968. The system Ag_3AuS_2-Ag_2S. *American Mineralogist*, **53**, 496-500.

Kiukkola, K., Wagner, C. 1957. Measurements on galvanic cells involving solid electrolytes. *Journal of the Electrochemical Society*, **104**, 379-386.

Osadchii, E.G., Rappo, O.A. 2004. Determination of standard thermodynamic properties of sulfides in the Ag-Au-S system by means of a solid-state galvanic cell. *American Mineralogist*, **89**, 1405-1410.

Sitte, W., Brunner, A. 1988. Investigation of the binary system Ag-Te in the temperature range between 25 and 200^{o}C using solid silver electrolytes. *Solid State Ionics,* **28-30**, 1324-1328.

Wiegers, G.A. 1976. Electronic and ionic conduction of solid solutions $Ag_{2-x}Au_xSe$ ($0 \le x \le 0.5$). *Journal of the Less-Common Metals,* **48**, 269-283.