DETERMINATION OF STANDARD THERMODYNAMIC PROPERTIES OF FISCHESSERITE (Ag_3AuSe_2) BY HIGHTEMPERATURE GALVANIC CELL METHOD

Rappo O.A., Echmaeva E.A., Lunin S.E., Osadchii E.G. (IEM RAS)
euo@iem.ac.ru

The silver-gold-selenium system contains three stable stoichiometric selenides (Fig.1.): naumannite (Ag_2Se), fischesserite (Ag_3AuSe_2) and gold selenide (AuSe).

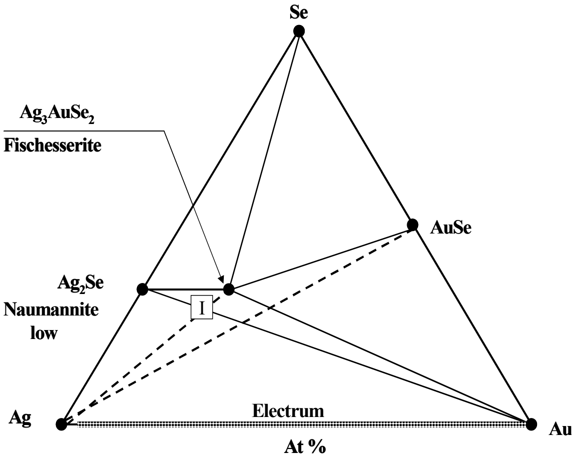

Fig 1. Phase diagram Ag-Au-Se

Thermodynamic properties of the reaction

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

were determined in the galvanic cell

$$(-)Pt|Ag\ |Ag_4RbI_5|\ Ag_3AuSe_2, Ag_2Se, Au\ |Pt(+) \quad (A)$$

with Ag_4RbI_5 superionic compound as a solid electrolyte, which has a specific Ag^+ conduction in temperature range 316-404 K.

The cell consists of a silver disc (reference system), a tablet of a solid electrolyte and a tablet of a sample system (Fig.2). The solid electrolyte tablet (2 mm in thickness and 5-6 mm in diameter) was cut out of a block of crystalline transparent yellow green Ag_4RbI_5, and then mirror polished. The cell in the form of tablet stack was placed into a silica glass tube (6.5 mm ID) between Pt disks, which were connected with copper leads, and adjusted by spring to improve the electrical contact. The small distance between the electrodes (less than 1 cm) enabled 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 sprouts. Measurements were performed under permanent dried argon gas flow of 0.5-1 cm^3 per minute.

The cells were placed into the isothermal (at least, 20 mm in height) zone of a vertical resistance (direct current) furnace (18 mm ID and 250 mm high). The temperature was maintained constant within ± 0.1 K by the electronic temperature controller "PROTHERM-100" and measured in the middle of the cell with the 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 the accuracy of (0.01 ± 0.005) mV with a multi-channel millivoltmeter and recorded using a computer data acquisition system. High-input impedance (~ 10^{13} Ω) channels were used for the EMF measurements.

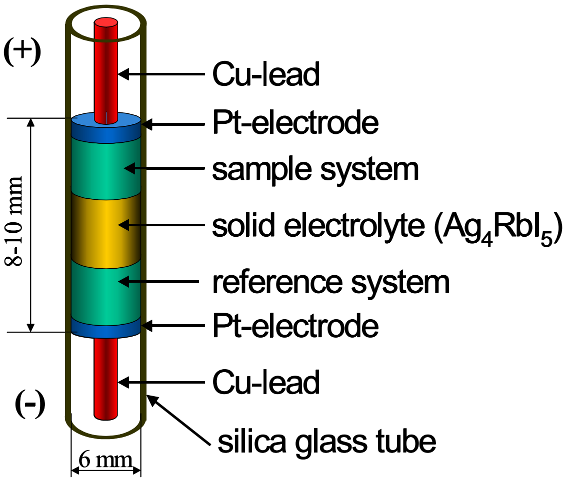

Fig 2. Principal sketch of Cell (A).

The measurements were performed as a "temperature titration". Temperature was changed in 5-10 degrees 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. The equilibrium was assumed, when the EMF remained unchanged within ± 0.03 mV.

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

$$E(\mathrm{A})=(85.86\pm1.72)+(0.1463\pm0.001)\cdot T/\mathrm{K},\ (316<\mathrm{T/K}<404),\ \mathrm{R}^2=0.988 \qquad (1)$$

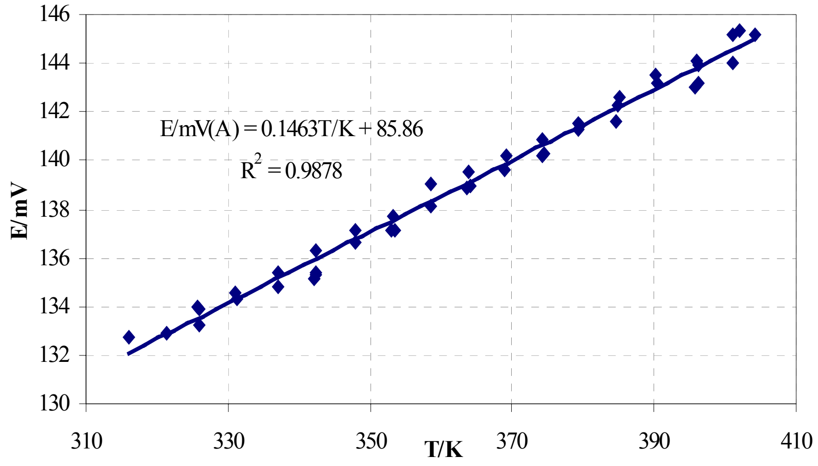

Fig. 3. Temperature dependence of EMF of Cell (A)

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

$$\Delta G=-\mathrm{n}\mathrm{F}E,\ \mathrm{b}\cdot\mathrm{F}=\Delta S \text{ и } \Delta G=\Delta H\text{-}T\Delta S, \qquad (2,3,4),$$

where n=1 is the number of electrons participating in the cell reaction $\mathrm{Cu}=\mathrm{Cu}^{+}+\mathrm{e}$;
F=96484,56 $\mathrm{C\cdot mol^{-1}}$ stands for the Faraday constant;
E is the cell EMF in volts.

Standard thermodynamic properties of reaction (I) were calculated using auxiliary data [1].

Table 1. Standard thermodynamic properties of fischesserite $\mathrm{Ag_3AuSe_2}$(cr, 298.15 K).

$\Delta_r G^o$ ($\mathrm{J\cdot mol^{-1}}$)	$\Delta_r S^o$ ($\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$)	$\Delta_r H^o$ ($\mathrm{J\cdot mol^{-1}}$)
-(12493±300)	14.116±0.008	-(8284±300)

Existence of the only ternary compound $\mathrm{Ag_3AuSe_2}$ in the Ag-Au-Se system was confirmed by solid-phase-annealing method in temperature range 373-673 К. Data about existence of AgAuSe phase are mistaken.

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Reference

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