DETERMINATION OF STANDARD THERMODYNAMIC PROPERTIES OF AG_3AUS_2 AND AU_2S BY USE SOLID STATE GALVANIC CELL TECHNIQUE

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Binary silver and gold sulphides appear as mineral uytenbogaardtite (Ag_3AuS_2) and petrovskaite (AgAuS). Thermodynamic properties of these phases and Au_2S are not enough investigated. To estimate thermodynamic properties of sulphides in the system Ag-Au-S [1] used experimental data on their equilibrium with electrum between (100-850) ^oC. The goal of the present work is to determine the Gibbs energy of formation of Ag_3AuS_2 and Au_2S using solid-state galvanic cell technique (emf- method).

The Gibbs free energies of equilibrium reactions

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

$$2Au(cr) + S(cr) = Au_2S(cr) \quad (2)$$

were determined by emf measuring in respective galvanic cells

$$Pt, Ag \mid Ag_4RbI_5 \mid Ag_3AuS_2, Ag_2S, Au, Pt \quad (I)$$

$$Pt, AgAuS, Au, S \mid Ag_4RbI_5 \mid AgAuS, Au_2S, Au, Pt \quad (II)$$

with Ag_4RbI_5 solid electrolyte within temperature range (310-382) K.

Synthesis experiments were done using standard silica glass tube technique. The reagents used were qualification “extra purity” (99.999%) Ag, Au, and S. Syntheses have been carried out in three consecutive stages of (10-12) days exposition at 450, 550, and 620^oC with homogenisation substances in a mortar under acetone after each temperature exposition. Gold sulphide Au_2S was synthesised according to [2]. The prepared compounds were then verified by powder X-ray diffraction and under optical microscope. The obtained Au_2S contains a small amount (less then 1 vol. %) of very fine (3-7μ) and well-formed crystals of metallic gold. It should be noted that the presence of gold in the gold sulphide as well as in sulphide electrodes does not prevent from making emf measurements.

Sulphide electrodes were prepared in the shape of pressed pellet (120 kg/cm^2) of 6 mm in diameter and 2 mm in thickness. Gold wire in the form of the Archimedes spiral was pressed into the top and bottom of the pallet surfaces. Metallic electrodes were cut in disk form of 0.5 mm in thickness. Solid electrolyte was pressed from powder or cut from polycrystalline block.

Electrodes and solid electrolyte mirror polished were packed into silica glass tube and pressed down with a spring. The cell arrangement was placed into silica glass flow-through container and emf measurements were conducted in argon flow. The cell set up was heated in vertical resistance furnace where temperature was supported with the accuracy ±0.3 K by the temperature controller “Proterm-100”. Emf values have been measured by the computer connected high impedance input voltmeter (10^{12} Ohm) with closeness ±0.01 mV. Equilibrium emf values were determined by “temperature titration” method in the regime of waiting constant emf value at the given temperature. The measurements were made in two ways at increasing and decreasing temperature. Thus, each neighbour T/E-point (fig. 1) was obtained at contrary temperature trend. As usual equilibrium was reached during (2-7) days.

Temperature dependence emf (E/mV) was approximate by the linear equation in the assumption $\Delta C_p = 0$:

$$E(I) = 0.1707T + 58.47 \qquad (R^2 = 0.988;\ 339<T/K<382)$$

$$E(II) = 1.474T - 588.2 \qquad (R^2 = 1;\ 310<T/K<320)$$

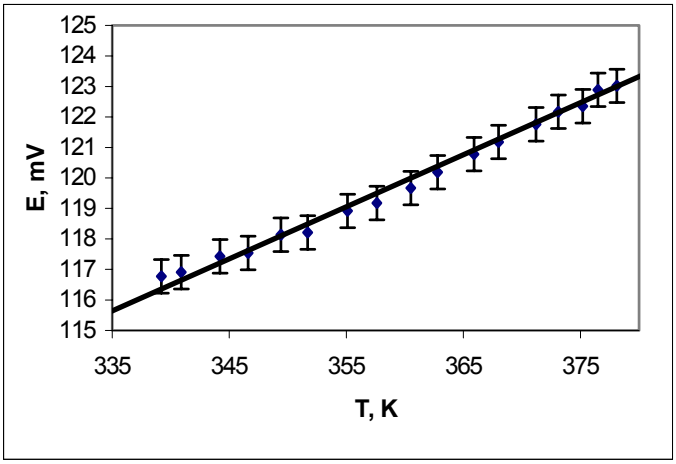

Fig. 1. Temperature dependence emf of cell (I).

At equilibrium cell reaction $\Delta G = -nFE$, where n- number of electrons taking place in the reaction (n=1 for both reactions), F=96484.56 C – the Faraday constant. According to the base thermodynamic equations entropy and enthalpy change of the reaction are defined as $\Delta S = -(d\Delta G/dT)_p = nF(dE/dT)_p$ and $\Delta H = \Delta G + T\Delta S = -nF[E - T(dE/dT)_p]$ respectively, where $(dE/dT)_p$ – temperature coefficient in $V.K^{-1}$ at standard pressure 1 atm (0.101325 MPa).

The calculated standard thermodynamic functions of reaction (I) and crystalline sulphides are represented in table 1. Auxiliary data for calculation of thermodynamic properties of Ag_3AuS_2(cr) are taken from Barin [3].

Table 1.

Thermodynamic properties of reaction (1), Ag_3AuS_2(cr), and Au_2S(cr). (Standard state of sulphur – $S_{rhombic}$)

Reaction, Phase	Source	$\Delta G^o_{298.15}$ J mol^{-1}	$(\Delta)S^o_{298.15}$ J mol^{-1} K^{-1}	$\Delta H^o_{298.15}$ J mol^{-1}
Reaction (I)	Our data	-10550 ±350	16.5 ±5.0	-5640
Ag_3AuS_2(cr) (lower)	Our data	-70500 ±350	276.4 ±5.0	-59540
	Barton, 1980	-63450 ±6300	-	-
Au_2S(cr)	Our data	14350 ±3000	-	-
	Barton, 1980	10800 ±3100	-	-

A metastable state (E<0, ΔG>0) of gold sulphide Au_2S was determined. However, we have not enough experimental data (only two points) for precise determination of thermodynamic properties and the data presented should be considered as the previous ones.

References

1. *Barton, M.* (1980). The Ag-Au-S system. Economic Geology. V.75. P.303-316.
2. *Renders, P., Seward, T.* (1989). The stability of hydrosulphido – and sulphide complexes of Au(I) at 25°C // Geochim. Cosmochim. Acta. V. 53. P.244-253.
3. *Barin, I.* (1995) Thermodynamic data of pure substances.