EXPERIMENTAL DETERMINATION OF STANDARD THERMODYNAMIC PROPERTIES OB AUROSTIBITE ($AuSb_2$)

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Thermodynamic properties of aurostibite ($AuSb_2$) were determined using electromotive force (EMF) method in galvanic cell with Ag_4RbI_5/Ag^+ as a solid electrolyte:

$$Pt, Ag_3Sb, Sb \mid Ag_4RbI_5 \mid Ag_3Sb, AuSb_2, Au, Pt \qquad (A).$$

Half cell reactions of cell (A) can be written as:

$$6Ag + 6e + 2Sb = 2Ag_3Sb \quad \text{(left hand side electrode, Ag-Sb eutectic)}$$

$$2Ag_3Sb + Au = 6Ag + 6e + AuSb_2 \quad \text{(right hand side electrode, Au-Sb eutectic + } Ag_3Sb\text{)}.$$

The overall cell reaction can therefore be described as:

$$2Sb(cr) + Au(cr) = AuSb_2(cr) \qquad (I).$$

It should be noted that the presence of discrasite (Ag_3Sb) in cell (A) is eliminated. The EMF values measured for cell (A) as a function of temperature are presented as linear equation $E = a + b \cdot T$, which implies $\Delta_r C_p$ = constant, but not equal to zero, fitted to obtained experimental data yielded:

E(A)/mV = (12.13 ±0.2) + (-0.018 ±0.003)·T, ($230 < T$ /K< 430, $R^2 = 0.95$).

The Gibbs free energy and entropy change of the reaction (I) can be calculated from EMF of galvanic cell (A) using the following equations:

$$\Delta_r G \text{ (J·mol}^{-1}\text{)} = -n \cdot 10^{-3} \cdot F \cdot E$$

$$\Delta_r S \text{ (J·K}^{-1}\text{·mol}^{-1}\text{)} = n \cdot 10^{-3} \cdot F \cdot (dE/dT$$

$$\Delta_r H \text{ (J·mol}^{-1}\text{)} = -n \cdot 10^{-3} \cdot F \cdot [E - (dE/dT) \cdot T],$$

where n is the number of electrons participating in the cell reaction, F stands for the Faraday constant 96484.56 C·mol^{-1}, and E is the cell EMF in milivolts. The standard Gibbs energy and standard entropy at 298.15 K and 1 bar pressure of $AuSb_2$(cr) were calculated as follows:

$$\Delta_f G^o(AuSb_2, cr) = - \Delta_r G^o(I)$$

$$S^o(AuSb_2, cr) = 2S^o(Sb, cr) + S^o(Au, cr) + \Delta_r S^o(I).$$

$$\Delta_f G^o(AuSb_2, cr, 298.15 \text{ K}) = (-4000 \pm 300) \text{ J mol}^{-1}$$

$$\Delta_r S(I) = (-10.48 \pm 0.5) \text{ J·K}^{-1}\text{·mol}^{-1}$$

$$\Delta_r H^o(AuSb_2, cr, 298.15 \text{ K}) = (-7100 \pm 400) \text{ J·mol}^{-1}$$

$$S^o(AuSb_2, cr) = (128 \pm 7) \text{ J·K}^{-1}\text{·mol}^{-1}.$$

Due to very sluggish reaction the date above should be considered as previous. Presumably phase transition pyrite - marcasite takes place in aurostibite in temperature interval (435-450 K).

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