Thermodynamic study of monoclinic pyrrhotite in equilibrium with pyrite in the Ag-Fe-S system by solid-state electrochemical cell technique

DMITRIY A. CHAREEV^{1,*}, MIKHAIL V. VORONIN¹ AND EVGENIY G. OSADCHII¹

¹Institute of Experimental Mineralogy, Russian Academy of Sciences, Chernogolovka, Moscow District, 142432, Russia

ABSTRACT

An equilibrium mixture of monoclinic pyrrhotite and pyrite was synthesized in the eutectic AlCl₃-KCl melt at 525 K. The reaction 7FeS₂(cr) + 12Ag(cr) = 8Fe_{0.875}S(cr) + 6Ag₂S(cr) was studied by an electromotive force technique in an all-solid-state electrochemical cell with an Ag⁺-conductive solid electrolyte in Ar at atmospheric pressure: (–) Pt | Ag | AgI | Ag₂S, Fe_{0.875}S, FeS₂ | Pt (+). In the 490–565 K temperature range a linear electromotive force vs. temperature trend was obtained from which the temperature dependence of the sulfur fugacity was determined for the monoclinic pyrrhotite-pyrite equilibrium: $logf_{s_2}(mpo+py) = 14.079 - 14406 \cdot T^{-1}$, (500 < T/K < 565). In addition, standard thermodynamic functions were calculated for monoclinic pyrrhotite Fe_{0.875}S at 298 K and atmospheric pressure: $\Delta G_f(mpo, 298.15 \text{ K}) = -(136200 \pm 3000) \text{ J/mol}$, S°(mpo, 298.15 K) = (66.7 ± 1.3) \text{ J/(mol·*K*)}, $\Delta H_f(mpo, 298.15 \text{ K}) = -(157400 \pm 3000) \text{ J/mol}$. Gaseous sulfur, S₂—ideal gas at 1 bar (10⁵ Pa) pressure—was taken as a standard state for sulfur.

Keywords: Monoclinic pyrrhotite, thermodynamic properties, sulfur fugacity, electrochemical cell technique, salt flux technique