DETERMINATION OF THERMODYNAMIC PROPERTIES OF REACTION 'FES'(CR) S(CR) =FES$_2$(CR) +2AG(CR) FOR THE TEMPERATURE RANGE 560-650 K BY SOLID-STATE GALVANIC CELL TECHNIQUE

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At the triple system Ag-Fe-S at temperature interval 560-650 K there are no triple compounds, and there are three co-stable bynaric phases: argentite Ag_2S, pyrite and pyrrhotite, and below 518K Ag and pyrite is co-exist, which are forming from β- pyrrhotite and argentite.

Thermodynamic properties of the reaction

'FeS'(cr) +Ag_2S(cr) = FeS_2(cr)+ 2Ag(cr) (i)

(where 'FeS' is the solid solution of stoichiometric pyrrhotite in hypothetical compound $V_{Fe}S_S$) have been investigated via electromotive force (EMF) measurements for the temperature range 560-650 K and standard pressure in solid-state galvanic cells with common inert gas atmosphere with $AgI_{0.8}Br_{0.2}$ as a solid electrolyte:

Pt, Ag | $AgI_{0.8}Br_{0.2}$ | 'FeS', FeS_2, Ag_2S, Pt (A)

The electrodes, pressed samples and solid electrolyte, having the form of tablets, were polished up to mirror shine and gathered in a required sequence in a quartz tube and for improvement of contacts were drawn in by a spring.

The measurements were conducted by the "Temperature titration" technique. This method consists in change of temperature on 5-20K and expectations of equilibrium values of e.m.f. Reproducibility of the equilibrium was confirmed with the carried out measurements at the beginning at temperature rising, then at downturn. Values of temperature and e.m.f. were measured in an automatic mode by the computer. Achievement of equilibrium was established visually, when values e.m.f. did not change (± 0.03 mV) within 12 hours.

In dependence of potential on temperature there is a characteristic break at temperature about 600K which may be explained by phase transition pyrrhotite from β to γ-modification. Approximation was conducted by the two linear equations $E = a + b\cdot T$, which implies $\Delta_r C_p$ is constant and it's equal to zero. The crossing point of these lines is the temperature of phase transition.

The e.m.f. values as a function of temperature for reaction with participation of β and γ-pyrrotite yielded the following equations:

$E(A, 1)\ /mV = -(223.4\pm6.9) + (0.457\pm0.012)\ T/K$ $(560<T/K<600)$,

$E(A,2)/mV =-(268.4\pm6.5)+0.532\pm0.011)\cdot T/K$ $(600<T/K<660)$,

which implies $\Delta_r C_p$ is equal to zero. The combinent solution of the equations 1 and 2 gives heat of phase transition, which occurs at temperature 600.73K and equal to 6513 J.mol-1. The changing of Gibbs free energy and entropy of the given electrochemical reaction can be calculated from e.m.f. of the galvanic cell by following main thermodynamic equations:

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

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

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

where n- electrons, which take participle at the reaction, F – Faraday constant (96484.56 $C.mol^{-1}$), E – e.m.f. of the cell, mV.

Standard thermodynamic properties of reaction (i) are given in the table

Equation	$\Delta_f G°$ ($J.mol^{-1}$)	$\Delta_f H°$ ($J.mol^{-1}$)	$S°$ ($J.K^{-1}.mol^{-1}$)
1	12600	32330	66.18
2	15880	38840	77.06

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