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Determination of standard thermodynamic properties of daubreelite ($FeCr_2S_4$) in the system Ag-Cr-Fe-S by the solid state galvanic cells method

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Daubreelite is a common mineral in enstatite chondrites, but its thermodynamic properties have not been studied. This greatly complicates the study of the physico - chemical parameters of enstatite chondrites formation in their parent bodies.

Analysis of the quaternary system Ag-Cr-Fe-S showed that at temperatures below 423 K can be stable phase association Ag_2S + Cr_2S_3 + FeS_2 + $FeCr_2S_4$, potential silver which can be defined in a completely solid state galvanic cell:

(-) Pt | Ag | $RbAg_4I_5$ | Ag_2S, Cr_2S_3, FeS_2, $FeCr_2S_4$ | Pt (+),

with a $RbAg_4I_5$ as a solid electrolyte with a specific conductivity of Ag^+ ion.

The overall potential forming process in the cell corresponds to a chemical reaction:

$2Ag + Cr_2S_3 + FeS_2 = Ag_2S + FeCr_2S_4$

Gibbs energy of this reaction is associated with the electromotive force of galvanic cells by fundamental equation of thermodynamics $\Delta_r G = -nFE$, where n = 2 - the number of electrons in the electrochemical process, F = 96485 $C \cdot mol^{-1}$ - Faraday constant, and E-electromotive force (emf) of galvanic cell in volts.

Temperature dependence of the emf was determined in an electrochemical cell, a device which is described in detail in the works Osadchii and Chareev (2006), and Osadchii and Echmaeva (2007). The results were approximated by a linear dependence of E(T), which corresponds to the condition $\Delta_r C_p$ constant and equal to zero:

$E(mV)=76.32+0.2296 \cdot T$, $339<T<400$, $R^2=0.9936$, k=38 (number of E/T points).

The Gibbs energy, entropy and enthalpy changes of the reaction were calculated from E(T) dependence using base thermodynamic equations:

$\Delta_r G=-nFE \cdot 10^{-3}$, $\Delta_r S=nF(dE/dT) \cdot 10^{-3}$, $\Delta_r H=-nF \cdot [E-(dE/dT)T] \cdot 10^{-3}$.

Using auxiliary data Barin (1995) and Mills (1974) were determined standard thermodynamic properties formation of daubreelite from elements at 1 bar pressure:

$\Delta_f G^\circ(298.15\ K) = -483.8\ kJ \cdot mol^{-1}$,
$S^\circ(298.15\ K) = 187.53\ J \cdot mol^{-1} \cdot K^{-1}$,
$\Delta_f H^\circ(298.15\ K) = -488.4\ kJ \cdot mol^{-1}$.

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