



## **Determination of standard thermodynamic properties of daubreelite (FeCr<sub>2</sub>S<sub>4</sub>) in the system Ag-Cr-Fe-S by the solid state galvanic cells method**

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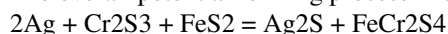
Daubreelite is a common mineral in enstatite chondrites, but its thermodynamic properties have not been studied. This greatly complicates the study of the physico - chemical parameters of enstatite chondrites formation in their parent bodies.

Analysis of the quaternary system Ag-Cr-Fe-S showed that at temperatures below 423 K can be stable phase association Ag<sub>2</sub>S + Cr<sub>2</sub>S<sub>3</sub> + FeS<sub>2</sub> + FeCr<sub>2</sub>S<sub>4</sub>, potential silver which can be defined in a completely solid state galvanic cell:

(-) Pt | Ag | RbAg<sub>4</sub>I<sub>5</sub> | Ag<sub>2</sub>S, Cr<sub>2</sub>S<sub>3</sub>, FeS<sub>2</sub>, FeCr<sub>2</sub>S<sub>4</sub> | Pt (+),

with a RbAg<sub>4</sub>I<sub>5</sub> as a solid electrolyte with a specific conductivity of Ag<sup>+</sup> ion.

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



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,  $F = 96485 \text{ C}\cdot\text{mol}^{-1}$  - 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:

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

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

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

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

$$\Delta_f G^\circ(298.15 \text{ K}) = -483.8 \text{ kJ}\cdot\text{mol}^{-1},$$

$$S^\circ(298.15 \text{ K}) = 187.53 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1},$$

$$\Delta_f H^\circ(298.15 \text{ K}) = -488.4 \text{ kJ}\cdot\text{mol}^{-1}.$$

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