

Prediction of enthalpies of formation of hydrous sulfates

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ABSTRACT

A method for the prediction of the enthalpies of formation ΔH_f° for minerals of hydrous sulfates is proposed and is decomposed in the following two steps: (1) an evaluation of ΔH_f° for anhydrous sulfates based on the differences in the empirical electronegativity parameter $\Delta_{Hf}O^- M^{+}(c)$ characterizing the oxygen affinity of the cation M^{+} ; and (2) a prediction of the enthalpy of hydration based on the knowledge of the enthalpy of dissolution for anhydrous sulfates.

The enthalpy of formation of sulfate minerals from constituent oxides is correlated to the molar fraction of oxygen atoms bound to each cation and to the difference of the oxygen affinity $\Delta_{Hf}O^- M^{+}(c)$ between any two consecutive cations. The $\Delta_{Hf}O^- M^{+}(c)$ value, using a weighing scheme involving the electronegativity of a cation in a given anhydrous sulfate, is assumed to be constant. This value can be calculated by minimizing the difference between the experimental enthalpies and calculated enthalpies of formation of sulfate minerals from constituent oxides.

The enthalpy of hydration is closely related to the nature of the cation in the anhydrous salt, to the number of water molecules in the chemical formula and to the enthalpy of dissolution for the anhydrous salt. The results indicate that this prediction method gives an average value within 0.55% of the experimentally measured values for anhydrous sulfates and 0.21% of the enthalpies of hydration or hydrous sulfates. The relationship between $\Delta_{Hf}O^- M^{+}(sulfate)$, which corresponds to the electronegativity of a cation in a sulfate compound, and known parameter $\Delta_{Hf}O^- M^{+}(aq)$ was determined. These determinations allowed the prediction of the electronegativity of some anhydrous transition metal double sulfate and contributed to the prediction of the enthalpy of formation for any hydrous double sulfate.

With a simplified prediction of the entropy of a hydrous sulfate, calculations of Gibbs free energy of formation can be evaluated and contribute to the knowledge of the stability of some hydrous sulfates in different environmental conditions such as temperature or air moiety. Therefore, to check the reliability of the predictive model, stability fields for some hydrous ferric sulfates such as pentahydrate ferric sulfate, lawsonite, kornelite, coquimbite, and quenstedtite vs. temperature and relative humidity were studied and compared with experimental measurements.

Keywords: Enthalpy of formation, hydrous double sulfate, entropy, enthalpy of hydration, double sulfates, sulfate, relative humidity, hydrous ferric sulfate, kornelite, lawsonite, coquimbite, quenstedtite, halotrichite, pickeringite, glauconite, picromerite, tamarugite, kalinite, syngenite, mendozite, tschermigite, krausite, goldichite, apthitalite, bilinite, romerite, solubility product, Gibbs free energy, temperature