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The Gibbs free energies and enthalpies of formation of U^{6+} phases: An empirical method of prediction

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ABSTRACT

Uranyl minerals form as a result of the oxidation and alteration of uraninite, UO_{2+x}. These uranyl phases are also important alteration products of the corrosion of UO_2 in used nuclear fuels under oxidizing conditions. However, the thermodynamic database for these phases is extremely limited. The Gibbs free energies and enthalpies for uranyl phases are estimated based on a method that sums polyhedral contributions. The molar contributions of the structural components to ΔG^0_f and ΔH^0_f are derived by multiple regression using the thermodynamic data of phases for which the crystal structures are known. In comparison with experimentally determined values, the average residuals associated with the predicted ΔG^0_f and ΔH^0_f for the uranyl phases used in the model are 0.08 and 0.10%, respectively, well below the limits of uncertainty for the experimentally determined values. To analyze the reliability of the predicted ΔG^0_f values, activity-activity diagrams in SiO_2-CaO-UO_3-H_2O and CO_2-CaO-UO_3-H_2O systems at 298.15 K and 1 bar were constructed using the predicted $\Delta G^0_{f,298.15}$ values for the relevant U^{6+} phases. There is good agreement between the predicted mineral stability relations and field occurrences, thus providing confidence in this method for the estimation of ΔG^0_f and ΔH^0_f of the U^{6+} phases.