

# Temperature Effect on the Complexation of Uranium(VI) with Sulfate and Fluoride Anions.

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Reliable models for predicting the chemical behavior of uranium in aqueous processing and in the repository of high-level nuclear wastes must properly take into consideration the temperature effect on the complexation of uranium with ligands that may be present, because the temperature under these conditions could be significantly above the ambient temperature (20 - 25°C). However, the majority of available thermodynamic data on uranium complexation are obtained at or near 25°C. Very few data are available at elevated temperatures [1]. Approximation methods [2], including the "constant enthalpy" approach, the "constant heat capacity" approach, the DQUANT equation and the revised HFK equation, have not been extensively tested for uranium because of the lack of experimental data. Therefore, we have started investigations on the complexation of uranium with a number of ligands at variable temperatures. In this presentation, we report the results of the complexation of U(VI) with sulfate and fluoride, two ligands believed to exist in the groundwater of the Yucca Mountain Repository in the United States, at 10 – 70°C.

The stability constants and enthalpy of U(VI)/sulfate and U(VI)/fluoride complexes have been determined by variable-temperature spectrophotometry and microcalorimetry. From these data, the entropy and the heat capacity of the complexation were also calculated. Discussions were made on the application of the SIT (Specific Ion Interaction Theory) approach to obtain the thermodynamic parameters at infinite dilution and variable temperatures.

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2. Puigdomenech, I.; Plyasunov, A. V.; Rard, J. A.; Grenthe, I. *Temperature corrections to thermodynamic data and enthalpy calculations*, in "Modeling in Aquatic Chemistry", Grenthe, I.; Puigdomenech, I. Eds. NEA/OECD, Paris, 1997, Chapt. X.