Estimating temperature dependence of Ln and An complexes using isocoulombic reactions

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Most of the available thermodynamic data concerning radioactive waste disposal are restricted to values of reaction constants at 25 °C and 1 bar. Estimation methods such as isocoulombic reactions can be used for extrapolating the properties of reactions involving aqueous species and minerals to elevated temperatures. Energetic, electrostatic, volumetric and structural differences between products and reactants must be minimal [1]. "Model reactions" are combined with the reactions of interest to generate isocoulombic reactions. Available literature data for the formation of Ln and An complexes were used to investigate what kind of model reactions can be combined with the reactions whose temperature trends are unknown, in order to produce the best estimates for the reaction constants (logK) of unknown reactions at elevated temperatures [2, 3]. From the compiled data, a set of selected "test" species was excluded from the dataset. The remaining species were used as a learning dataset to find a pattern for the best estimates of logK values at elevated temperatures. Subsequently, the properties of the complexation reactions of the "test" species were blindly predicted. The isocoulombic method was tested against experimental data retrieved in the ThermAc project [4] on the complexation of actinides (III, IV and VI) with ligands such as chloride, carbonate, sulfate, etc. Having only logK at 25 °C is sufficient to get quite reasonable estimates of logK values at elevated temperatures using isocoulombic reactions that exchange ions with similar hydrated ionic radius. The ThermoMatch code [5] was used to generate the reactions and combine them into isocoulombic reactions for systematic evaluation. The properties of substances and reactions were calculated at given T and P using the ThermoFun [5] library.

[1] Gu et al. (1994) Geochim. Cosmochim. Acta 17, 3545-3560.
[2] Migdisov et al. (2016) Chem.Geol. 7, 13-42.
[3] NEA Thermochemical Database (TDB). www.oecd-nea.org/dbtdb/
[4] Altmaier et al. (2016) Goldschmidt2016 abstr., 274.
[5] Miron et al. (2019), in preparation. www.thermohub.org