8.3 Intercomparison of thermodynamic databases

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Eh-pH diagrams give us fundamental information to understand solubility and sorption behavior in aqueous solution. Comprehensive diagrams of Pourbaix (1966) and Brookins (1987) are well known for the corrosion, immunity, passivation behavior of materials and for the geochemical behavior of elements, respectively. The author compiled the Eh-pH diagrams using the various thermodynamic databases (TDB's) for the purpose of showing the state-of-the-art, intercomparison, and usefulness of quick lookup of the diagrams.

Compilation of the TDB covers 6 databases; 1) FACT (bundled with FactSage® 5.2), 2) SUPCRT (updated with 98Updates distributed by Everett Shock on the Internet), 3) default TDB based on Lawrence Livermore National Lab. Data0.3245r4 (LLNL) bundled with Geochemist's Workbench® 4.0 (GWB), 4) JNC-TDB (011213g0.tdb and 011213g2.tdb), 5) OECD-NEA TDB, 6) ZZ-HATCHES-15. Elements selected for Eh-pH diagrams are those for which thermodynamic data are available (excluding inert gases) including not only radionuclide species but also non-radioactive species. Programs used for calculation are FactSage for FACT, GWB for LLNL, JNC-TDB, and AIST in-house software FLASK-AQ for SUPCRT, OECD-NEA, and HATCHES. Eh-pH diagrams for the system “Element-H-O” in 25°C, 1x10^5 Pa, total concentration 1x10^10 mol/kg are drawn. All species (either stable or unstable) considered for the calculation of Eh-pH diagram are listed in table for comparison.

As a result, elements showing good agreement among TDB's on the Eh-pH diagram are as follows; halogen, alkali, alkali earth elements (except Be and Ba), B, C, N, Si, P, S, Zn, As, Se, Nb, Ru, Ag, Cd, I, Au, Th, and U. Elements showing disagreement in the alkali Eh-pH area are Be, Fe, Co, Ni, Cu, Ba, Pb, La, Ce, Nd, Sm, Eu, Am, and Cm. Elements showing disagreements in the other area are Al, V, Cr, Mn, Zr, Mo, Tc, Pd, Sn, Sb, I, Hg, Ti, Bi, Np, and Pu. Elements difficult to evaluate due to less usable thermodynamic data are Sc, Ga, Y In, Lu, W, Re, Pt, Po, Pr, from Gd to Yb, (only contradictory two TDB's) Ge, Rh, Te, Hf, Os, Fr, Pm, Ac, and Pa (only one TDB). Throughout this work, characteristics of TDB were also made clear. As for the FactSage, aqueous species given only standard state thermodynamic data are dropped from the calculation other temperature than 25°C. This causes artifact of great difference of Eh-pH diagrams. SUPCRT lacks thermodynamic data of elemental minerals and oxide minerals for Se, Cr, Mn, V, Bi, Sc, Y, Lanthanide, Th, In, M, Pb, Ti, W, Zr, however it has advantage for capability to calculate equilibrium in the temperature other than 25°C. LLNL and JNC-TDB data provide only log_{10}K equilibrium constants, and cannot be traced back to enthalpy, entropy, Gibbs free energy data. JNC-TDB has a problem on chemical formula expressions. To discuss geochemical processes in alkali solution caused by groundwater-cement reaction and in thermal solution heated by waste deposit, further data is required for TDB's.

References