
Mission impossible: Building the all-purpose chemical thermodynamic database

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All major existing thermodynamic databases have been built with some applications in mind. If we use these databases outside their original focus we may calculate slightly, sometimes grossly wrong results, depending on how strongly we “misuse” them. However, merging all these databases to “the all-purpose thermodynamic database” will not work either.

The basic problem behind this “mission impossible” is that we do not have a proper fundamental theory of aqueous electrolyte solutions. Thermodynamic parameters have to be derived from experimental data by model assumptions (simplifications) about ionic interactions.

For modelling surface and subsurface aqueous systems (rivers and freshwater lakes, groundwater, sea water, brines and salt lakes) different model approaches have been used, i.e. variants of the extended Debye-Hückel equation, the specific ion interaction theory (SIT), and the Pitzer formalism. These different model approaches lead to different thermodynamic databases which cannot be merged to a single consistent database without re-fitting the basic experimental data.

The simplest approach in the realm of hydrothermal systems (high temperatures and pressures, i.e. $T > 300\text{ °C}$ and $P > 500\text{ bar}$) assumed solid phase equilibria with H_2O and CO_2 as the only components in the fluid phase. A more elaborate approach (SUPCRT) considered ionic species in the fluid phase with salt effects restricted to NaCl solutions.

In the first group of databases, developed for modelling surface and subsurface aqueous systems, temperature and pressure effects are either ignored, or limited to $T < 150\text{ °C}$ and saturated vapour pressure. By contrast, in databases developed for modelling hydrothermal systems temperature and pressure effects are the main focus, and 25 °C and 1 bar are mere “reference conditions” far outside their field of application. Attempts to merge databases from these “two worlds” lead to impressive looking data collections which revealed their deficiencies and needed additional data evaluation work whenever they were used in whatever field of application.