

Additional constraints and work terms in Gibbs energy minimisation with ChemApp and ChemSheet

Risto Pajarre

VTT Technical Research Centre of Finland Ltd.

The traditional scope of equilibrium solver ChemApp has been extended by including new energy (work) terms to the thermodynamic description of the system. The energy terms are introduced by defining additional system components to the system stoichiometry. Such terms can be associated with e.g. surface energy, membrane equilibrium and ion exchange in fibre suspensions, or external electric and magnetic fields. The chemical potential of the new component is proportional to the relevant physical potential or energy term (such as surface energy, osmotic pressure difference, membrane potential or magnetic field) when the corresponding stoichiometric coefficient is set proportional to the molar quantity (surface area, volume, charge or magnetization)

The same technique can be used to model the time development of reactive systems. Here the new stoichiometric coefficients relate to the stoichiometries of the constrained or slow reactions while the chemical potentials of the added components give the affinity of those constrained reactions. Other application areas of the added constraints include para-equilibrium systems and phase equilibria in nanoparticles.

Extending the application of equilibrium solvers enables the examination of new kinds of systems using existing thermodynamic software and, as far as possible, established data. As the method relies on the ability to redefine the system stoichiometry, it currently requires the related data file to be available in a plain text format. The application examples discussed have been mostly implemented using the ChemSheet program and could be applied in any ChemApp based code.