The Constrained Free Energy Method for Multi-Phase Systems

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The multi-phase analysis of complex systems by Gibbs free energy minimization has gained increasing popularity with the development of efficient computers and advanced data-bases. The advantages of the multi-phase methods have been widely recognized and they are becoming accepted in different applications, ranging from chemistry and metallurgy to materials processing, steel-making, pulp and paper production and energy and environment technologies.

The Gibbs energy minimization requires the use of the chemical potentials (partial molar Gibbs energies) of the constituents of the system. Usually, these appear at their equilibrium values as a result of the minimization calculation, the mass balance constraints being the necessary subsidiary conditions. Yet, there are several such physical circumstances, where chemical potentials appear constrained also by other factors. In this paper a method will be presented, by which constrained chemical potentials can be applied with multi-phase Gibbs energy minimization software. The constrained potentials arise typically due to a displacement in a generalized work-coefficient in the system or they are due to a pre-defined affinity. In the Gibbs energy minimization, performed by the Lagrange method, the constraints are set as additional Lagrangian coefficients.

Examples of the constrained potential method will be presented in terms of the electrochemical Donnan equilibria in aqueous systems containing semi-permeable interfaces [1], the phase formation in surface-energy controlled systems [2] and in systems with affinities controlled by chemical reaction kinetics [3]. For each of these applications data-bases are being developed, which can be utilized with the existing multi-phase thermodynamic (Gibbs energy) data by using advanced software tools. The proposed method has been successfully applied in calculating distribution coefficients for metal ions together with pH-values in pulp suspensions, in calculation of surface tension of alloys and in thermochemical process modeling involving chemical reaction rates.

[1] P. Koukkari, R. Pajarre, E. Räsänen, *Multi-phase Thermodynamics of Pulp Suspensions., in Chemical thermodynamics for industry*, Letcher, T.M. (Ed), Royal Society of Chemistry, Cambridge (2004).
[2] R. Pajarre, P. Koukkari, T. Tanaka and J. Lee: *Computing Surface Tensions of Binary and Ternary Alloys Systems with the Gibbs'ian Method*, Calphad, accepted for publication.
[3] P. Koukkari, and R. Pajarre,: *Calculation of Constrained Equilibria by Gibbs Energy Minimization*, Calphad, accepted for publication.