

Calculation of phase diagrams for non-equilibrium reaction systems with constrained Gibbs Energy minimization

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In the Constrained Gibbs Free energy minimization (CFE) method the conjugate variables driving force (D) and extent of reaction (ξ) appear as a key concepts for the calculation procedure [1,2]. As the CFE method often is applied for non-equilibrium systems and for partial equilibria, the driving force (affinity) may be given as a target input or is received as the result of the calculation [3]. The advancement of the internal process (extent of a chemical reaction) is either given as an external constraint (independent variable) or becomes defined from the internal conditions of a metastable system and acts as a dependent variable of the system.

For chemically reactive systems, some reactions typically can be identified as the rate-determining (slow) steps, while in a multicomponent system several other reactions may reach local chemical equilibrium. Then, the slow reactions may be constrained in the Gibbs'ian calculation and the reaction path can be followed in terms of their advancement and affinity. Correspondingly, using the driving force and the extent of the constrained reaction(s) as independent variables phase diagrams for reactive non-equilibrium conditions have been calculated.

[1] Koukkari, P. and Pajarre, R.. Calculation of constrained equilibria by Gibbs energy minimization, *Calphad*, 30, 1 (2006): pp. 18-26

[2] Hillert, M.: *Phase Equilibria, Phase Diagrams and Phase Transformations*, Cambridge University Press, Cambridge, 2008.

[3] Koukkari, P., Pajarre, R., Kangas, P., Thermo-dynamic affinity in constrained free-energy systems. *Monatshefte für Chemie* 149, 38, (2018). 1–394.