Discrete Thermodynamics of Chemical Equilibria

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Current paradigm of chemical thermodynamics deals with isolated chemical systems at “true” thermodynamic equilibrium, yielding the unknown “far-from-equilibrium” states to non-equilibrium theory. The situation changes as we switch from continuous differential equations for thermodynamic affinity to difference equations. Such an approach leads to discrete thermodynamics of chemical equilibria with its logistic equations; their solutions, graphically represented as inverse bifurcation diagrams are binding the entire spectrum of possible states of the chemical system - from “true” equilibrium to true chaos - into its domain of states by the unique idea. The domain of states contains distinctive areas of “true” thermodynamic equilibrium, where the body of classical chemical thermodynamics exactly falls in, then the area of open equilibrium within still unbroken thermodynamic branch, and the area of pitchfork bifurcations eventually heading to chaos. The logistic equation of states is composed of a classical term (e.g. in case of isothermic-isobaric system, as first approximation it is the change of Gibbs’ free energy), and a non-traditional parabolic term, a function of the system deviation from "true" equilibrium. In isolated system, the second term turns to zero, the system moves to the area of “true” equilibrium and obeys the classical rules. The presentation discusses the importance of the system response to external perturbation on its domain of states and its impact on the system evolution, the similarities between the chemical and biological populations, and peculiarities of thermodynamic simulation out of the area of isolated equilibria.