



Global optimization algorithms to compute thermodynamic equilibria in large complex systems with performance considerations [☆]



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ABSTRACT

Several global optimization methods are reviewed that attempt to ensure that the integral Gibbs energy of a closed isothermal isobaric system is a global minimum to satisfy the necessary and sufficient conditions for thermodynamic equilibrium. In particular, the integral Gibbs energy function of a multi-component system containing non-ideal phases may be highly non-linear and non-convex, which makes finding a global minimum a challenge. Consequently, a poor numerical approach may lead one to the false belief of equilibrium. Furthermore, confirming that one reaches a global minimum and that this is achieved with satisfactory computational performance becomes increasingly more challenging in systems containing many chemical elements and a correspondingly large number of species and phases. Several numerical methods that have been used for this specific purpose are reviewed with a benchmark study of three of the more promising methods using five case studies of varying complexity. A modification of the conventional Branch and Bound method is presented that is well suited to a wide array of thermodynamic applications, including complex phases with many constituents and sublattices, and ionic phases that must adhere to charge neutrality constraints. Also, a novel method is presented that efficiently solves the system of linear equations that exploits the unique structure of the Hessian matrix, which reduces the calculation from a $O(N^3)$ operation to a $O(N)$ operation. This combined approach demonstrates efficiency, reliability and capabilities that are favorable for integration of thermodynamic computations into multi-physics codes with inherent performance considerations.

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1. Introduction

Computational thermodynamics plays an integral role in facilitating engineering design of a wide array of materials and processes. Many equilibrium solvers have been developed to assist in this process, which rely on numerical methods and algorithms to compute thermodynamic equilibria. Upon initial impression, the number of publications in the open literature pertaining to this subject matter appears rather exhaustive. However, the majority of articles describing global optimization methods applied to computational thermodynamics deal with relatively small systems, such

as liquid–vapor equilibria, or are aimed at solving only a handful of calculations [1–7]. Although these methods work well for relatively small systems or when only a few calculations are needed, they were not developed to handle very large systems or for integration of thermodynamic calculations into multi-physics codes, which puts much greater demands on reliability and efficiency. This has been the impetus of developing THERMOCHEMICA [8] for integration into multi-physics codes, such as the BISON [9] nuclear fuel performance code. The goal of this paper is to review some of the more promising algorithms with greater mathematical rigor and to focus on performance issues that become more prominent as the size and complexity of thermodynamic systems increases.

The computation of thermodynamic equilibria rests on the minimization of the integral Gibbs energy of a closed isothermal–isobaric system subject to linear equality and inequality constraints represented by conservation of mass and the Gibbs phase rule. The Gibbs energy function of non-ideal phases may be non-convex, yielding multiple local minima. Local minima correspond to different compositions of phases that may be believed to be stable (e.g., a miscibility gap), which may not necessarily

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correspond to the true equilibrium composition. Finding the global minimum of this function among the many local minima within the domain space can be a daunting challenge, especially in large complex thermodynamic systems containing many highly non-ideal solution phases. Consequently, an inadequate numerical approach may lead one to the false belief of thermodynamic equilibrium, which may be far from the true equilibrium state.

There are several significant issues with finding a global minimum of the integral Gibbs energy function. First, *no global optimization technique guarantees the ability of finding a global extremum of a nonconvex function* [10]. One can, however, gain a certain level of confidence in applying a particular algorithm to a specific type of problem within a well defined perimeter of application. Second, searching for a global minimum becomes increasingly more difficult as the size of the system increases. And finally, the computational effort associated with performing this task can increase very rapidly in large systems, which can be a significant obstacle to integrating thermodynamic computations into multi-physics codes. The necessary and sufficient conditions for thermodynamic equilibrium at constant temperature and pressure are reviewed in Section 2 and several global optimization techniques that have been applied to the thermodynamic equilibrium problem are reviewed in Section 3. Three particular methods that have been found effective in computational thermodynamics are further examined in five case studies of varying complexity in Section 4. Finally, the behavior and suitability of these methods are discussed in Section 5.

2. Necessary and sufficient conditions for thermodynamic equilibrium at constant temperature and pressure

The necessary conditions for thermodynamic equilibrium require satisfaction of mass conservation and Gibbs' phase rule. The sufficient condition for equilibrium in a closed system at constant temperature and pressure corresponds to a global minimum of the integral Gibbs energy function. Ensuring that the mass balance constraints and the Gibbs phase rule have been satisfied is straightforward; however, special attention must be given to confirming that the Gibbs energy of a system, G , is at a global minimum.¹ For sake of completeness, the necessary conditions are briefly reviewed while the manuscript as a whole is dedicated to the sufficient condition of equilibrium.

First, the mass balance constraints must be satisfied. The total mass of system component j is represented by b_j and is computed by

$$b_j = \sum_{\lambda=1}^{\Lambda} n_{\lambda} \sum_{i=1}^{N_{\lambda}} x_{i(\lambda)} a_{i(\lambda)j} + \sum_{\omega=1}^{\Omega} n_{\omega} a_{\omega j} \quad (1)$$

where N_{λ} denotes the number of species in solution phase λ , and Λ and Ω represent the total number of stable solution phases and pure condensed phases in the system. The mole fraction of species i in solution phase λ is represented by $x_{i(\lambda)}$, and n_{λ} and n_{ω} represent the total number of moles of solution phase λ and pure condensed phase ω , respectively. The stoichiometry coefficients of component j in species i and pure condensed phase ω are $a_{i(\lambda)j}$ and $a_{\omega j}$ (g-at-mol⁻¹), accordingly. Clearly, n_{λ} and n_{ω} must be non-negative and $0 < x_{i(\lambda)} < 1$.

A solution phase may be represented as a multi-sublattice model, whereby the species are represented by a fixed combination of constituents that contain only a single constituent on each

sublattice. Thus, constituents are a subset of the species. Furthermore, the species may then be interpreted as stoichiometric compounds representing the extremes of composition and are commonly referred to as "compound end members". The mole fraction of species i , or compound end member, is related to the site fractions of constituents, $y_{i(s)}$, on all sublattices in the phase corresponding to i through the following formalism

$$x_{i(\lambda)} = \prod_{s=1}^{N_s} y_{i(s)} \quad (2)$$

where s is the sublattice index and N_s is the number of sublattices.

Second, the equilibrium condition must also abide Gibbs' phase rule, which requires that the number of thermodynamic degrees of freedom, F , be non-negative. For a closed isothermal-isobaric system, F is defined as the difference between the number of system components, C , and the total number of stable phases, Φ (i.e., $\Phi = \Lambda + \Omega$) as

$$F = C - \Phi \quad (3)$$

where maintaining constant temperature and pressure removes two degrees of freedom. Thus, Gibbs' phase rule requires that the number of co-existing phases at equilibrium in an isothermal isobaric closed system must be less than or equal to the number of system components (i.e., $1 \leq \Phi \leq C$). A system component is the most basic form of representing part of a thermodynamic system, which is often taken as a chemical element or by a fixed integer combination of chemical elements. The term "system component" is used here to distinguish from a "phase component", which typically represents a species in a solution phase.

Finally, the sufficient condition for equilibrium requires that G is at a global minimum with respect to the quantities of all species and phases. The integral Gibbs energy of a multicomponent multi-phase system can be represented as

$$G = \sum_{\lambda=1}^{\Lambda} n_{\lambda} g_{\lambda} + \sum_{\omega=1}^{\Omega} n_{\omega} g_{\omega} \quad (4)$$

where g_{λ} and g_{ω} are the molar Gibbs energies of solution phase λ and pure condensed phase ω , respectively. The latter is fixed, whereas the formulation of g_{λ} is model dependent and is a non-linear function of $x_{i(\lambda)}$. This term is responsible for the non-convexity of G .

A local minima² in G , which may differ from the global minimum, is indicated by $dG = 0$. An equivalent statement yields the following linear equality³ [14,15]

$$\mu_i = \sum_{j=1}^C a_{ij} \Gamma_j \quad (5)$$

where μ_i is the chemical potential of species i and Γ_j is the chemical potential of system component j . Eq. (5) states that the chemical potential for each system component must have the same value in all stable phases within the system [15]. This equation is often graphically represented as a tangent line between phases on a molar Gibbs energy plot in a binary system or equivalently as a hyperplane in higher order systems. This is sometimes called the "Gibbs plane", whereby the corners of the Gibbs plane are given by Γ_j and any point on this plane is μ_i .

The linear equality represented by Eq. (5) is used to justify the selection of stable phases and ensuring that no metastable phase

¹ Of course, thermodynamic equilibrium can be calculated for other conditions, such as fixed enthalpy or chemical potential of a component. The conditions described herein exclusively pertain to a closed system at constant temperature and pressure.

² Numerical methods that locally minimize G subject to mass balance constraints have been extensively documented in the literature [8,11–13] and are not discussed herein.

³ A thorough derivation and discussion of this necessary condition is provided by Piro et al. [14].

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