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CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry

Updating the estimated assemblage of stable phases in a Gibbs energy minimizer

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ABSTRACT

Several numerical strategies are presented that can be used to effectively and efficiently update the estimated assemblage of stable phases in a Gibbs energy minimizer. Decisions must be made in selecting which phase should be added to or withdrawn from the system, the order in which certain combinations should be considered, testing procedures of the appropriateness of a candidate system for further consideration, etc. The manner in which these methods are performed have a profound effect on the performance and reliability of such calculations; without effective strategies, the solution may not converge. While these matters are somewhat straightforward for relatively small systems, far greater challenges are experienced in large systems containing many chemical elements. These matters will be discussed and effective solutions that have been integrated into THERMOCHIMICA throughout the course of its development will be presented.

1. Introduction

Computational thermodynamic software have served countless scientific and engineering investigations well, whereby conventional applications typically include point calculations (e.g., a single temperature, pressure, and composition) and the construction of phase diagrams. Contemporary applications are evolving towards more sophisticated thermodynamic representations of complex systems with many chemical elements (e.g., nuclear fuel [1]) and the integration of those calculations into multi-physics codes (e.g., coupling thermochemistry with nuclear physics, and heat and mass transfer to simulate irradiated nuclear fuel behaviour [2,3]). Despite significant advances in computer hardware and parallel computing methodologies, the numerical methods that are employed must be made with adequate efficiency to bare a reasonable computational cost.

Previous investigations have demonstrated great progress in the development of numerical methods used in various aspects of a Gibbs energy minimizer, such as initialization algorithms [4,5], the non-linear solver [6–10], and numerical procedures to ensure that the necessary [11] and sufficient [12–17] conditions for thermodynamic equilibrium have been satisfied. However, to the best of the knowledge of the author, only a small handful of articles in the open literature have discussed numerical strategies for updating the estimated assemblage of stable phases, none of which have revealed any great detail for implementation in a general computational framework. The reason for

this is likely that comprehensive numerical methods to handle complicated problems are mainly needed for software that have broad capabilities, virtually all of which fall within the commercial domain. Clearly, commercial interests incentivize one to closely guard trade secrets.

The issues pertaining to the manner that an estimated assemblage of stable phases is updated are of great importance in general equilibrium thermodynamic solvers because convergence may not be assured without adequate numerical strategies to update the system. Another concern is that the number of global iterations[1] required to achieve convergence may be unnecessarily high when using inadequate numerical methods. As is often the case, the devil's in the details; the impetus of this article is to lay bare those details and to offer some strategies to solve them that have been conceived throughout the development of THERMOCHIMICA [10]. A background to this numerical problem is given in Section 2 and several effective strategies are described on how the phase assemblage can be updated are given in Section 3.

2. Background

2.1. Constraints

A phase may need to be withdrawn from, it may need to be added to, or it may need to substitute another phase that is currently

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[1] The global iteration cycle involves changes to the system as a whole where changes can be made to the selection of phases, whereas the local iteration cycle belongs to a line search method that attempts to locally satisfy the Wolfe conditions. Local iterations occur within a single global iteration.

predicted to be stable in the system. First, the criterion for withdrawing a phase is dictated by the numerical constraints imposed on the mass conservation equations. Second, the criterion for adding a phase is governed by the sufficient condition for equilibrium, which is derived from the second law of thermodynamics. Finally, the criterion for substituting a phase is made in part to adhere to Gibbs' phase rule. These three broad criterions will be described below.

The mass balance equation for each system component[2] j is given by

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

where N_λ denotes the number of species in solution phase λ, and Λ and Ω represent the total number of stable solution and stoichiometric phases in the system, respectively. 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 stoichiometric phase ω, respectively. The stoichiometry coefficients of component j in species i and stoichiometric phase ω are $a_{i,j}$ and $a_{\omega,j}$ (g-at·mol^{-1}), accordingly.

Eq. (1) is subject to the following constraints:

$$x_{i(\lambda)} > 0, \quad n_\lambda > 0, \quad n_\omega > 0, \quad \forall\, (i, \lambda, \omega) \tag{2}$$

In addition to satisfying the mass balance equations, the integral Gibbs energy of the system, G, must be at a global minimum at thermodynamic equilibrium. An equivalent statement of a local minima given by $dG=0$ is represented by the following linear equality [11,18].

$$\mu_i = \sum_{j=1}^{C} a_{i,j} \Gamma_j \tag{3}$$

where μ_i is the chemical potential of i, Γ_j is the chemical potential of system component j, and C is the number of system components. In the Gibbs energy minimization approach, μ_i and Γ_j are separate variables. Specifically, μ_i is computed based on the mole fractions of species within the same phase (as appropriated by the specific model), whereas Γ_j is an undetermined Lagrangian multiplier that is solved by the non-linear solver, which subsequently provides incremental updates to μ_i. Therefore, there is necessarily a residual associated with Eq. (3).

A common interpretation of Eq. (3) is that it represents a line (or plane or hyperplane) that is tangent to the molar Gibbs energy surfaces of phases that are predicted to be stable. One of the necessary conditions for equilibrium requires that the chemical potentials of all species in stable solution phases and stoichiometric phases lie on this plane [11], while the sufficient condition requires that the molar Gibbs energy surfaces of all metastable phases lie above this plane [17]. The difference between the molar Gibbs energy of any metastable solution phase and the corresponding value computed by the chemical potentials of the system components is often referred to as the "driving force" [19] or "tangent plane distance function" [14], which is defined for solution phase λ as

$$\pi_\lambda = \min_x \sum_{i=1}^{N_\lambda} x_{i(\lambda)} \left(\mu_{i(\lambda)} - \sum_{j=1}^{C} a_{i,j} \Gamma_j \right) \tag{4}$$

One can also compute this value for a stoichiometric phase, π_ω, which is trivial to compute since the molar Gibbs energy of a stoichiometric phase, g_ω, by definition has a unique composition. Furthermore, Eq. (4) equally applies to phases represented by the Compound Energy Formalism (CEF) with multiple sublattices. The mole fractions and chemical potentials associated with the compound end members are used in Eq. (4), which are related to the constituents on all sublattices.

At equilibrium, π_λ and π_ω for all metastable phases must be positive and non-zero.[3] Therefore, the criterion for adding a phase is whether π_λ or π_ω is negative at any point in the iteration cycle, which adheres to the sufficient condition for equilibrium:

$$\pi_\lambda > 0, \quad \pi_\omega > 0 \tag{5}$$

In addition to ensuring that the integral Gibbs energy of the system is a minimum at equilibrium, the number of stable phases must abide Gibbs' phase rule, which requires that the number of thermodynamic degrees of freedom, F, be non-negative. The current discussion considers closed isothermal-isobaric systems exclusively. In this case, F is defined as the difference between the number of system components, C, and the total number of stable phases, Φ (i.e., $\Phi = \Lambda + \Omega$), where maintaining constant temperature and pressure removes two degrees of freedom, as

$$F = C - \Phi, \tag{6}$$

which is subject to the following constraint:

$$F \geq 0 \tag{7}$$

Therefore, the criterion for whether a phase needs to substitute another phase in the system is made – at least in part – to obey Gibbs' phase rule. To summarize, the criterion for withdrawing a phase is made with respect to Eq. (2), adding a phase is made with respect to Eq. (5), and substituting a phase is made partially with respect to Eq. (7). These criteria provide the foundation for specific methods for updating the estimated assemblage of stable phases, which will be discussed in Section 3. The following sub-section will describe aspects of the optimization process pertinent to updating the active set of constraints.

2.2. Optimization

Solving the system of non-linear equations represented by the Hessian matrix, **H**, yields a direction vector, **p**, which provides direction in which the system's independent variables change. Updating the estimated assemblage of stable phases has a direct effect on the construction of **H**, which therefore affects changes to the system variables. The Hessian matrix that minimizes the Lagrangian function of the integral Gibbs energy of the system has been derived by Eriksson and Rosen [6] and is summarized below:

$$\mathbf{H} = \begin{bmatrix} r_{j=1,k=1} & \cdots & r_{j=1,k=C} & \kappa_{j=1,\lambda=1} & \cdots & \kappa_{j=1,\lambda=\Lambda} & a_{j=1,\omega=1} & \cdots & a_{j=1,\omega=\Omega} \\ \vdots & \ddots & \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ r_{j=C,k=1} & \cdots & r_{j=C,k=C} & \kappa_{j=C,\lambda=1} & \cdots & \kappa_{j=C,\lambda=\Lambda} & a_{j=C,\omega=1} & \cdots & a_{j=C,\omega=\Omega} \\ \kappa_{j=1,\lambda=1} & \cdots & \kappa_{j=C,\lambda=1} & 0 & \cdots & 0 & 0 & \cdots & 0 \\ \vdots & \ddots & \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ \kappa_{j=1,\lambda=\Lambda} & \cdots & \kappa_{j=C,\lambda=\Lambda} & 0 & \cdots & 0 & 0 & \cdots & 0 \\ a_{j=1,\omega=1} & \cdots & a_{j=C,\omega=1} & 0 & \cdots & 0 & 0 & \cdots & 0 \\ \vdots & \ddots & \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ a_{j=1,\omega=\Omega} & \cdots & a_{j=C,\omega=\Omega} & 0 & \cdots & 0 & 0 & \cdots & 0 \end{bmatrix} \tag{8}$$

The notation here is simplified with the variables

$$r_{j,k} = \sum_{\lambda=1}^{\Lambda} \sum_{i=1}^{N_\lambda} n_{i(\lambda)} a_{i,j} a_{i,k} \tag{9}$$

and,

$$\kappa_{j,\lambda} = \sum_{i=1}^{N_\lambda} n_{i(\lambda)} a_{i,j} \tag{10}$$

where $n_{i(\lambda)}$ is the number of moles of species i in solution phase λ. The system of linear equations that is to be solved is therefore,

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