A globally convergent saturation state algorithm applicable to thermodynamic systems with a stable or metastable omni-component phase

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Abstract

A new algorithm is proposed for determining the saturation condition of a multi-component solution with respect to a thermodynamic system of phases that are in exchange equilibrium. The procedure is simple to implement, analytic in construction, and guaranteed to converge. The algorithm finds application in the computational thermodynamics of equilibrium phase relations in multi-component systems and provides a means of discriminating computed assemblages that are potentially metastable from those that are globally stable. The algorithm can be applied to any chemical system of arbitrary complexity.
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1. INTRODUCTION

There are many challenges associated with performing computational thermodynamics in systems with multi-component solution phases, but perhaps the most daunting is identification of the potential phases and their compositions in the equilibrium assemblage. By contrast, in systems comprising a collection of pure phases, this exercise is straightforward and the resulting equilibrium assemblage is uniquely defined; most computational procedures for single-component phase collections start with the unlikely assumption that all possible phases are present in the system, and optimize this initial guess using linear programming (e.g., simplex method) to achieve a minimal energy solution (Smith and Missen, 1982). Importantly, in such a procedure the numerical algorithm retains compositional information about the universe of possible phases at each numerical step in the evolution to the minimum, with optimality prescribed by the molar abundance (which may be zero) of each phase in the final assemblage. If the phases in the equilibrium system are solutions of varying composition however, a complication emerges: In the course of

energy minimization a particular solution phase may disappear from the assemblage, indicated by the molar abundance of all of its components tending towards zero; in subsequent numerical steps to the energy minimum, as further phases are discarded and compositions of remaining phases are adjusted, the earlier discarded phase may reenter the assemblage to become a member of the final equilibrium configuration of phases. In this scenario, the complication is how to determine the stability of any discarded solution phase so that it may be evaluated for reintroduction into the assemblage? This procedure is not trivial because, unlike the single component case, simply adding a tiny amount of the phase to the assemblage and noting the direction of change of total energy does not apply, given that the solution phase composition is not known *a priori*. Randomly selecting a composition to evaluate potential solution phase inclusion simply does not work because most such random guesses will be metastable, and Monte Carlo-like evaluation of potential compositions is too time-consuming for phases with four or more components. The answer to this dilemma is an algorithmic procedure that correctly determines the relative stability of a given phase *vis-a-vis* a collection of (meta)stable phases. In general, such procedures are referred to as saturation state algorithms because they are derived historically from

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methods utilized in determining the relative saturation condition of solid phases in potential association with aqueous solution (Helgeson et al., 1970; Reed, 1982).

Most saturation state algorithms take advantage of the presence of a (meta)stable phase that contains all of the thermodynamic components in the system. An aqueous fluid or a magmatic liquid are excellent examples of such phases. We denote these *omni-component* phases, using the Latin prefix *omni*, meaning everything. Strictly speaking, all phases are omni-component phases, but in practical computations compositions of solutions are restricted by available thermodynamic data and solution models. Importantly, as will be demonstrated below, an omni-component phase can always be defined for a collection of arbitrary phases in exchange equilibrium (metastable or stable), so algorithms that rely on the existence of an omni-component phase for determining saturation state conditions are universally applicable.

In this paper, a new algorithm is presented for determination of the saturation state of a phase relative to an omni-component phase. While many such algorithms have been proposed (e.g., Reed, 1982; Ghiorso, 1994) and utilized in practice (Ghiorso and Sack, 1995; Ghiorso et al., 2002; Tirone et al., 2009), the algorithm developed below is unique in that it does not rely on the solution of non-linear systems of equations, a numerical procedure which may be time-consuming or yield locally minimal (i.e. potentially incorrect) solutions. Nor does the algorithm proposed below require an initial numerical guess. Both of these features are advantages in that together they foster achievement of a solution that is globally convergent. The paper begins with a statement of the new algorithm, then applies the algorithm to thermodynamic systems with a stable or metastable omni-component phase, and finally addresses the issue of algorithm convergence and other practical matters of implementation.

2. SATURATION STATE ALGORITHM – DESCRIPTION

Consider an omni-component (oc) phase with n thermodynamic components. We pose the problem: What is the saturation state of a target-phase relative to a specified composition of the oc-phase at some given temperature (T) and pressure (P). The problem is illustrated in Fig. 1 for a model two component system. Composition is denoted on the abscissa as mole fraction (X) of the second component in solution, and the molar Gibbs free energy (G) is plotted on the ordinate. The specified composition of the oc-phase is labeled "L." The dashed line is tangent to the Gibbs energy curve at "L," and for the illustrated cases, this tangent line projects to lower Gibbs free energies than those of the target-phase. Consequently, the target-phase is undersaturated relative to the chosen composition of the oc-phase. In quantitative terms, the degree of undersaturation is given by the chemical affinity (A), which is the *minimal* energy difference between the projected tangent line from the oc-phase and the Gibbs free energy curve of the target-phase for some composition where the slopes of both energy curves are identical.

Determining the saturation state of a target-phase is therefore an exercise in finding the target-phase composition that satisfies these geometrical requirements in energy-composition space. Although Fig. 1 illustrates this geometrical construction for a two-component case, the situation readily generalizes to Gibbs free energy surfaces with tangent hyperplanes and gradient vectors for arbitrary numbers of components.

The geometrical condition of the previous paragraph is embodied in the set of thermodynamic equations

$$\mu_{i,\text{oc-phase}} = A + \mu_{i,\text{target-phase}} \tag{1}$$

for all c components of the target-phase, where μ denotes the chemical potential, which is indexed on i, and $1 \leqslant i \leqslant c$, $c \leqslant n$. For simplicity and without loss of generality both phases are described with the same component stoichiometry; in practice a mapping may be required to balance stoichiometric differences between difference sets of components adopted for each phase. Alternately, the method of Lagrange multipliers may be utilized to construct the left-hand-side of (1), as described below in Section 3. Note that in Eq. (1) the chemical affinity is not indexed on i, implying that the disequilibrium energy offset is identical for all components of the target-phase. The proof of this result is given by Ghiorso (1987, Appendix b). If the affinity is zero, then the phases are mutually tangent (Fig. 1) and Eq. (1) reduces to the standard Gibbs requirement of heterogeneous phase equilibrium.

Eq. (1) expands to

$$\mu_{i,\text{oc-phase}} = A + \mu_{i,\text{target-phase}}^o + RT \ln a_{i,\text{target-phase}} \tag{2}$$

where a denotes the activity of a component in the target-phase and the superscript zero refers to the standard state condition of unit activity of the pure substance at any T and P. The activity may be further expanded into a product of mole fraction and activity coefficient (i.e., $a_{i,\text{target-phase}} = X_i \gamma_i$), which permits Eq. (2) to be rearranged as:

$$\mu_{i,\text{oc-phase}} - \mu_{i,\text{target-phase}}^o - RT \ln \gamma_i = \Phi_i = A + RT \ln X_i \tag{3}$$

In Eq. (3) the activity coefficient terms are brought to the left-hand-side of the expression and are included in the definition of Φ_i.

2.1. Saturation state algorithm

The saturation state algorithm proceeds as follows:

(I) Assume initially that the target-phase is ideal, which implies all $RT \ln \gamma_i$ are zero. This assumption renders Φ_i independent of X_i (Eq. (3)).

(II) Form difference expressions from Eq. (3), as

$$\Phi_{i+1} - \Phi_i = RT \ln X_{i+1} - RT \ln X_i$$

which may be rearranged to give

$$r_i = \exp\left(\frac{\Phi_{i+1} - \Phi_i}{RT}\right) = \frac{X_{i+1}}{X_i} \tag{4}$$