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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.

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

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

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:

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

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

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

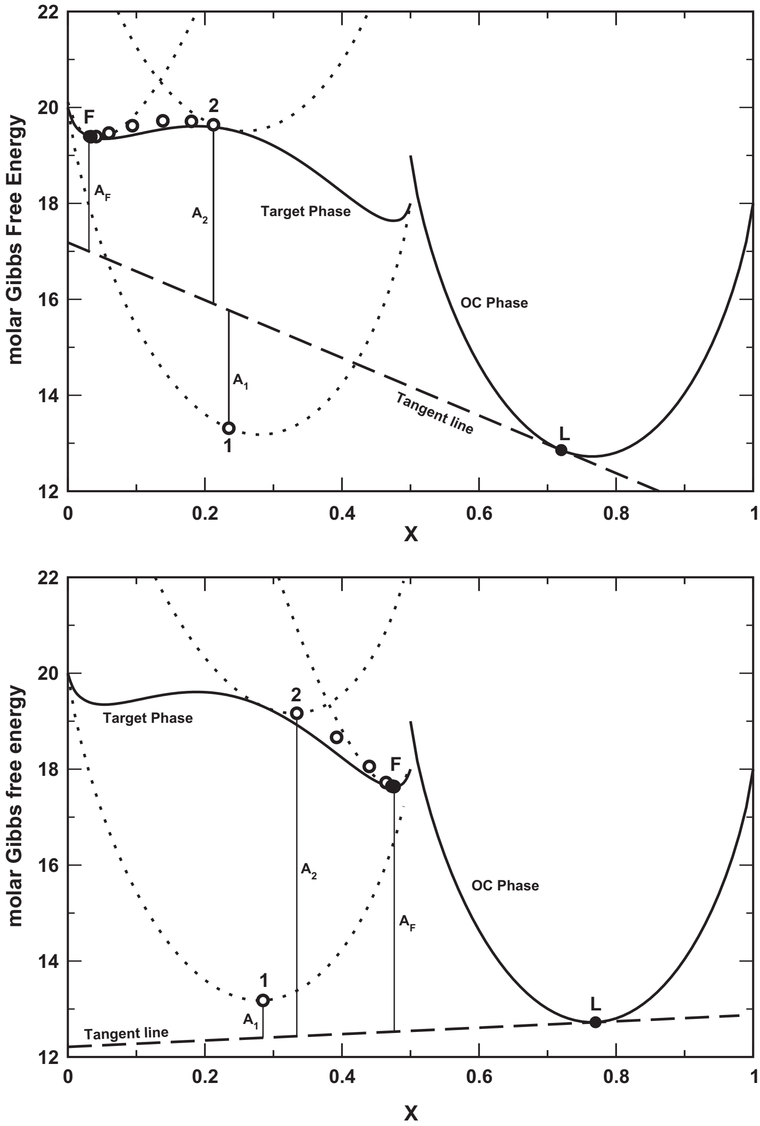

Fig. 1. Illustration of saturation state algorithm for a target phase referenced to an omni-component phase (oc) of composition X_L. The Gibbs free energies of the two phases are illustrated by the heavy solid curves. The dashed line labeled "tangent line" is tangent to the oc-phase at X_L. It has the same slope as the tangent to the target phase at X_F. 1, 2, etc. refer to the sequence of intermediate solutions which converge to F. The chords labeled A_i are geometrical representations of the chemical affinity. The dotted curves are "ideal mixing" approximations of the target phase, as described in the text. The upper and lower panel differ only in location of X_L.

(III) Solve analytically for X_1 using an expression derived by repeated application of Eq. (4) to the closure constraint on the sum of mole fractions,

$$X_1 + X_2 + X_3 + \ldots + X_{c-1} + X_c = 1$$

as:

$$X_1 + r_1 X_1 + r_1 r_2 X_1 + \ldots + (r_1 r_2 \ldots r_{c-2}) X_1 + (r_1 r_2 \ldots r_{c-2} r_{c-1}) X_1 = 1$$

$$X_1 = \frac{1}{1 + r_1 + r_1 r_2 + \ldots + (r_1 r_2 \ldots r_{c-2}) + (r_1 r_2 \ldots r_{c-2} r_{c-1})} \quad (5)$$

(IV) Solve analytically for the remaining X_i by repeated substitution of Eq. (4):

$$X_i = (r_{i-1} r_{i-2} \ldots r_2 r_1) X_1$$

(V) Solve for the affinity by appropriately transforming Eq. (3):

$$A = \Phi_1 - RT \ln X_1$$

(VI) Use values for the $X_1 \ldots X_c$ calculated in steps III and IV to evaluate $RT \ln \gamma_i$ for the target-phase. Treat these quantities *as constants* and from them calculate new values of Φ_i using Eq. (3).

(VII) Preserve the current values $X_1 \ldots X_c$ and A. Perform algorithmic steps II through VI again. Evaluate convergence criteria: Are the newly computed values of $X_1 \ldots X_c$ and A "sufficiently" close to the preserved values from the last iteration? If not, go to step VI. If so, exit the procedure. On exit, if the affinity is a positive quantity, the target-phase is undersaturated. If negative, supersaturated.

Note: When implementing the algorithm for target-phases that have configurational entropies of mixing that reflect site multiplicity (i.e., α symmetrically equivalent sites in the formula unit), convergence may be accelerated by modifying Eq. (3) and its dependencies as: $\mu_{i,\text{oc-phase}} - \mu^{o}_{i,\text{target-phase}} - RT\ln\gamma_i = \Phi_i = A + \alpha RT\ln X_i$.

The algorithm works by taking advantage of the fact that the solution of the saturation state problem is analytic if the target phase is ideal (Ghiorso, 1994). By holding the molar excess Gibbs free energies ($RT\ln\gamma_i$) constant and transferring their contribution onto the standard state term (i.e. left-hand-side of Eq. (3)), a succession of pseudo-ideal systems are evaluated until the final one gives a result that is identical to the desired solution for the thermodynamically non-ideal target phase. This succession of solutions can be seen visually in Fig. 1. Two cases are evaluated in the figure corresponding to saturation state conditions for a target-phase that exhibits a large miscibility gap. The dotted curve labeled "1" is the molar Gibbs free energy of solution for the equivalent hypothetical ideal target-phase (Algorithmic step I), and the point/chord labeled "1" and "A_1" are the algorithmic solutions for the saturation condition. The dotted curve labeled "2" is the "ideal" molar Gibbs free energy of solution for the case where the standard state properties of the target-phase are adjusted by the $RT\ln\gamma_i$ calculated from the composition at "1." Note that the dotted curve "2" matches by construction the actual Gibbs curve of the target-phase at composition "1." The composition at "2" and the affinity, A_2, are solutions of the saturation state algorithm (steps II through VI) applied to curve "2;" note that composition "2" is closer to the ultimate solution (at "F") than composition "1." Repeated construction of pseudo-ideal Gibbs curves leads to a succession of approximations which terminate when the pseudo-ideal curve is topologically identical to the actual target-phase Gibbs curve in the local compositional interval about the saturation surface solution. In the figure this solution is denoted by the composition at point "F" along with the associated affinity, labeled "A_F." The pseudo-ideal Gibbs free energy curve for this point is also illustrated for reference.

The algorithm described and illustrated above converges rapidly, and has been evaluated for target-phases with up to seven components. It is more robust than the algorithm of Ghiorso (1994; later applied in Asimow and Ghiorso, 1998) which relies on the solution of sets of non-linear equations. The one apparent restriction is that the algorithm requires all component mole fractions of the target-phase to be positive quantities. As many thermodynamic solutions violate this assumption, it is necessary to introduce a modification, which is described in the next section.

2.2. Saturation state algorithm – Modifications for reciprocal solutions

Often the implicit assumption of positive mole fractions of component concentrations in the target-phase is violated. Typically this situation occurs in reciprocal solutions (Wood and Nicholls, 1978), where the number of natural endmembers of the solution exceeds the number of thermodynamic components. Quadrilateral pyroxenes serve as a nice example of a reciprocal solution. These pyroxenes have compositions with natural endmembers $CaMgSi_2O_6$ (Di), $CaFeSi_2O_6$ (Hd), $Mg_2Si_2O_6$ (En), and $Fe_2Si_2O_6$ (Fs). Often the natural endmembers of a reciprocal solution are referred to as *solution species* and in this case the composition of a pyroxene interior to the quadrilateral can be described in terms of mole fractions of species (i.e., X^s_{Di}, X^s_{Hd}, X^s_{En}, X^s_{Fs}) or alternately mole fractions of thermodynamic components, of which there are three, and we might choose X^c_{Di}, X^c_{Hd}, and X^c_{En}. Note that if there are s species and c components, $s \geqslant c$, and that the species mole fraction are always positive. Note also that with this choice of components, compositions more Fe-rich than those along the En-Hd join will of necessity have negative mole fractions of the component Di (e.g. Fs: $X^c_{\text{Di}} = -2$, $X^c_{\text{Hd}} = 2$, $X^c_{\text{En}} = 1$).

Numerical procedures in computational thermodynamics often avoid the use of species concentrations because such quantities are not linearly independent. There is, however, no such requirement of linear independence in manipulating the mole fractions in the algorithm described previously, so species mole fractions can readily be substituted for component mole fractions, and the saturation state condition evaluated in "species"-space rather than "component"-space. For example, in the case of the quadrilateral pyroxenes the target-phase thermodynamic model would provide values of μ_{Di}, μ_{Hd}, and μ_{En}. The required value of μ_{Fs} for the saturation state algorithm would be obtained from the condition of homogeneous equilibrium: $\mu_{\text{Fs}} = \mu_{\text{En}} + 2\mu_{\text{Hd}} - 2\mu_{\text{Di}}$, which must always hold. The algorithm would yield X^s_{Di}, X^s_{Hd}, X^s_{En}, and X^s_{Fs}, which could then be mapped back to the component set:

$$
\begin{aligned}
X^c_{\text{Di}} &= X^s_{\text{Di}} - 2X^s_{\text{Fs}}\\
X^c_{\text{Hd}} &= X^s_{\text{Hd}} + 2X^s_{\text{Fs}}\\
X^c_{\text{En}} &= X^s_{\text{En}} + X^s_{\text{Fs}}
\end{aligned}
$$

By defining a suitable set of natural endmembers, the saturation state algorithm described above can be utilized with target-phases that posses the properties of reciprocal solutions.

3. GENERALITY OF THE OMNI-COMPONENT PHASE

It is not uncommon for a model thermodynamic system to contain an omni-component phase. The liquid phase in a magma certainly qualifies as does the aqueous phase in a fluid-rock system, or the condensing gas phase of the early solar nebula. In all these cases application of the saturation state algorithm described above is straightforward, and such an algorithm can form an integral part of a computational scheme to evaluate the phase proportions and compositions in the system at equilibrium. For calculation of phase equilibria in systems that do not contain a model omni-component phase, it is desirable to construct a metastable or hypothetical equivalent that functions as a proxy for saturation surface evaluation. Asimow and Ghiorso (1998) advocate this notion and their use of a metastable pseudo-liquid phase is integral to the calculation of subsolidus phase relations in magmatic systems (e.g. MELTS, pMELTS). The method of Asimow and Ghiorso (1998) can be generalized for arbitrary collections of phases that are in *exchange* equilibrium.

A collection of phases are in exchange equilibrium if at a given bulk composition, T and P, the phase proportions and compositions define a local minimum in the Gibbs free energy of the system. This state is only equivalent to the global equilibrium state if all potential phases not currently included in the assemblage are *undersaturated* relative to the phases in the assemblage. For any collection of phases in exchange equilibrium, the Gibbs–Duhem theorem (Prigogine and Defay, 1954) provides a means of stipulating a set of system chemical potentials of appropriate thermodynamic components; if the system is not in exchange equilibrium, such potentials have no meaning nor definition. For example, suppose the bulk composition of a system may be expressed as 25% spinel of composition Sp_{50} ($0.5\ MgAl_2O_4 + 0.5\ FeAl_2O_4$), 25% olivine of composition Fo_{90} ($0.1\ Fe_2SiO_4 + 0.9\ Mg_2SiO_4$) and 50% quartz ($SiO_2$). At a given T and P, this assemblage may be metastable relative to the assemblage spinel–olivine–orthopyroxene, or spinel–orthopyroxene–quartz, but regardless of this possible metastability, the Fe/Mg ratios of the spinel and olivine will have values that zero the free energy change of the exchange reaction

$$\begin{aligned} &2MgAl_2O_4\ (spn) + Fe_2SiO_4\ (olv) \\ &\quad = 2FeAl_2O_4\ (spn) + Mg_2SiO_4(olv) \end{aligned} \tag{6}$$

if the assemblage is in *local equilibrium*. Under this special condition the chemical potentials of SiO_2, Al_2O_3, FeO and MgO are uniquely defined by application of the Gibbs–Duhem theorem, which requires μ_{SiO_2}, $\mu_{Al_2O_3}$, μ_{FeO}, μ_{MgO} to satisfy *simultaneously*:

$$\begin{aligned} \mu^{spn}_{MgAl_2O_4} &= \mu_{MgO} + \mu_{Al_2O_3} \\ \mu^{spn}_{FeAl_2O_4} &= \mu_{FeO} + \mu_{Al_2O_3} \\ \mu^{olv}_{Mg_2SiO_4} &= 2\mu_{MgO} + \mu_{SiO_2} \\ \mu^{olv}_{Fe_2SiO_4} &= 2\mu_{FeO} + \mu_{SiO_2} \\ \mu^{qtz}_{SiO_2} &= \mu_{SiO_2} \end{aligned} \tag{7}$$

because exchange equilibrium (Eq. (6)) dictates that

$$2\mu^{spn}_{FeAl_2O_4} + \mu^{olv}_{Mg_2SiO_4} - 2\mu^{spn}_{MgAl_2O_4} - \mu^{olv}_{Fe_2SiO_4} = 0 \tag{8}$$

Values of chemical potentials consistent with Eqs. (7) and (8) may be used to construct the Gibbs free energy (and related thermodynamic properties) of a hypothetical omni-component phase, whose composition is equivalent to the bulk composition of the system. This omni-component phase may in turn be utilized to evaluate saturation state conditions for other potential phases that might populate the system at equilibrium, e.g. orthopyroxene. If all possible potential phases are undersaturated relative to this hypothetical omni-component phase, then the true equilibrium assemblage has been found. If not, the indicated supersaturated phase may be introduced to the assemblage, the Gibbs free energy minimized, which will place the revised assemblage in exchange equilibrium, and the properties of a new hypothetical omni-component phase computed, from which, the true global equilibrium state of the system may be reevaluated. This process is robust, in the sense that from any initial guess to the compositions and proportions of phases in a system, an omni-component phase can be constructed for each local equilibrium step to the global minimum, and the convergence of local minima to the global minimum can be evaluated to verify the uniqueness of the final assemblage.

4. COMMENTS AND CONCLUSIONS

The saturation state algorithm described in this paper can always be applied to test for attainment of the global minimum in the energy of a thermodynamic system. In practice, a test for global convergence of this kind should always be applied in every calculation whose aim is to establish the identity and proportions of phases in an equilibrium assemblage. Such testing is performed by the MELTS family of calculators (Ghiorso and Sack, 1995; Ghiorso et al., 2002; Gualda et al., 2012) as well as PhasePlot (phasePlot.org), which operates on thermodynamic data/model collections that may not contain an explicit omni-component phase. The algorithms of Brown and Skinner (1974), Connolly and Kerrick (1987), Voňka and Leitner (1995), and Tirone et al. (2009) also implement tests to guarantee that all potential solution phases are present in the final equilibrium phase assemblage. Failure to implement saturation surface checking of the kind described here can lead to apparent equilibrium phase assemblages that are in reality metastable. In particular, algorithmic procedures for the computation of phase equilibrium that are initialized by inclusion of all possible phases, and proceed by adjusting phase composition and proportions and discarding unstable phases en route to an energy minimum, may not attain the global minimum. The numerical procedures described by Connolly (1990) and Stixrude and Lithgow-Bertelloni (2011) fail to perform saturation state testing and potentially may pre-maturely converge to a metastable assemblage. The saturation state of all discarded phases must be evaluated prior to a declaration that the equilibrium assemblage has been achieved, as there is no guarantee that a phase discarded once may not re-stabilize again after other phase composition/proportion adjustments take place. The computational path to equilibrium is irreversible and littered with local minima ready to fool the unsuspecting numerical algorithm into a false sense of security. Only in the case of pure component phases will the minima found always be unique and global. Computational procedures in systems containing solution phases should always employ checks to insure global convergence. Fortunately, as every model thermodynamic system in exchange equilibrium either posses intrinsically or can be made to represent an omni-component phase, the algorithm described in this paper may be utilized to perform these tests and establish definitively the global equilibrium state of the system.

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