



The geodynamic equation of state: What and how

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[1] Geodynamic models commonly assume equations of state as a function of pressure and temperature. This form is legitimate for homogenous materials, but it is impossible to formulate a general equation of state for a polyphase aggregate, e.g., a rock, as a function of pressure and temperature because these variables cannot distinguish all possible states of the aggregate. In consequence, the governing equations of a geodynamic model based on a pressure-temperature equation of state are singular at the conditions of low-order phase transformations. An equation of state as a function of specific entropy, specific volume, and chemical composition eliminates this difficulty and, additionally, leads to a robust formulation of the energy and mass conservation equations. In this formulation, energy and mass conservation furnish evolution equations for entropy and volume and the equation of state serves as an update rule for temperature and pressure. Although this formulation is straightforward, the computation of phase equilibria as a function of entropy and volume is challenging because the equations of state for individual phases are usually expressed as a function of temperature and pressure. This challenge can be met by an algorithm in which continuous equations of state are approximated by a series of discrete states: a representation that reduces the phase equilibrium problem to a linear optimization problem that is independent of the functional form used for the equations of state of individual phases. Because the efficiency of the optimization decays as an exponential function of the dimension of the function to be optimized, direct solution of the linearized optimization problem is impractical. Successive linear programming alleviates this difficulty. A pragmatic alternative to optimization as an explicit function of entropy and volume is to calculate phase relations over the range of pressure-temperature conditions of interest. Numerical interpolation can then be used to generate tables for any thermodynamic property as a function of any choice of independent variables. Regardless of the independent variables of the governing equations, a consistent definition of pressure, and the coupling of equilibrium kinetics to deformation, is only possible if the continuity equation accounts for dilational strain.

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1. Introduction

[2] For decades phase equilibria have been accounted for in geodynamic models by parameterizations that permit separation of chemical and nonchemical energetic effects [e.g., *Richter*, 1973; *Christensen and Yuen*, 1985; *Connolly and Thompson*, 1989; *Tackley et al.*, 1993; *Podladchikov et al.*, 1994]. This artificial separation has led to formulations of the energy and continuity equations that are not well suited to models in which equilibria are evaluated from continuous equations of state [e.g., *Petrini et al.*, 2001; *Gerya et al.*, 2001; *Rupke et al.*, 2002], a possibility that has become practical with advances in computational methods [e.g., *Saxena and Eriksson*, 1983; *Wood and Holloway*, 1984] and the availability of thermodynamic data [e.g., *Holland and Powell*, 1998; *Stixrude and Lithgow-Bertelloni*, 2005; *Xu et al.*, 2008]. In particular, geodynamic models commonly presume an equation of state as a function of temperature (T), pressure (P), and chemical composition (m_1, \dots, m_{k-1}). This assumption is legitimate in homogeneous systems, but in heterogeneous systems, the T – P coordinates of coexisting phases degenerate during discontinuous phase transformations. This degeneracy gives rise to a singularity known as the Stefan problem, which can only be resolved exactly by the introduction of cumbersome internal boundary conditions [e.g., *Oezisik*, 1993]. In practice this solution is rarely implemented; instead, the energy consumption and dilational strain due to phase transformations are accounted for by ad hoc approximations [*Richter*, 1973] or costly iterative techniques [*Connolly*, 1997; *Tirone et al.*, 2009]. An equation of state as a function of the relative proportions of extensive properties, i.e., specific entropy (s) and volume (v), and chemical composition, eliminates these difficulties because all phase transformations are continuous in terms of these variables. These concepts are reviewed here with the goal of persuading geodynamicists that the s – v – m formulation is not only practical, but more efficient than the T – P – m formulation.

[3] There seem to be no examples of an s – v – m equation of state being used to close the governing equations of a geodynamic model, but s – P – m formulations in which energy conservation is reformulated as an entropy advection equation are not uncommon [e.g., *Glatzmaier*, 1988]. A recent example [*Hebert et al.*, 2009], couples the geodynamic governing equations to computed multicomponent phase equilibria to evaluate mantle dynamics with mass transfer under the assumptions that mass transfer is reversible and isochoric, the latter assumption

requiring that pressure be equated to load. Although the phase equilibrium solver [*Ghiorso and Kelemen*, 1987] used by *Hebert et al.* [2009] computes equilibria as a function of s – P – m coordinates, it does so by iterative solution of a T – P – m formulation that cannot be used to characterize low-variance phase fields in which pressure and temperature partial derivatives are not defined. The s – P – m formulation is essentially the enthalpy method of chemical engineering [*Oezisik*, 1993], which has been applied to geodynamic models with parameterized phase equilibria [*Katz*, 2008].

[4] The equation of state of a heterogeneous system provides a map of the systems thermodynamic properties as a function of its independent state variables. This map is obtained by finding the combination of the phases that optimize the appropriate thermodynamic energy function. The optimized energy is thus the desired equation of state and in the geodynamic case is the specific internal energy $u(s, v, m_1, \dots, m_{k-1})$. Such an optimization is more complicated than typical phase equilibrium problems, wherein the specific Gibbs energy $g(m_1, \dots, m_{k-1})$ is optimized at constant temperature and pressure, because of the increased dimension of the problem and because conventional compilations of thermodynamic data do not provide explicit functions for $u(s, v, m_1, \dots, m_{k-1})$. Thus, although the geodynamic implementation of the s – v – m formulation is more efficient than the conventional T – P – m formulation, the optimization necessary to construct the requisite equation of state poses technical difficulties. A secondary goal of this paper is to address these difficulties.

[5] The phase equilibrium problem is generic, but the type of problem to be attacked makes distinctly different demands on its solver. Geochemical and petrological problems often require resolution of components present in concentrations that span many orders of magnitude, but because the results are of primary interest, human expertise can be invoked to steer the solver to the correct result. In contrast, geodynamical and geophysical applications typically require resolution of only major chemical components, but because the results are often used within computationally intensive models, it is desirable to avoid solvers that require human interaction. In view of this distinction, *Connolly* [2005] advocates an algorithm proposed by *White et al.* [1958] that solves a linearized formulation of the phase equilibrium problem for geodynamic applications. A unique virtue of the linearization, which is of particular relevance here,

is that it can be used to extract $u(s, v, m_1, \dots, m_{k-1})$ for a heterogeneous system even if the equations of state for the individual phases are expressed as a function of a different set of state variables [Connolly, 1990]. The weakness of the linearized formulation is that its cost increases exponentially with the dimension of the optimization problem. An iterative linearized optimization strategy that results in orders of magnitude increases in speed and accuracy is introduced here as a means of reducing this cost. This strategy was implemented in the *Perple_X* computer program [Connolly, 2005] in late 2006, in the interim it has been applied in numerous geodynamic studies that make use of the T – P – m formulation. The description of the strategy here serves the additional purpose of documenting the algorithm.

[6] Section 2 of this paper is a review of elementary thermodynamic principles that is intended to clarify the concept of an equation of state for a heterogeneous system as well as the nature and choice of state variables. Section 3 outlines the optimization problem that must be solved to obtain the equation of state and the algorithm advocated for this purpose, and sections 4 and 5 address the manner in which the equation of state can be implemented in geodynamic models.

2. What: Equations of State

[7] The complete differential of the internal energy of a hydrostatic system in the reversible limit is usually written

$$dU = TdS - PdV + \sum_i^k \mu_i dM_i \quad (1)$$

where T , S , P and V are temperature, entropy, pressure and volume, respectively, and μ_i and M_i are the chemical potential and mass of the k independently variable kinds of mass in the system of interest (see Table 1 for a summary of notation). Equation (1) may be expressed more succinctly [e.g., Callen, 1960; Hillert, 1985] as

$$dU = \sum_i^{k+2} \theta_i d\Psi_i \quad (2)$$

where the intensive differential coefficients are defined in terms of the independent extensive variables by the relation

$$\theta_i \equiv \frac{\partial U}{\partial \Psi_i}. \quad (3)$$

As the properties $\theta_1, \dots, \theta_{k+2}$ are gradients in energy with respect to properties $\Psi_1, \dots, \Psi_{k+2}$ they are referred to here as potentials [Hillert, 1985]; thus, T , $-P$, and μ_i are the potentials for the transfer of S , V , and M_i , respectively. For any real process, the second law of thermodynamics requires

$$dU < \sum_i^{k+2} \theta_i d\Psi_i. \quad (4)$$

It follows that a system must be in a state of stable equilibrium, i.e., a state in which no macroscopic processes are possible, if all its variables have extremal values. Gibbs exploited this requirement with his minimum energy stability criterion

$$dU_{\Psi_1, \dots, \Psi_{k+2}} > 0, \quad (5)$$

which, if true for all variations in state at constant $\Psi_1, \dots, \Psi_{k+2}$, is sufficient to demonstrate stability. An unfortunate consequence of this logic is that it appears to suggest, in violation of energy conservation, that if a system is unstable it may lower its energy at constant $\Psi_1, \dots, \Psi_{k+2}$. For this reason, the maximum entropy criterion is preferable from a didactic perspective. Despite this advantage, energy criteria are used here because they allow a more compact formulation.

[8] When the independent variables of the Gibbs differential (equation (3)) are inconvenient, the Legendre transform

$$\Omega \equiv U - \sum_{i=n+1}^{k+2} \Psi_i \theta_i \quad (6)$$

combined with the Gibbs differential yields a free energy function in the variables $\Psi_1, \dots, \Psi_n, \theta_{n+1}, \dots, \theta_{k+2}$,

$$d\Omega = \sum_{i=1}^n \theta_i d\Psi_i - \sum_{i=n+1}^{k+2} \Psi_i d\theta_i \quad (7)$$

that measures the maximum amount of energy that can be extracted from a system at constant $\theta_{n+1}, \dots, \theta_{k+2}$. The common forms of Ω are the Helmholtz energy $A(T, V, M_1, \dots, M_k)$, the enthalpy $H(S, P, M_1, \dots, M_k)$, and the Gibbs energy $G(T, P, M_1, \dots, M_k)$; and the internal energy $U(S, V, M_1, \dots, M_k)$ is recovered from equation (7) if $n = k + 2$. Given $\Omega(\Psi_1, \dots, \Psi_n, \theta_{n+1}, \dots, \theta_{k+2})$, the properties corre-

Table 1. Frequently Used Notation

Symbol	Meaning
A, a	extensive and specific Helmholtz energy
c	number of independent conservative extensive properties
e_Ψ	unit quantity of property Ψ
G, g	extensive and specific Gibbs energy
H, h	extensive and specific enthalpy
k	number of independent kinds of mass
M, m	extensive and specific mass
n	number of independent extensive properties
P	pressure
S, s	extensive and specific entropy
T	Temperature
U, u	extensive and specific internal energy
V, v	extensive and specific volume
x^j	relative amount of phase j , $\alpha^j/\alpha^{\text{system}}$
α	amount, defined by equation (22) or (26)
μ	chemical potential
θ	thermodynamic potential for property Ψ
Ψ	an extensive property
ψ	the specific property Ψ/α
$\bar{\psi}$	specific property with α as defined in equation (26)
Ω	extensive free energy, equation (7)
ω	specific free energy, equation (14) or (25)

sponding to the dependent differential coefficients of equation (7) are obtained as

$$\theta_i = \frac{\partial \Omega}{\partial \Psi_i}, \quad i = 1, \dots, n \quad (8)$$

and

$$\Psi_i = -\frac{\partial \Omega}{\partial \theta_i}, \quad i = n+1, \dots, k+2 \quad (9)$$

By the same logic used to obtain Gibbs' stability criterion (equation (5)), it follows from equations (4) and (7) that a system is in stable equilibrium if

$$d\Omega_{\Psi_1, \dots, \Psi_n, \theta_{n+1}, \dots, \theta_{k+2}} > 0 \quad (10)$$

is true for all variations in state. Although it is possible to express Ω as a function of any arbitrary choice of $k+2$ state variables, with the caveat that at least one variable must be extensive, equation (10) provides a stability criterion only at constant values for the independent variables of equation (7). For this reason the independent variables of equation (7) are considered to be the natural variables of the function Ω [Callen, 1960].

[9] A state of matter is distinguished by the relative proportions of its $k+2$ extensive attributes. These proportions define the thermodynamic composition of the matter and are designated specific variables

[de Groot and Mazur, 1984]. Specific variables are defined as

$$\psi_i \equiv \frac{\Psi_i}{\alpha}, \quad u \equiv \frac{U}{\alpha}, \quad \omega \equiv \frac{\Omega}{\alpha} \quad (11)$$

where α is an arbitrarily chosen extensive property or linear combination of extensive properties (e.g., total mass). From equation (11), the total variation in energy may be expressed as the sum of variations due to changes in state and amount

$$dU = \alpha du + u d\alpha \quad (12)$$

thus, the specific energy is formally an equation of state. At constant amount, from equations (2), (11), and (12), the variation in the specific energy due to a reversible change in state is

$$du = \sum_{i=1}^{k+2} \theta_i d\psi_i. \quad (13)$$

Although the right-hand side of equation (13) has $k+2$ differentials, only $k+1$ of the differentials are independent; as only $k+1$ independent proportions can be formed from the $k+2$ independent extensive properties of equation (2). Thus, u is a function of $k+1$ specific properties, i.e., $u(\psi_1, \dots, \psi_{k+1})$. The specific free energy function

$$d\omega = \sum_{i=1}^n \theta_i d\psi_i - \sum_{i=n+1}^{k+2} \psi_i d\theta_i \quad (14)$$

is the Legendre transform of equation (13). As in the case of u , for a variation in state at constant amount, only $k+1$ of the differentials on the right-hand side of equation (14) are independent, i.e., $\omega(\psi_1, \dots, \psi_{n-1}, \theta_{n+1}, \dots, \theta_{k+2})$. With the proviso that the amount α is defined as a function of Ψ_1, \dots, Ψ_n , or a subset of these properties, and that $n > 0$, then from equations (10) and (11)

$$d\omega_{\psi_1, \dots, \psi_{n-1}, \theta_{n+1}, \dots, \theta_{k+2}} > 0 \quad (15)$$

for all variations from a stable state at constant amount.

2.1. State of a Heterogeneous System

[10] The parts of an equilibrium system may differ in state. All parts in the same state constitute a phase of the system. Gibbs [1957] demonstrated that in an equilibrium system the potential θ_i must be the same in all phases where Ψ_i is a possible attribute. Thus, in contrast to specific variables, the

potentials θ_i cannot distinguish equilibrium phases and are only characteristic of the entirety of an equilibrium system. Gibbs' argumentation not only demonstrated the necessity for the uniformity of the potentials, but also requires that the number of phase states in an equilibrium system is

$$p \leq k + 2 \quad (16)$$

a condition known as the Gibbs phase rule. From equation (15), the relative amounts of the phases of a stable system minimize

$$\omega^{\text{system}} = \sum_{j=1}^p x^j \omega^j \quad (17)$$

at constant $\theta_{n+1}, \dots, \theta_{k+2}$ subject to the imposed constraints

$$\psi_i^{\text{system}} = \sum_{j=1}^p x^j \psi_i^j, \quad i = 1, \dots, n \quad (18)$$

where the relative amounts of the phases $x^j = \alpha^j / \alpha^{\text{system}}$ sum to unity and are subject to the physical constraint

$$1 \geq x^j \geq 0, \quad j = 1, \dots, p. \quad (19)$$

Thus, the equilibrium properties and phase relations of a system can be mapped by finding the phase assemblage that minimizes ω as a function of the variables $\psi_1, \dots, \psi_{n-1}, \theta_{n+1}, \dots, \theta_{k+2}$. From equations (17) and (18), such a map is an indirect representation of $\omega(\psi_1, \dots, \psi_{n-1}, \theta_{n+1}, \dots, \theta_{k+2})$ in that this function can be recovered given knowledge of the relative amounts and state of a systems

constituent phases. For a system in which all phases have the same chemical composition (i.e., $k = 1$), and defining specific properties such that $\alpha \equiv M$, there are four such maps corresponding to the natural variables of the specific internal energy ($n = 3, u(s, v)$), enthalpy ($n = 2, h(s, P)$), Helmholtz ($n = 2, a(T, v)$) and Gibbs ($n = 1, g(T, P)$) free energy functions (Figure 1). The resulting $k + 1$ dimensional map is composed of phase fields that identify the stable phase assemblage of the system as a function of the map variables. As the state of a system is defined via equations (17) and (18), if the relative amounts and

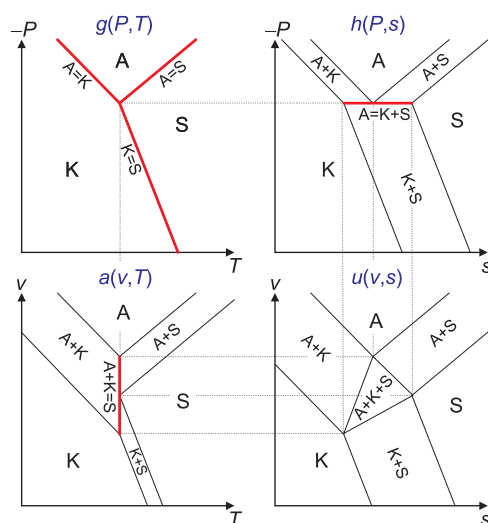


Figure 1. Schematic phase relations (A, andalusite; K, kyanite; S, sillimanite) of the Al_2SiO_5 ($k = 1$) system, with specific variables defined by $\alpha \equiv M_{\text{Al}_2\text{SiO}_5}$, as a function of the natural variables of the internal energy ($n = 3, u(s, v)$) and the enthalpy ($n = 2, h(s, P)$), Helmholtz ($n = 2, a(T, v)$) and Gibbs ($n = 1, g(T, P)$) free energy functions. Because the P – T – μ coordinates of coexisting phases are identical, phase fields of $p > n$ phases become geometrically degenerate (heavy red lines) if mapped as a function of one or more potentials. In these phase fields the state of the system is not defined because the relative amounts of the phases cannot be established from the map (or the corresponding energy function). In the case that a degenerate field involves $n + 1$ phases, the field is said to represent a first-order, or discontinuous, phase transformation. If a first-order phase transformation occurs at constant Ψ_1, \dots, Ψ_n , then the proportions of the phases are constrained to vary according to a unique reaction equation that balances the quantities Ψ_1, \dots, Ψ_n and Ω among the coexisting phases. In the T – P map there are three first-order transformations corresponding to reactions that balance mass and Gibbs energy, whereas in the s – P and T – v maps there is only one first-order transformation which corresponds to the degenerate 3-phase field of the P – T map. In the s – P map, the corresponding reaction ($A = K + S$) balances mass, entropy, and enthalpy and in the T – v map the reaction ($K = A + S$) balances mass, volume, and Helmholtz energy. Such singularities cannot occur in the s – v map because the coordinates are sufficient to resolve the maximum number ($k + 2$) of phases that may coexist in an equilibrium system; for this reason $u(s, v, m_1, \dots, m_{k-1})$ is the only equation of state for heterogeneous systems. This example demonstrates that the classification of phase transformations as discontinuous or continuous is not based on any intrinsic attribute of the transformation, but rather is dependent on the boundary conditions (i.e., whether Ψ_i or θ_i is independently controlled) assumed for a given thermodynamic system. Thus, if discontinuous phase transformations give rise to difficulties in solving the governing equations of a geodynamic model, then the simplest solution is to adopt a thermodynamic formulation that eliminates them, i.e., by mapping phase relations as a function of the internal energy.

state of its constituent phases are known, the state of the system is defined in fields where $p \leq n$ phase coexist as the amounts of the phases must satisfy equation (18), i.e.,

$$\begin{vmatrix} \psi_1^p & \dots & \psi_1^p \\ \vdots & \ddots & \vdots \\ \psi_n^1 & \dots & \psi_n^p \end{vmatrix} \begin{vmatrix} x^1 \\ \vdots \\ x^p \end{vmatrix} = \begin{vmatrix} \psi_1^{\text{system}} \\ \vdots \\ \psi_n^{\text{system}} \end{vmatrix}. \quad (20)$$

However, fields of $p > n$ phases are geometrically degenerate, with dimension $k + n + 1 - p$; thus, the amounts of the phases are not defined by the map and the state of the system is indeterminate. That this condition reflects a degeneracy in the underlying free energy function follows from the observation that if $p > n$ phases coexist then a phase transformation may occur at constant $\theta_1, \dots, \theta_{k+2}$ such that

$$d\psi_i^{\text{system}} = \sum_j \psi_i^j dx^j = 0, \quad i = 1, \dots, n$$

and as

$$d\omega^{\text{system}} = \sum_i \theta_i d\psi_i^{\text{system}} = 0, \quad (21)$$

ω cannot distinguish the possible states of the system and the dependent specific properties cannot be defined by differentiation of equation (14). Thus, while ω is an equation of state for a homogeneous system, it is only an equation of state for heterogeneous systems consisting of $p \leq n$ phases. In many geodynamic models such degeneracies are problematic because the mathematical formulations presume any specific property can be expressed via an equation of state as a continuous function of its conjugate potential, e.g., $s(T)$ or $v(P)$. The equation of state is then used to eliminate the specific property from the phenomenological equations with the result that the reformulated governing equation itself becomes singular at the conditions of a phase transformation involving $p > n$ phases. This problem, known as the Stefan problem [Oezisik, 1993], can be resolved approximately by iteration or exactly by the introduction of internal boundary conditions, but in cases where the phase transformations cannot be anticipated these methods are tedious. Because $u(\psi_1, \dots, \psi_{k+1})$ is continuous for all possible states, a simpler approach is to employ the sole legitimate equation of state, u , and to leave the phenomenological equations in their original form. The key obstacle to this approach is to find an effective strategy for establishing $u(\psi_1, \dots, \psi_{k+1})$.

2.2. Amount

[11] The only constraint on the definition of amount is that it must be an extensive property, i.e., a first-order homogeneous function; thus, amount is most easily defined by taking $\alpha \equiv \Psi_n$. However, the nondimensional definition

$$\alpha \equiv \sum_i^n \Psi_i / e_{\Psi_i} \quad (22)$$

where e_{Ψ_i} is a unit quantity of Ψ_i and

$$\sum_i^n \Psi_i / e_{\Psi_i} = 1 \quad (23)$$

has the advantage that it is possible to choose the independent properties Ψ_1, \dots, Ψ_n so that all the states of a system at constant $\theta_{n+1}, \dots, \theta_{k+2}$ can be represented on a $n - 1$ dimensional simplex with vertices at $\psi_1/e_{\Psi_1}, \dots, \psi_n/e_{\Psi_n}$ [Connolly, 1990]. Such representations define the physical composition of matter in a way that is directly analogous to the triangular and tetragonal diagrams used in petrology to describe the composition of ternary and quaternary chemical systems. When amount is defined as in equation (22), the dependent differential in equation (14) is

$$d\psi_n = -e_{\Psi_n} \sum_i^{n-1} d\psi_i / e_{\Psi_i} \quad (24)$$

and equation (14) may be rearranged as

$$d\omega = \sum_{i=1}^{n-1} \left(\theta_i - \frac{e_{\Psi_i}}{e_{\Psi_n}} \theta_n \right) d\psi_i - \sum_{i=n+1}^{k+2} \psi_i d\theta_i \quad (25)$$

From equation (25), it follows that if $\omega(\psi_1, \dots, \psi_{n-1})$ is plotted as above its simplicial coordinates $\psi_1/e_{\Psi_1}, \dots, \psi_{n-1}/e_{\Psi_{n-1}}$, then the ω coordinate of a tangent to $\omega(\psi_1, \dots, \psi_{n-1})$ at $\psi_i/e_{\Psi_i} = 1$ is equal to $\theta_i e_{\Psi_i}$ (Figure 2).

[12] Because the definition of amount provided by equation (22) is symmetrical with respect to the independent specific variables it is convenient for discussion of the optimization problem. However, in practice it is preferable to define amount

$$\alpha \equiv \sum_i^c \Psi_i / e_{\Psi_i} \quad (26)$$

in terms of the c conservative material properties of the representative element of a physicochemical system. For example, it is common that the

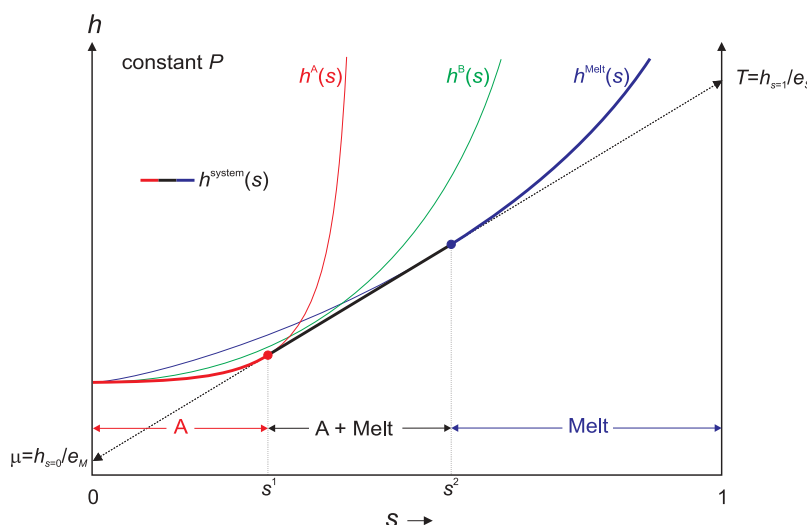


Figure 2. The phase equilibrium problem at constant pressure and specific entropy s^{sys} for an isochemical system ($k = 1$) in which the possible states of matter are described by three equations of state $h^A(s)$, $h^B(s)$, and $h^{\text{Melt}}(s)$. For specific entropy defined by equations (11) and (22), the third law of thermodynamics requires that all states degenerate at $s = 0$ (i.e., $T = 0$ K); the illustration is otherwise generic to problems with $n = 2$ at constant $\theta_{n+1}, \dots, \theta_{k+2}$ assuming the identities $\omega = h$, $\psi_1 = s$. The minimum enthalpy surface of the system (heavy curves) is the isobaric equation of state for the system and coincides with $h^A(s)$ for $s \leq s^1$; thus, for these conditions the stable state consists of one phase described by $h^A(s)$. Likewise, as the surface coincides with $h^{\text{Melt}}(s)$ for $s \geq s^2$ the system is composed entirely of melt. For $s^1 < s < s^2$, the minimum h surface is simultaneously tangent to $h^A(s)$ and $h^{\text{Melt}}(s)$ and corresponds to states in which phases described by $h^A(s)$ and $h^{\text{Melt}}(s)$ with entropies of s^1 and s^2 , respectively, stably coexist. For these states, $s^{\text{sys}} = x^A s^1 + (1 - x^A) s^2$ and $h^{\text{sys}} = x^A h^1 + (1 - x^A) h^2$, where h^1 and h^2 are the h coordinates of the minimum h surface at s^1 and s^2 , x^A is the relative amount of phase A, and $x^{\text{Melt}} = 1 - x^A$. From equation (25), if a tangent to any point along the minimum enthalpy surface is extrapolated to $s = 1$, then the value of its h coordinate is the temperature of the state; likewise, the value of the h coordinate at $s = 0$ is the chemical potential of the state. This construction illustrates the origin of the Stefan problem in that if the stable system is heated (isobarically), its temperature and chemical potential will remain constant between s^1 and s^2 ; it follows that the isobaric isothermal free energy function $g(T, P) = \mu$ cannot discriminate between these states. An equivalent formulation of the phase equilibrium problem is to maximize s at specified h .

representative elements of geodynamic models are isochemical, i.e., closed with respect to mass, but open with respect to entropy and volume, in which case the c conservative properties are the k chemically distinct kinds of mass. The advantage of this form is that the specific internal energy is

$$d\bar{u} = \sum_{i=1}^{c-1} \left(\theta_i - \frac{e_{\psi_i}}{e_{\psi_c}} \theta_c \right) d\bar{\psi}_i + \sum_{i=c+1}^{k+2} \theta_i d\bar{\psi}_i \quad (27)$$

where the bar superscript distinguishes specific properties defined by equations (11) and (26), and the potentials of primary geodynamic interest are

$$\frac{\partial \bar{u}}{\partial \bar{\psi}_i} = \theta_i, \quad i = c + 1, \dots, k + 2. \quad (28)$$

In the context of the geodynamic application $d\bar{\psi}_1 = \dots = d\bar{\psi}_c = 0$; therefore, the functional form of the equation of state may be abbreviated as $\bar{u}(\bar{\psi}_{c+1}, \dots,$

$\bar{\psi}_{k+2})$, e.g., $\bar{u}(\bar{s}, \bar{v})$ for an isochemical representative element.

2.3. Pressure and Nonhydrostatic Systems

[13] An inconsistency between chemical thermodynamics and geodynamics is that the former typically assumes hydrostatic conditions, whereas the primary concern of the latter is the understanding of a nonhydrostatic process, i.e., shear deformation. In principle, this inconsistency can be resolved by formulating an equation of state in terms of the elastic deviatoric strain tensor in addition to the specific volume, which is used to characterize mechanical state in the hydrostatic case [Callen, 1960; Stixrude and Lithgow-Bertelloni, 2005]. If thermodynamic equilibrium prevails, then the dilational deformation is effectively time-independent because the time scale for chemical equilibration is much greater than that for molecular relaxation [Batchelor, 2005], i.e., bulk viscos-

ity is effectively infinite. Thus, for viscoelastic rheologies dilation must be elastic, whereas dilation resulting from nonassociated plasticity (e.g., pressure dependent yielding) is more complex because it occurs as a consequence of shear deformation [Hill, 1950]. Regardless of the details of the irreversible rheology, mean stress can only be affected via the dependence of the equation of state on elastic deviatoric strain, thus, if this strain has no significant effect on phase relations, the mean stress and compressibility of a system is only a function of the state variables used to define the hydrostatic equation of state. For a Hookean elastic equation of state, the deviatoric strain energy of an isotropic system is

$$\delta u^{\text{strain}} = \bar{v}_0 \left(\left\{ \frac{8G_S}{3} - K_S \right\} \cdot [\varepsilon_{11}^2 + \varepsilon_{33}^2 + \varepsilon_{11}\varepsilon_{33}] + G_S[\varepsilon_{12}^2 + \varepsilon_{13}^2 + \varepsilon_{23}^2] \right) \quad (29)$$

where \bar{v}_0 is the volume of the unstrained state, K_S and G_S are the adiabatic bulk and shear moduli, respectively, and the ε_{ij} are the independent components of the deviatoric elastic strain tensor. Approximating G_S as $K_S/3$, if elastic strain is small compared to irreversible strain, and the independent components of the stress tensor are of the order of $\Delta\sigma$, then equation (29) is

$$\delta u^{\text{strain}} \approx \frac{15\bar{v}_0}{4K_S} \Delta\sigma^2 \quad (30)$$

Taking parameters for forsterite for purposes of illustration ($K_S = 128$ GPa, $\bar{v}_0 = 43$ J/MPa [Xu *et al.*, 2008]), demonstrates that deviatoric stresses of ~ 1 GPa are necessary to generate elastic strain energies comparable to error in the reference energy of forsterite (~ 3 kJ/mol [Xu *et al.*, 2008]), an unusually well characterized phase. Thus, it is reasonable to conclude that under ordinary geodynamic conditions strain energy is insignificant and the pressure or mean stress can be computed from a hydrostatic equation of state.

[14] The foregoing analysis presumes that the representative element of geodynamic models is appropriate for the resolution of the grain-scale processes of thermodynamic equilibration. This presumption is the most tractable basis for incorporating phase equilibria in many geodynamic problems. Exceptions to this generalization are porous media problems in which kinetic effects result in distinct pressure fields for the solid matrix and low-viscosity interstitial fluid. Dahlen [1992] notes that in this case, the most reasonable model is

to assume that phase equilibria involving the fluid are governed by the pressure of the fluid. Rigorous treatment of such problems would entail the use of a separate equation of state for the fluid and solid matrix. Dahlen's [1992] logic can be used to justify approximating the pressure used for purposes of computing phase equilibria to the vertical load in systems where a hydrostatic interstitial fluid is connected to the Earth's surface. This assumption is reasonable at depths within the Earth of ~ 10 km, but at greater depths the pressure of a hydrostatic interstitial fluid may take on any value between those of the principal tectonic stresses [Connolly and Podladchikov, 2004]. Failing additional information in such circumstances, the most plausible model for the phase equilibrium pressure is the mean stress, i.e., the mechanical pressure.

[15] The density effects of phase transformations are often accounted for in geodynamic problems by the Boussinesq approximation [Batchelor, 2005] because many geodynamic codes for large-scale deformation presume incompressible flow. A consequence of this approximation is that the effect of phase transformations on pressure cannot be evaluated and the pressure for phase equilibrium computations is taken as the mean stress or, more commonly, the vertical load. While such approximations may be adequate for certain geodynamic purposes, they are thermodynamically inconsistent. This inconsistency can only be resolved by formulations that rigorously account for dilational deformation.

3. How: The Optimization Problem

[16] The phase equilibrium problem, summarized by equations (17)–(19), is to find the relative amounts and states of the phases that minimize the energy of a system at constant $\psi_1, \dots, \psi_{n-1}$, $\theta_{n+1}, \dots, \theta_{k+2}$ given equations of state that describe all potentially stable phases of the system. This problem is nonlinear because a single equation of state may describe as many as $k + 2$ phases, and neither the identity nor the states of the stable phases are known at the outset. While numerous nonlinear optimization strategies have been implemented for geoscientific problems (for a brief review, see Connolly [2005]), nonlinear strategies tend to be costly, numerically unstable and require starting guesses to assure convergence to the correct result. For these reasons, these methods are not well suited for computationally intensive geodynamic models. Additionally, nonlinear strategies require that the equations of state are functions of

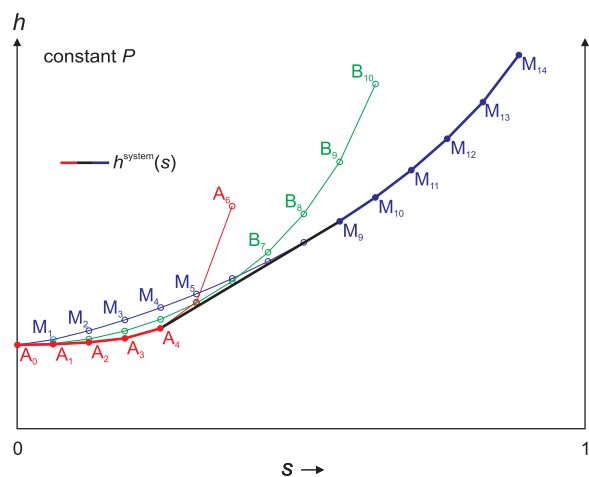


Figure 3. The linearized approximation of the phase equilibrium problem illustrated in Figure 2. Equations of state $h^A(s)$, $h^B(s)$, and $h^{\text{Melt}}(s)$ are represented by finite sets of states generated by incrementing s by δ_s . For a system with specified s , the stable state is obtained by finding the set of discrete states that minimizes the enthalpy. If the set of discrete states include two or more states corresponding to a single equation of state, the spacing of the states can be used to establish whether the states represent more than one real phase. For example, for s intermediate between A_2 and A_3 the fact that these states differ by the increment δ_s can be used to infer that within the resolution of the approximation the true state of the system would be a homogeneous phase described by $h^A(s)$. The discretization need not be done at constant δ_s ; thus, if the equations of state are known only as analytic functions of temperature, $h^A(T)$, $h^B(T)$, and $h^{\text{Melt}}(T)$ may be discretized as a function of temperature. Regardless of the variable used for discretization, the optimization returns the equation of state $h^{\text{system}}(s)$.

$\psi_1, \dots, \psi_{n-1}, \theta_{n+1}, \dots, \theta_{k+2}$. This requirement creates a practical difficulty in that equation of state parameterizations provided in thermodynamic databases are almost invariably for the natural variables of the specific Gibbs energy $g(T, P, m_1, \dots, m_{k-1})$; and while a Legendre transform of $g(T, P, m_1, \dots, m_{k-1})$ yields any desired state function, it does so in terms of the natural variables of g , e.g., from $\bar{g}(T, P)$ and equation (6)

$$\bar{u}(T, P, m_1, \dots, m_{k-1}) = \bar{g} - T \frac{\partial \bar{g}}{\partial T} - P \frac{\partial \bar{g}}{\partial P}. \quad (31)$$

Provided the partial derivatives in equation (31) are unique, it is possible to obtain $u(s, v, m_1, \dots, m_{k-1})$ by iteratively optimizing a function of $g(T, P, m_1, \dots, m_{k-1})$ [Ghiorso and Kelemen, 1987]. However, such a strategy fails for low-variance phase equilibria where the partial derivatives are undefined, e.g., the two- and three-phase fields of the aluminosilicate phase diagram (Figure 1).

[17] Linearization of the phase equilibrium problem offers a means of circumventing the difficulties endemic to nonlinear solvers. In the linearized formulation the continuous spectrum of states defined by each equation of state is approximated by a finite number of discrete phase states. The approximated problem is thereby reduced to the linear optimization problem of finding the amount of matter in each discrete state that minimizes

$$\omega^{\text{system}} = \sum_{j=1}^{\Pi} x^j \omega^j$$

at constant $\theta_{n+1}, \dots, \theta_{k+2}$ subject to the constraints

$$\begin{aligned} \psi_i^{\text{system}} &= \sum_{j=1}^{\Pi} x^j \psi_i^j, \quad i = 1, \dots, n \\ 1 \geq x^j &\geq 0, \quad j = 1, \dots, \Pi, \end{aligned}$$

where Π is the total number of phase states generated by discretization and, for an arbitrarily specified state of the system, the amounts of n discrete phase states are nonzero. If more than one discrete state of a phase described by the same continuous equation of state is stable, then within the resolution of the discretization the states that are adjacent in the $\psi_1, \dots, \psi_{n-1}$ parameter space correspond to a single phase state in the real problem; whereas discrete states that are separated by unstable states of the same phase represent distinct states of the same phase in the real problem (e.g., immiscible states).

[18] The primary virtues of the linearized formulation, which has been implemented in various incarnations of the Perple_X computer program, are its extraordinary simplicity and that an optimization algorithm (Simplex [White et al., 1958]) can be selected that assures convergence to a global extremum. A cryptic virtue of linearization that is of relevance here is that the discretization of phase states can be done as a function of any choice of independent variables (Figure 3); thus, it is possible to obtain the equation of state $u(s, v, m_1, \dots, m_{k-1})$ for a system even if the equations of state of the individual phases are expressed as $u(T, P, m_1, \dots, m_{k-1})$.

3.1. Iterative Refinement of the Linearized Problem

[19] The disadvantage of the linearized formulation is that discretization of the states of a phase with many compositional degrees of freedom generates a large number of potential phase states. To illustrate the magnitude of this problem, it is helpful

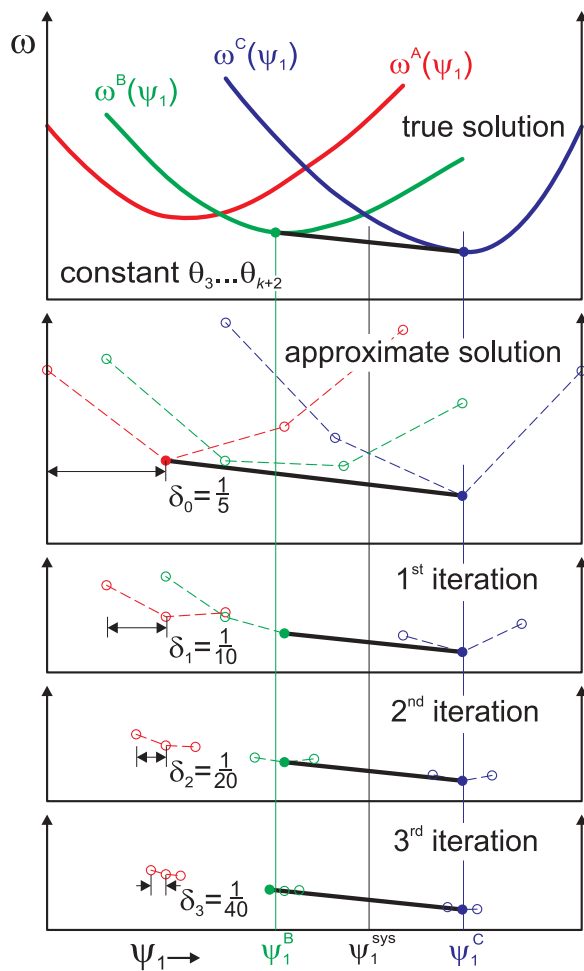


Figure 4. The strategy for the iterative refinement of a linearized problem in which ω is to be optimized at $\psi_1 = \psi_1^{\text{sys}}$ at constant $\theta_3 \dots \theta_{k+2}$. In the exact solution, the stable phases of the system are $\omega^B(\psi_1)$ at $\psi_1 = \psi_1^B$ and $\omega^C(\psi_1)$ at $\psi_1 = \psi_1^C$. The problem is initially linearized by representing the continuous equations of state $\omega^A(\psi_1)$, $\omega^B(\psi_1)$, and $\omega^C(\psi_1)$ by a finite set of states generated at increments of $\delta_0 = 1/5$ in ψ_1 . Because the initial resolution is poor, the solution for the initial approximation incorrectly identifies a phase described by $\omega^A(\psi_1)$ as stable. With iteration parameters $i_0 = 2$, $i_2 = 1$, and $\varepsilon = 0$, new states are generated in successive iterations with twice the resolution of the previous approximation around each stable state. Additionally, resolution is increased about the i_2 metastable states closest to the approximate solution; thus, refinement of the metastable discrete state of $\omega^B(\psi_1)$ identified in the initial resolution leads to the identification of the correct phases after one iteration. Successive iterations progressively improve the accuracy of the estimate for ψ_1^B , but the estimate for ψ_1^C does not change because the initial estimate is accurate within the resolution of the iteration scheme.

to define amount as in equation (22) in which case it is possible to define an $n - 1$ dimensional simplicial compositional space that includes all possible states of a given phase. Discretization of this space on a uniform Cartesian grid with spacing δ generates

$$\pi \approx \frac{1}{2} \left(\sum_{i=n-2}^{n-1} \frac{(l/\delta + 1)^i}{(i-1)!} + n - 1 + \sum_{i=1}^{n-1} \frac{(l/\delta - 1)^i (n-1)!}{(i!)^2 (n-1-i)!} \right). \quad (32)$$

phase states, where l is the length of the orthogonal axes. Thus, discretization of the entire composition space (i.e., $l = 1$) of a phase with eight variable chemical components resolved at $\delta = 10^{-2}$ would generate $\sim 10^{11}$ states, well beyond the limit of $\sim 10^6$ imposed by present-day computational standards (i.e., ~ 2 Gb of addressable memory). In previous applications [Connolly, 2005], this obstacle was circumvented by relying on expertise to restrict the range of the composition space considered for complex phases. The innovation introduced here is a strategy in which iterative refinement of the linearization is used to achieve resolution that is limited by machine precision rather than memory [White *et al.*, 1958].

[20] The refinement strategy begins with the solution of a low-precision linearization (Figure 4). In successive iterations, phase states that are highly unstable are eliminated and the precision of the linearization is increased in the vicinity of phase states that are stable or nearly stable. The necessity for refining nearly stable states is that phases initially identified as being metastable may become stable in subsequent iterations (Figure 4). In detail, if the initial precision is δ_0 , then in the m th iteration phase states are generated with precision

$$\delta_m = \frac{2\delta_0}{1 + \varepsilon_0} \left(\frac{1 + \varepsilon_0}{1 + i_0} \right)^m \quad (33)$$

on a grid with orthogonal axes of length

$$l_m = i_0 \delta_m \quad (34)$$

about each phase state retained from the previous iteration. The relative resolution of the grid l_m/δ_m in each iteration is constant and specified by the integer parameter i_0 . Algebraically, the real parameter ε_0 must be $< i_0$ and i_0 must be > 1 for iteration to increase resolution. Assuming that the precision of the linearization at any level is $\pm \delta$, setting $\varepsilon_0 = 0$ is adequate to assure that iteration converges to stable phase states. Despite this expectation, ε_0 is retained as a free parameter, of the order of the value for δ required to obtain the maximum desired resolution, to eliminate degeneracies that may arise by the

refinement of adjacent phase states. In the implementation of this scheme phase states are discretized on a regular Cartesian grid over the composition space or, if desired, on a conformal transformation [Roberts, 1970] of the composition space. Provision is made for the conformal transformation to permit accurate resolution of highly nonlinear equations of state; when such transformations are used, equation (32) gives the resolution of the conformal Cartesian grid and not the variable resolution of the true compositional variables.

[21] Discounting the minor influence of the ε_0 parameter, four parameters characterize the iteration scheme: δ_0 , the initial spacing for discretization; i_0 , the relative resolution in each iteration; i_1 , the maximum number of iterations; and i_2 , the number of metastable phase states to be refined in each iteration. For any desired final precision, these parameters may be chosen to optimize either speed or accuracy. Accuracy improves with precision and is limited by memory. To illustrate the choice of parameters in this case, consider the calculation of phase relations for an isobaric-isothermal closed chemical system with eight chemical components (i.e., $n = 8$) with $\Pi \sim 100$ possible phases all but one (e.g., a melt) of which are stoichiometric. Further, suppose memory limits the number of phase states that can be treated to $\pi \sim 10^6$ and the desired final precision is 10^{-5} . As there is only one phase state for each stoichiometric phase, the number of phase states under consideration is approximately the number of phase states used to represent the melt. Solving equation (31) with $\pi = 10^6$, $n = 8$, the initial precision is then $\delta_0 = 0.05$. In each iteration $n + i_2$ phase states are retained and in the worst case every one of these states may correspond to the nonstoichiometric phase. Thus, the number of phase states that can be used for the refinement of an individual phase state from the previous iteration is $\pi_i = \pi/(n + i_2)$, where i_2 is the number of metastable phase states to be refined. This result implies that refining metastable states ($i_2 > 0$) reduces the attainable relative precision for memory-limited problems. The negative consequences of this reduction must be weighed against the possibility that retaining these states may eliminate discretization errors (Figure 4). Thus, in practice i_2 is found by experiment, i.e., the parameter is increased until a threshold is reached beyond which the optimization results are not significantly affected. Such experimentation typically gives $i_2 < 10$; for the present example $i_2 = 2$ is assumed so that $\pi_i = 10^5$ and solving equation (32) for the relative resolution l/δ (i_0) yields $i_0 = 13$. For

$\delta_0 = 0.05$, $i_0 = 13$, and $i_2 = 2$, from equation (32) the integral number of iterations necessary to achieve a final precision of $\delta < 10^{-5}$ is 4, i.e., $i_1 = 4$.

[22] Because operation counts for linear programming algorithms are strongly dependent on the number of variables, for a given value of δ_0 , speed is optimized by minimizing the relative resolution of the iterative refinement (i.e., setting parameter $i_0 = 2$). Thus, for the example discussed above it would be faster to achieve the desired final precision with $i_1 = 9$ iterations with a relative resolution $i_0 = l_m/\delta_m = 2$, than $i_1 = 4$ iterations with a relative precision $i_0 = l_m/\delta_m = 14$. There is no algorithmic constraint on the resolution of the initial discretization ($1/\delta_0$); therefore, as with parameter i_2 , the optimal value must be determined by experiment. In this regard, because the initial discretization is static, the high cost of initializing the solver for the initial discretization can be eliminated by storing the data for the initial and the iteratively refined discretizations in separate arrays.

[23] The quantitative phase relations calculated by the algorithm for the Al_2SiO_5 system (Figure 5) are essentially those previously illustrated schematically (Figure 1), but extended to include melting. The Al_2SiO_5 system was chosen as an example because discontinuous phase transitions are prevalent in simple chemical systems; thus, paradoxically, simple chemical models, as often assumed in parameterizations of phase equilibria, are the most likely to lead to ill-conditioned geodynamic problems. The calculated phase relations provide a quantitative demonstration of the profound energetic and density effects of phase transformations, in that the variations in entropy and volume caused by the five 2-phase transformations are much greater than the variations within the three subsolidus 1-phase fields. Because the $\bar{s} - \rho$ coordinates of the representative elements of a geodynamic model vary continuously in response to heat flow and deformation, these effects imply that a $T - P$ phase equilibrium solver, or a solver that relies on $T - P$ partial derivatives, would fail more often than it would succeed for the subsolidus aluminosilicate system, i.e., such a solver would fail for the $\bar{s} - \rho$ conditions of any phase field for $k > p$ phases.

4. How: Putting Phase Equilibria Into Geodynamic Governing Equations

[24] To illustrate a closed geodynamic formulation based on the internal energy equation of state,

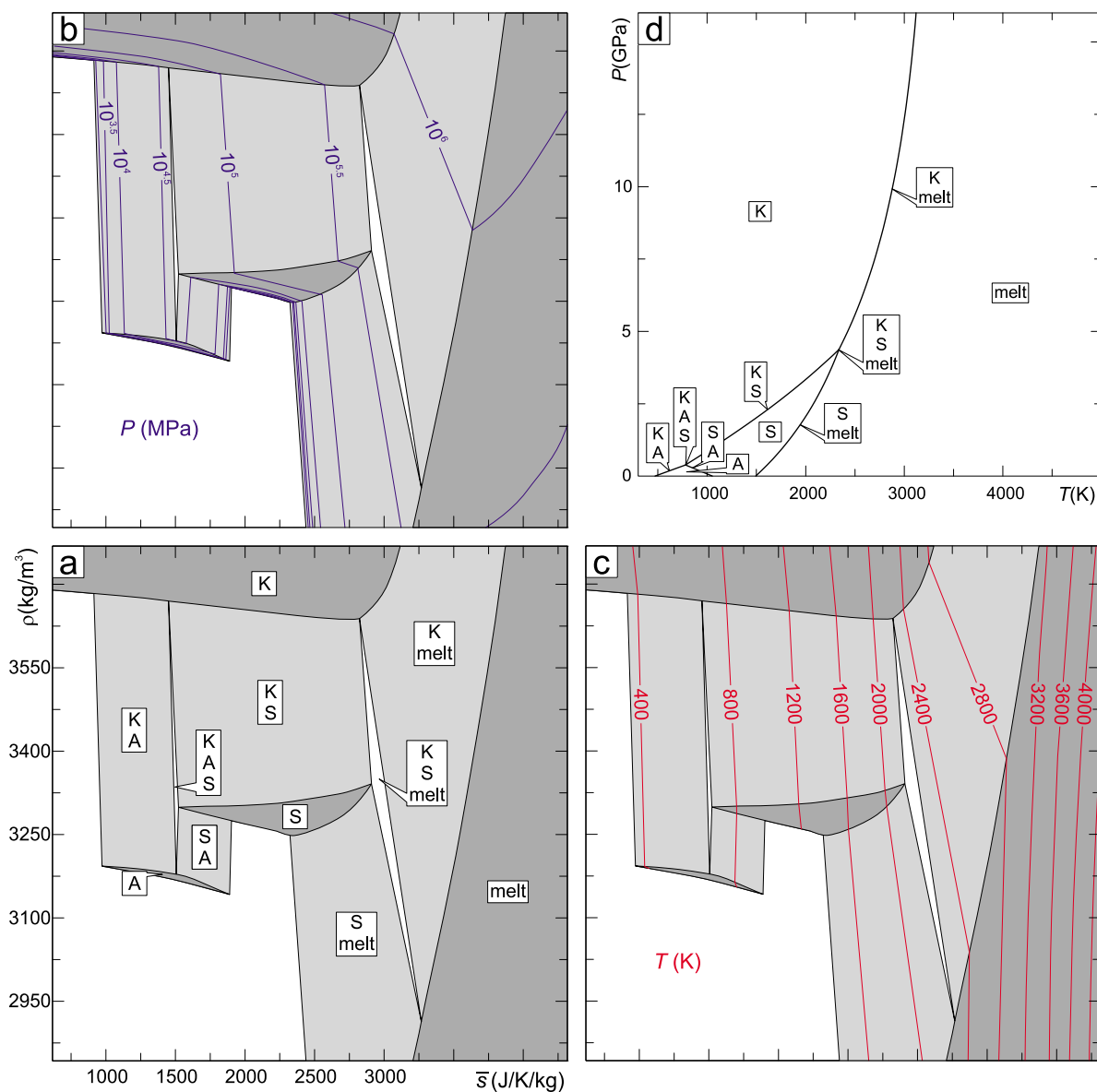


Figure 5. (a) Phase relations computed by minimizing $\bar{u}(\bar{s}, \bar{v})$ for the Al_2SiO_5 ($k = 1$) system as a function of density ($\rho = 1/\bar{v}$) and specific entropy (\bar{s}). The $\bar{s} - \rho$ coordinates of geodynamic systems vary continuously in response to heat flow and deformation; therefore, if phase equilibria are calculated dynamically within a thermomechanical code, it is essential that the phase equilibrium solver function for any arbitrary $\bar{s} - \rho$ coordinate. A solver that minimizes $\bar{u}(\bar{s}, \bar{v})$ meets this requirement, but solvers that rely on a $P-T-m$ formulation fail for phase equilibria involving $p > k$ phases. Such equilibria dominate the Al_2SiO_5 phase diagram; thus, for this system a $P-T-m$ dependent solver would be likely to fail more often than it would succeed. This difficulty is endemic to dynamic implementations of $P-T-m$ solvers but can be circumvented in static implementations wherein phase equilibria are calculated and summarized in look-up tables prior to the thermomechanical calculation (Figure 7). Thermodynamic data from *Holland and Powell* [1998, revised 2002], phase notation: andalusite (A), sillimanite (S), and kyanite (K). The white region in the bottom left corner represents physical conditions at which pressure is negative given the possible phases. From a practical perspective these conditions are indicative of geologically unrealistic $\bar{s} - \rho$ conditions, but from a thermodynamic perspective the negative pressures reflect the absence of a vapor phase in the model. (b) Isotherms and (c) isobars obtained by differentiation of the optimized function $\bar{u}(\bar{s}, \bar{v})$. (d) The phase relations as a function of pressure and temperature. The $P-T$ conditions correspond roughly to the conditions for the $\bar{s} - \rho$ calculation. The melting phase relations are an approximation in that sillimanite is metastable, at least at low pressure, with respect to mullite [Pask, 1996]. The files for these calculations are accessible from perplex.ethz.ch/perplex_usv.html.

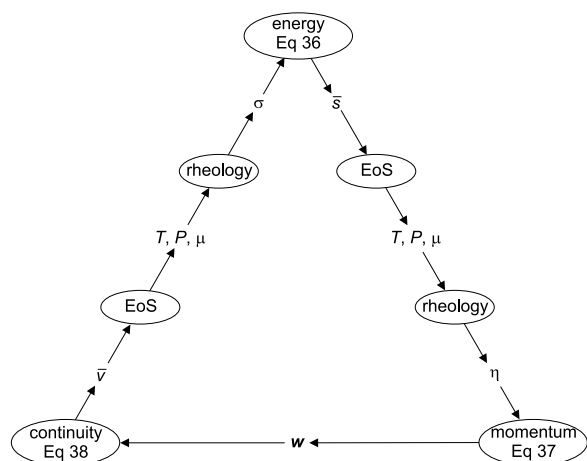


Figure 6. Iterative cycle for an implicit numerical solution of the governing equations for an isochemical geodynamic model. The governing equations are closed by constitutive relations (rheology) and the equation of state (EoS). The variables updated by each equation, or set of equations, are indicated for the clockwise cycle. Constitutive relations usually describe rheology as a function of thermodynamic potentials; therefore, if the deviatoric stress tensor or effective viscosity is required by a governing equation, both the equation of state and the constitutive relations are employed if a governing equation modifies a state variable. For a nonisochemical geodynamic system, i.e., a system in which the transfer of $k-c$ kinds of mass is possible, the governing equations would be augmented by conservation equations for the $k-c-1$ independent specific masses $m_{k-c-1}, \dots, m_{k-1}$ [e.g., Katz, 2008; Tirone et al., 2009].

consider a thermomechanical model for viscoelastic deformation without mass transfer, i.e., the representative elements are isochemical and characterized by the equation of state $\bar{u}(\bar{s}, \bar{v})$. If the internal energy of a representative element associated with a material point varies only through heat conduction, irreversible shear deformation, and reversible dilation, then conservation of energy requires [de Groot and Mazur, 1984]

$$\frac{d\bar{u}}{dt} = \bar{v}(\sigma : \dot{\epsilon} - \nabla \cdot q) - P \frac{d\bar{v}}{dt} \quad (35)$$

where q is the heat flux, σ and $\dot{\epsilon}$ are the deviatoric stress and strain rate tensors, and t is time. Equation (35) describes the conversion of dissipative power ($\sigma : \dot{\epsilon}$) to heat or dilational or chemical work; however, energy may also be dissipated by microscopic elastic strain, i.e., damage. The neglect of this damage, as consistent with the assumption that $\bar{u}(\bar{s}, \bar{v})$ is the complete equation of state, implies that equation (35) describes the maximum

effect of mechanical dissipation on the state of the system [Regenauer-Lieb et al., 2009].

[25] Equating equation (35) to the time derivative of the equation of state

$$\frac{d\bar{u}}{dt} = T \frac{d\bar{s}}{dt} - P \frac{d\bar{v}}{dt}$$

and, making use Fourier's law to express heat flux as a function of thermal conductivity (K) and temperature, the result is rearranged to obtain an evolution equation for entropy

$$\frac{d\bar{s}}{dt} = \bar{v} \frac{\nabla \cdot (K \nabla T) + \sigma : \dot{\epsilon}}{T}. \quad (36)$$

Equation (36) is readily solved numerically by using the right-hand side to estimate the spatial distribution of entropy and using the equation of state as an update rule for temperature (i.e., $T = \partial \bar{u} / \partial \bar{s}$). The strain rate tensor $\dot{\epsilon}$ in equation (36) is a function of the velocity field and, by making use of constitutive relations, the stress tensor σ can be expressed as a function of state variables and $\dot{\epsilon}$. Therefore, solution of equation (36) requires governing equations for the components (w_x, w_y, w_z) of the velocity (\mathbf{w}) and \bar{v} . The former are provided by the Stokes equation [Batchelor, 2005] with effective viscosity η

$$\nabla \cdot (\eta \nabla \mathbf{w}) = \nabla P, \quad (37)$$

where gravitational body forces have been omitted for simplicity, and continuity

$$\frac{d\bar{v}}{dt} = \bar{v} \nabla \cdot \mathbf{w} \quad (38)$$

closes the system of equations in $\bar{s}, \bar{v}, w_x, w_y, w_z$ in conjunction with the equation of state $\bar{u}(\bar{s}, \bar{v})$ and constitutive relations (Figure 6). In this formulation, just as conservation of energy provides an evolution equation for entropy, continuity provides the evolution equation for volume; and pressure and any state variables required by the constitutive relations are updated from $\bar{u}(\bar{s}, \bar{v})$.

[26] The restriction to an isochemical thermomechanical model in the foregoing is not essential. In general, if mass transfer occurs among representative elements, the equation of state is $u(s, v, m_1, \dots, m_{k-1})$ and an additional $k-1$ governing equations must be introduced to assure conservation of the independently variable kinds of mass [e.g., de Groot and Mazur, 1984]. Mass transfer is accomplished by advection of a low-viscosity fluid

through a more viscous solid is a problem of particular geodynamic relevance. Most commonly, the migration of the fluid is kinematically prescribed [Gerya *et al.*, 2004] or tracked by marker techniques [Gorczyk *et al.*, 2007; Hebert *et al.*, 2009]; however, some recent treatments [Katz, 2008; Tirone *et al.*, 2009] solve such problems rigorously by introducing a complete set of governing equations for the “fluid” and “solid” phases, either of which may in fact be an aggregate of thermodynamic phases.

[27] The conventional $T - P$ formulation for the heat flow equation is obtained from equation (35) by expanding the entropy differential as

$$d\bar{s} = \frac{\partial \bar{s}}{\partial T} dT + \frac{\partial \bar{s}}{\partial P} dP$$

and making use of the identities

$$\frac{\partial \bar{s}}{\partial T} = \frac{c_P}{T}, \quad \frac{\partial \bar{s}}{\partial P} = -\alpha_P \bar{v}$$

Equation (35) rearranges to

$$\frac{dT}{dt} = \left(\bar{v} [\nabla \cdot (K \nabla T) + \sigma : \dot{\epsilon}] + \alpha_P T \frac{dP}{dt} \right) / c_P. \quad (39)$$

Likewise, from the identity

$$K_T = -\bar{v} \left(\frac{\partial P}{\partial \bar{v}} \right)_T,$$

continuity (equation (38)) is

$$\frac{dP}{dt} = -K_T \nabla \cdot \mathbf{w}. \quad (40)$$

Absent first-order phase transitions, the governing equations (39), (40) and (37) are closed in P , T , w_x , w_y , w_z by rheology and the equation of state $\bar{g}(T, P)$ via

$$c_P = -T \frac{\partial^2 \bar{g}}{\partial T^2}, \quad v = \frac{\partial \bar{g}}{\partial P}, \quad \alpha_P = \frac{\partial^2 \bar{g}}{\partial T \partial P} / \frac{\partial \bar{g}}{\partial P}, \quad (41)$$

$$K_T = -\frac{\partial \bar{g}}{\partial P} / \frac{\partial^2 \bar{g}}{\partial P^2}.$$

The $\bar{s} - \bar{v}$ (equations (35) and (38)) and $T - P$ (equations (39) and (40)) formulations of the energy and continuity equations are mathematically equivalent, but the $T - P$ formulation is ill conditioned because $\bar{g}(T, P)$ is not a function of the state of a system undergoing a discontinuous phase transformation (equation (21)). To illustrate this ill condition, consider the description of an isobaric transformation of andalusite to sillimanite (Figure 5) by equation (39). At the transformation

temperature $\bar{g}^{\text{andalusite}} = \bar{g}^{\text{sillimanite}}$, yet the internal energy and other first-order properties of the system vary linearly with the amount of sillimanite generated by heating. It follows that the coefficients c_P and α_P (equation (41)) of the heat flow equation are infinite and therefore that the equation is singular. Moreover, at the transformation temperature $\bar{g}(T, P)$ cannot be differentiated to yield \bar{v} or the latent heat of the transformation required for ad hoc resolution of the singularity. The same problem emerges with the K_T coefficient of the continuity equation (equation 40) if a discontinuous phase transformation is induced by isothermal compression. In contrast, numerous engineering studies have demonstrated that the enthalpy method, the solution of the isostatic equivalent of equation (35), is well conditioned [Oezisik, 1993]. From an operational perspective, the $\bar{s} - \bar{v}$ formulation requires only two first-order derivatives of $\bar{u}(\bar{s}, \bar{v})$ for T and P , whereas the $T - P$ formulation requires the evaluation of six first- and second-order derivatives of $\bar{g}(T, P)$ for c_P , \bar{v} , α_P and K_T . Thus, even in systems where first-order phase transitions can be precluded, there is no prima facie ground to prefer the $T - P$ formulation.

5. Dynamic Versus Static Phase Equilibrium Implementations

[28] It is natural to ask how there can have been so many successful geodynamic applications of the $T - P$ formulation if it is ill conditioned? The answer to this question lies in the way in which equations of state are implemented in geodynamic models. This can be done in two ways distinguished here as static and dynamic methods. In the dynamic method the equation of state is evaluated during the application, whereas by the static method the equation of state is evaluated prior to the application and summarized in a table as a function of the desired state variables. In the static method, discontinuities associated with first-order phase transformations are smoothed by the finite resolution of the table. Consequently, there are no singularities in the $T - P$ formulation if finite difference approximations are used to evaluate the effective c_P , \bar{v} , α_P and K_T from $\bar{g}(T, P)$, as in equation (41), and the formulation is generally well conditioned. Thus, the use of static methods explains the numerical stability of the vast majority of geodynamic applications that have incorporated phase equilibria computed by free energy minimization over the last decade. Paradoxically, the unlimited resolution of phase relations provided

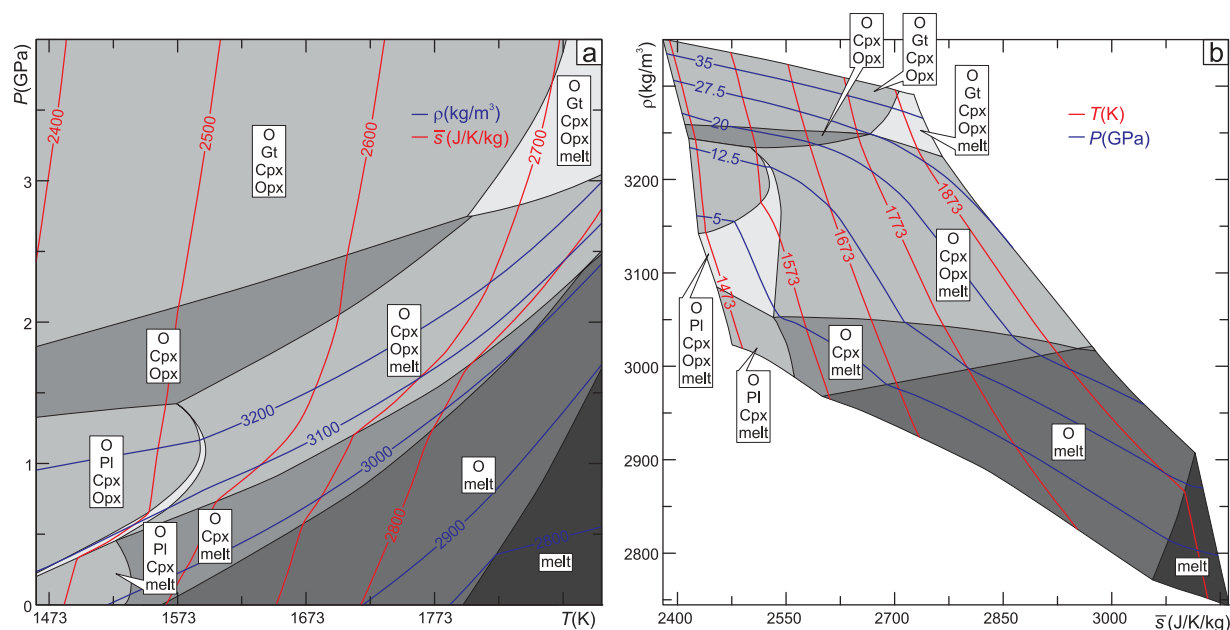


Figure 7. (a) Phase relations and physical properties mapped as a function of pressure and temperature, by optimizing $\bar{g}(T, P)$, transformed to (b) a map of phase relations and physical properties as a function of entropy and density. The transformation is accomplished by using numerical interpolation of $\bar{s}(T, P)$ and $\rho(T, P)$, the red and blue curves in the P – T map, to obtain $T(\bar{s}, \rho)$, and $P(\bar{s}, \rho)$, the red and blue curves in the \bar{s} – ρ map. These latter functions can be summarized in look-up tables and used to close the \bar{s} – \bar{v} formulation of geodynamic governing equations (e.g., equations (36)–(38); Figure 6). This transformation offers a pragmatic alternative to the direct optimization of $\bar{u}(\bar{s}, \bar{v})$ (Figure 5), from which $T(\bar{s}, \rho)$ and $P(\bar{s}, \rho)$ are obtained by numeric differentiation (i.e., $T = \partial \bar{u} / \partial \bar{s}$, $P = -\partial \bar{u} / \partial \bar{v}$). The phase relations are for a simplified version of the LOSIMAG [Hart and Zindler, 1986] mantle composition (molar composition: 0.707 SiO₂, 0.037 Al₂O₃, 0.0971 FeO, 0.867 MgO, 0.053 CaO, 0.005 Na₂O). Phase notation and solution model sources: olivine and garnet (O and Gt) [Holland and Powell, 1998], plagioclase (Pl) [Fuhrman and Lindsley, 1988], orthopyroxene and clinopyroxene (Opx and Cpx) [Holland and Powell, 1996], melt [Ghiorso et al., 2002]; end-member thermodynamic data for the melt model (“pMELTS”) modified to be consistent with the data of Holland and Powell [1998] (revised 2002) used for all other phases. The files for this calculation are accessible at perplex.ethz.ch/perplex_usv.html.

by dynamic methods is a source of numerical instability, both because of the aforementioned singularities and because the thermodynamic optimization as a function of pressure and temperature is numerically unstable at the conditions of first-order phase transformations. The feasibility of recent applications [Hebert et al., 2009; Tirone et al., 2009] that have employed dynamic methods is because first-order transformations are uncommon in complex chemical systems.

[29] Given the high cost of phase equilibrium calculations, from a computational perspective a dynamic strategy only makes sense if the cost of memory required for the static method is prohibitive. For example, in the reactive melt flow problem considered by Tirone et al. [2009] the state of the system is defined by pressure, temperature and the five chemical compositions. Resolution of each state variable at a percent of its range would require a table with 100^7 entries and is clearly impractical.

In contrast, the problem involving only pressure, temperature and water transport treated by Hebert et al. [2009] requires a table with only 100^3 entries, which is tractable by the static method given current computational standards. Given that conservative interpolation between table entries is feasible, the “percent level” resolution used here for the sake of argument is likely to vastly exceed the requirements of most geodynamic models.

[30] An additional advantage of the static method is that the equation of state for a system can be mapped as a function of the variables that are most convenient for the phase equilibrium calculation and then converted *post hoc* to tables as a function of the variables for the geodynamic calculation (Figure 7). For example, optimization as function of pressure and temperature yields

$$\bar{g}(T, P), \quad \bar{s}(T, P) = -\frac{\partial \bar{g}}{\partial T}, \quad \bar{v}(T, P) = \frac{\partial \bar{g}}{\partial P}.$$

Given these functions, $\bar{g}(\bar{s}, \bar{v})$, $T(\bar{s}, \bar{v})$, and $P(\bar{s}, \bar{v})$ are obtained by numerical interpolation (a script for this purpose is at www.perplex.ethz.ch/perplex_usv.html) onto a regular \bar{s} – \bar{v} coordinate frame and the equation of state $\bar{u}(\bar{s}, \bar{v})$ is constructed from the Legendre transformation (equation (6); compare to equation (31))

$$\bar{u}(\bar{s}, \bar{v}) = \bar{g}(\bar{s}, \bar{v}) + T(\bar{s}, \bar{v})\bar{s} - P(\bar{s}, \bar{v})\bar{v}.$$

This latter step is superfluous from a geodynamic perspective, as the \bar{s} – \bar{v} formulation of the geodynamic governing equations requires only $T(\bar{s}, \bar{v})$ and $P(\bar{s}, \bar{v})$ (Figures 6 and 7b).

6. Summary and Discussion

[31] This paper has outlined a consequence of assuming local equilibrium for the phase relations of geodynamic systems, an assumption that is equivalent to assuming the existence of an equation of state for a heterogeneous system. The conventional notion of an equation of state stems from homogeneous systems. The state of a homogeneous system with N independent extensive material attributes can be specified by any choice of $N-1$ independent state variables and because pressure and temperature are easily controlled in experimental systems, these variables are commonly chosen to specify thermal and mechanical state. This notion of an equation of state does not apply to heterogeneous systems such as rocks for both theoretical and practical reasons. As a heterogeneous system may consist of as many as N phases, its equation of state must be capable of distinguishing N phases; this is only possible if coexisting phases have unique coordinates in the representative space defined by the independent variables of the equation of state. A representative space defined by thermodynamic potentials, such as pressure and temperature, does not meet this requirement because the potentials are equal in coexisting phases; therefore, the independent equation of state variables must correspond to the $N-1$ specific properties that define the relative proportions of the N material attributes. For most geodynamic problems, the N attributes are the k kinds of mass, entropy, volume and five components of the elastic strain tensor. Elementary considerations reviewed here show that the contribution of elastic deviatoric strain to the total energy of geodynamic systems is unlikely to be significant; thus, from a practical perspective the N attributes for geodynamic systems are the k kinds of mass, entropy, volume and the equation of state is $u(s, v, m_1, \dots, m_{k-1})$ [cf. *Tantsev et al.*, 2009]. An implication of this

model is that the dilational rheology must be elastic. If the additional, and common, assumption that the representative elements of a geodynamic model conserve mass, then the equation of state simplifies to $\bar{u}(\bar{s}, \bar{v})$ and temperature and pressure are functions of the specific entropy and volume. For this configuration, the equation of state, constitutive relations, and governing equations for energy, mass (continuity) and momentum provide a closed system of equations in \bar{s} , \bar{v} and velocity. The energy and continuity equations are evolution equations for \bar{s} and \bar{v} , and $\bar{u}(\bar{s}, \bar{v})$ furnishes the update rule for pressure and temperature.

6.1. Optimization Method and Its Implementation

[32] The equation of state of a heterogeneous system is computed by finding the phase states that optimize the systems energy as a function of its independently variable properties; as such the equation of state is not amenable to analytic expression, in contrast to the equations of state for individual phases. Thus, in practice the equation of state of a heterogeneous system is a numeric function. The manner in which phase equilibria are implemented in a geodynamic model dictates the numerical method by which the equation of state is most efficiently computed. In static implementations, the equation of state is tabulated as a function of its independent variables. In this case, the choice of independent variables for the phase equilibrium calculation is irrelevant as the table can be reformulated in terms of whatever variables are optimal for the geodynamic model (Figure 7). For geodynamic models that treat multicomponent mass transfer [e.g., *Tirone et al.*, 2009] it may be desirable to dynamically optimize phase relations as an explicit function of the desired geodynamic variables. An obstacle to such optimizations is that the equations of state for the potential phases of geological systems are known invariably as functions of temperature rather than entropy and usually as functions of pressure rather than volume. Discretization provides a means of representing a functional form for the equation of state of a phase in terms of any choice of independent state variables. Thus, given $u(T, P, m_1, \dots, m_{k-1})$, the discrete function $u(s, v, m_1, \dots, m_{k-1})$ is easily obtained. The combination of these discretized functions is then optimized by linear programming. Compared to conventional isobaric-isothermal optimization problems, the increased dimension of the isentropic-isochoric problem poses numerical difficulties. This paper has detailed a successive linear programming strategy that directly

optimizes the total energy of a system to overcome these difficulties. Aside from numerical issues, the advantage of a direct optimization strategy is that no user expertise is required to resolve situations, e.g., immiscibility or boiling, in which distinct phases are represented by a single equation of state. The weakness of direct energy optimization strategies is they cannot resolve variations in specific variables that do not significantly affect the total energy of the system. Thus, they are poorly suited for the solution of problems in which it is necessary to resolve trace element geochemistry.

6.2. Looking for Something New?

[33] In emphasizing the formal definition of an equation of state, the case made here has been legalistic rather than demonstrative. Specifically, it is argued that the s - v - m formulation is preferable because it is better conditioned and more efficient from an operational perspective. While these issues can also have a significant impact on computational results [Schneider and Beckermann, 1991; Oezisik, 1993], the scale of geodynamic models is such that a P - T - m formulation based on effective thermodynamic properties will recover the same physical behavior. Given that accounting for the thermal effects of phase equilibria is now routine in geodynamic models, the only suggestion made here that offers the prospect of revealing new physical behavior is to account for the coupling of thermodynamic and mechanical pressure. The artificial decoupling of these measures of pressure is an inescapable consequence of the almost universal neglect of dilational strain in the continuity equation (equation (38) or (40)), as implicit in Boussinesq models. In lieu of a more rigorous relation, thermodynamic pressure is usually related to depth or load, an approximation that yields kinetics appropriate for inviscid materials, the antithesis of geodynamic systems. Such approximations have their greatest dynamic consequence for large strain phase transitions, e.g., melting or devolatilization [Connolly, 1997] or phase transformations at extreme pressure. In regard to the latter, the recent discovery of a postperovskite lower mantle phase is of particular interest [Oganov and Ono, 2004]; e.g., if the postperovskite transition has a Clapeyron slope of ~ 10 MPa/K, then the mechanical work done during this transformation at 2500 K and 125 GPa is five times its heat effect. The neglect of dilational strain in the continuity equation also violates conservation of mass; thus, the approximation may have significant conse-

quences for modeling the dynamics of the geoid [Hetenyi *et al.*, 2007; Afonso *et al.*, 2008].

6.3. Are Phase Equilibria Worth the Effort?

[34] Given the focus of this paper, it is relevant to conclude with thoughts on the value of incorporating phase equilibria computed from thermodynamic data in geodynamic modeling. A common *pro* argument is that phase transformations induce new types of behavior, whereas the *contra* argument is that the large number of parameters required for phase equilibrium computations increases the uncertainty of, and complicates, geodynamic modeling. These arguments cannot be refuted objectively, but there are points of weakness in both. Geodynamic models evolved from a stage in which phase transformations were entirely neglected to the current stage in which it is possible to account for continuous phase transformations via an intermediate stage in which natural phase transformations were simulated as discontinuous processes and represented by parameterizations. When compared to such parameterizations, more realistic phase equilibrium models sometimes do reveal new behavior, but the larger number of degrees of freedom associated phase equilibrium models tends to dampen the overall geodynamic consequences of phase transformations [Petrini *et al.*, 2001; Kaus *et al.*, 2005; Simon and Podladchikov, 2008; Nakagawa *et al.*, 2009]. Thus, simple parameterizations are useful for identifying extremal geodynamic scenarios. However, the construction of more elaborate parameterizations, even if only for a few phase transformations, rapidly leads to a parameter space that is too complex to explore thoroughly. Although such a parameter space may seem miniscule compared to that of a thermodynamic database, the case for the use of a thermodynamic model is less bleak than might be expected for two reasons. The zeroth and first-order parameters of thermodynamic databases are strongly correlated [Holland and Powell, 1998]; thus, errors on individual parameters provide a pessimistic basis for assessing uncertainties. These autocorrelations combined with the nonlinear phase equilibrium problem to make statistical error assessment a practical impossibility. Paradoxically this impossibility makes the case that, from a geodynamic perspective, individual thermodynamic databases should be regarded as a single parameter; as the only practical means for error assessment is comparison of computations done with alternative databases. The recognition that thermodynamic databases are a distillation of a complex body of

knowledge supports this view. As such, databases may not reproduce any individual observations perfectly; rather they are an attempt to minimize the compromises necessary to reconcile disparate observations. Thus, while the temptation to make *post hoc* adjustments to databases to improve agreement with new, or favored, individual observations is strong, such adjustments tend to damage the integrity of the database.

Acknowledgments

[35] I owe the idea of a geodynamic equation of state to Yuri Podladchikov. Two decades ago, a presentation by George Bergantz convinced me of the value of the enthalpy method in geodynamic applications. Mark Caddick motivated and tested the improvements described here to Perple_X's optimization algorithm. Discussions with George Hetenyi, Taras Gerya, Richard Katz, and Paul Tackley and reviews by George Bergantz and an anonymous reviewer improved this paper. I thank Peter van Keken for editorial guidance and handling. This work was supported by Swiss National Science Foundation grant 200020-107889.

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