

# A Primer in Gibbs Energy Minimization for Geophysicists<sup>1</sup>

J. A. D. Connolly

*Earth Sciences Department, Swiss Federal Institute of Technology, Zurich, 8092 Switzerland*  
*e-mail: james.connolly@erdw.ethz.ch*

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**Abstract**—Gibbs energy minimization is the means by which the stable state of a system can be computed as a function of pressure, temperature and chemical composition from thermodynamic data. In this context, state implies knowledge of the identity, amount, and composition of the various phases of matter in heterogeneous systems. For seismic phenomena, which occur on time-scales that are short compared to the time-scales of intra-phase equilibration, the Gibbs energy functions of the individual phases are equations of state that can be used to recover seismic wave speeds. Thermodynamic properties relevant to modelling of slower geodynamic processes are recovered by numeric differentiation of the Gibbs energy function of the system obtained by minimization. Gibbs energy minimization algorithms are categorized by whether they solve the non-linear optimization problem directly or solve a linearized formulation. The former express the objective function, the total Gibbs energy of the system, indirectly in terms of the partial molar Gibbs energies of phase species rather than directly in terms of the Gibbs energies of the possible phases. The indirect formulation of the objective function has the consequence that although these algorithms are capable of attaining high precision they have no generic means of treating phase separation and expertise is required to avoid local minima. In contrast, the solution of the fully linearized problem is completely robust, but offers limited resolution. Algorithms that iteratively refine linearized solutions offer a compromise between robustness and precision that is well suited to the demands of geophysical modeling.

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## INTRODUCTION

Gibbs energy minimization is a technique by which rock mineralogy, and ultimately its elastic and caloric properties, can be predicted as a function of pressure, temperature and bulk composition from thermodynamic data (Fig. 1). Although Gibbs energy minimization has long been advocated for geophysical problems (e.g., Saxena and Eriksson, 1983; Wood and Holloway 1984; Sobolev and Babeyko, 1994; Bina, 1998), it is only in the last decade that the availability of comprehensive thermodynamic data bases (e.g., Ricard et al., 2005; Khan et al., 2006; Stixrude and Lithgow-Bertelloni, 2007; Stixrude and Lithgow-Bertelloni, 2011) has made the application of such calculations feasible for geophysical models of the entire Earth's mantle. This paper outlines the Gibbs energy minimization problem, the classes of algorithms used to solve it, and the thermodynamic relations necessary to extract elastic and caloric properties.

Although Gibbs energy minimization computer programs are often applied in the modelling of petrological phase equilibria, the most popular program developed for this purpose (THERMOCALC, Powell 1978) is a phase equilibrium calculator. The distinction between calculators and minimization programs is that the former invokes assumptions about the stability of

one or more phases. Thus, in the THERMOCALC algorithm the phase assemblage is specified and the compositions of the phases are computed. The popularity of calculators, which are not considered further here, reflects both that the requisite assumptions can often be justified by petrological expertise and that calculators can be used to treat chemically complex systems. However reliance on expertise is generally impractical in large-scale geophysical applications.

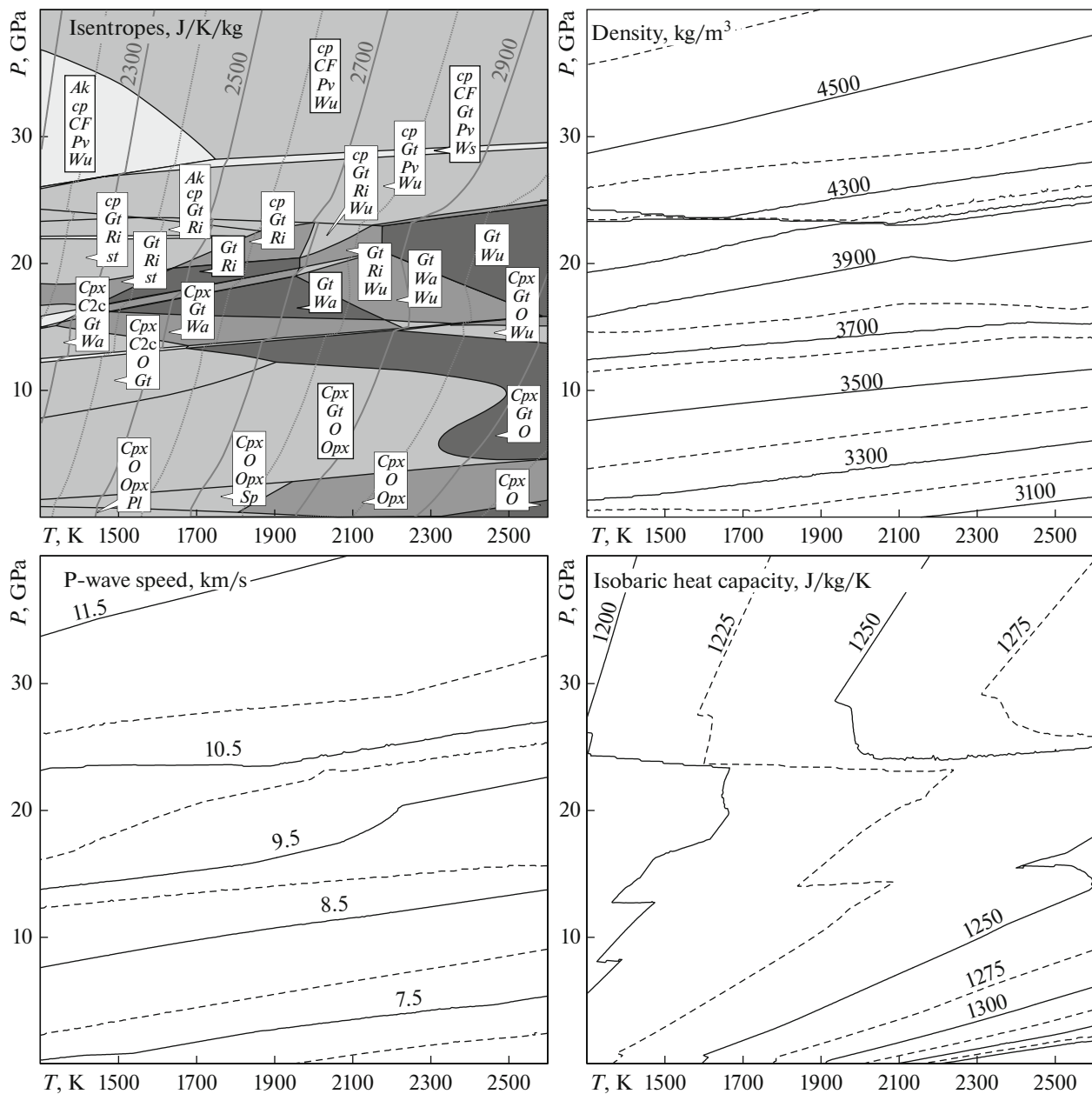
## THERMODYNAMIC PRELIMINARIES

In the presence of aqueous fluids rocks attain thermodynamic equilibrium at temperatures as low as ~600 K (Bucher and Frey, 1994) and even anhydrous silicate systems are reasonably well equilibrated at temperatures in excess of ~1100 K (Wood and Holloway, 1984). Thus, it is reasonable to assume that the mineralogy of the bulk of the interior of the earth can be predicted by thermodynamic methods. A combined statement of the first and second laws of thermodynamics expresses the variation in the internal energy ( $U$ ) of a system

$$dU \leq TdS - PdV + \sum_{k=1}^c \mu_k dN_k, \quad (1)$$

as a first order homogeneous differential in entropy ( $S$ ), volume ( $V$ ) and the molar amounts ( $N_k$ ) of the  $c$  inde-

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**Fig. 1.** Phase relations (a) and physical properties (b–d) for a Na<sub>2</sub>O–CaO–Al<sub>2</sub>O<sub>3</sub>–MgO–FeO–SiO<sub>2</sub> pyrolite bulk composition computed by Gibbs energy minimization. The isentropes (mantle adiabats) superimposed on the phase diagram section in (a) are obtained from the Gibbs energy minimization. The bulk moduli used to compute p-wave speed are the Voigt-Reuss-Hill averages of the corresponding moduli of the stable phases. Bulk composition and thermodynamic data, including solution models, are from Stixrude and Lithgow-Berterlloni (2011), the calculations were done using the *Perple\_X* program (Connolly, 2009). Phase notation: *Ak*—akimotoite; *cp*—Ca-perovskite; *CF*—calcium ferrite structure Na-Mg-Fe silicate; *Cpx*—clinopyroxene; *C2c*—high pressure pyroxene; *Gt*—garnet; *O*—olivine; *Opx*—orthopyroxene; *Pl*—plagioclase; *Pv*—bridgmanite; *Rng*—ringwoodite; *Sp*—spinel; *st*—stishovite; *Wad*—Wadleysite; *Wus*—wuestite. Lower case notation indicates stoichiometric (pure) phases.

pendently variable kinds of mass, i.e., the chemical components, and the differential coefficients are temperature ( $T$ ), pressure ( $P$ ) and chemical potentials ( $\mu_k$ ). The equality in Eq. (1) applies in the limit of reversible processes and the inequality accounts for entropy production, i.e., dissipation, associated with real processes. Equation (1) assumes, as is conventional in

chemical thermodynamics, and generally well justified in earth science applications, isostatic stress and the absence of strong electromagnetic and gravitational fields. To illustrate the predictive capacity of the second law, the entropy differential may be decomposed into the component ( $dS^{\text{external}}$ ) that arises through interactions between a system and its environment and

the component due to spontaneous internal processes ( $dS^{\text{internal}}$ ). For an isobaric, isothermal, chemically closed system (i.e.,  $dN_1 = \dots = dN_c = 0$ ), the only possible interactions with its environment are mechanical work ( $-PdV$ ) and heat exchange ( $TdS^{\text{external}}$ ). As these interactions are isothermal and isobaric, they must be reversible, therefore from Eq. (1)

$$dU - TdS^{\text{external}} + PdV \leq TdS^{\text{internal}}. \quad (2)$$

Since the left-hand side of Eq. (2) is zero by definition and the entropy production by any real internal process must be positive, it follows that the differential

$$dG \equiv dU - TdS + PdV \quad (3)$$

must be negative for any real process at constant temperature, pressure and composition, and therefore that the function  $G$ , known as the Gibbs energy, must have its lowest possible value when the system is in a state such that no spontaneous processes are possible, i.e., a state of stable thermodynamic equilibrium. The complete differential of  $G$  in the reversible limit is obtained by substituting the integral of Eq. (1) for an equilibrium system

$$U = TS - PV + \sum_{k=1}^c \mu_k N_k, \quad (4)$$

in Eq. (3) to obtain

$$dG = -SdT + VdP + \sum_{k=1}^c \mu_k dN_k. \quad (5)$$

Equation (5) expresses  $G$  as a function of both state and size; in practice, the size dependence is eliminated by normalizing extensive properties relative to a fixed amount of matter. The only rational normalization is to identify amount with one of the extensive variables of Eq. (1), unfortunately in chemical thermodynamics amount is almost invariably defined as

$$\alpha \equiv \sum_{k=1}^c N_k, \quad (6)$$

a definition adopted here in view of its broad use. The specific molar amounts of the different kinds of mass, i.e., the molar chemical compositions,  $x_k = N_k/\alpha$ , are then subject to the constraint

$$\sum_{k=1}^c x_k = 1. \quad (7)$$

Eliminating  $x_c$  through Eq. (7), the differential of the specific Gibbs energy is

$$dg = -sdT + vdP + \sum_{k=1}^{c-1} (\mu_k - \mu_c) dx_k, \quad (8)$$

where  $g = G/\alpha$ ,  $s = S/\alpha$ , and  $v = V/\alpha$ .

Compilations of thermodynamic data and solution models (e.g., Stixrude and Lithgow-Bertelloni, 2011) provide the information necessary to construct continuous functions  $g^i(P, T, x_k)$  that describe the various equilibrium states of matter possible in a given system. While the structure of such a function is important in that it determines the reliability of its interpolation and extrapolation, such details are of no relevance to the phase equilibrium problem and are therefore not considered here. The function  $g^i(P, T, x_k)$  is a complete equation of state in that it combines the information contained separately in what are often referred to as mechanical and caloric equations of state and solution models (i.e., chemical equations of state), e.g., from Eq. (8)

$$s^i = -\partial g^i / \partial T, \quad (9)$$

$$v^i = \partial g^i / \partial P. \quad (10)$$

While it is common to identify  $g^i$  with a particular phase, this usage is formally incorrect because every state represented by such a function is a possible phase of matter. Even if equilibrium is prescribed, the number of states of matter represented by a particular function  $g^i$  is not known a priori. For example, K-Na-Ca feldspar is described by a single function  $g^i$ , yet it is well known that under certain conditions three distinct phases of feldspar stably coexist (e.g., Fuhrman and Lindsley, 1988). Similarly, the description of critical phenomena in fluids requires that the subcritical liquid and gas states are defined by a single continuous equation of state (e.g., Prausnitz, 1969).

In the present context, the phase equilibrium problem is, given a collection of one or more equations of state  $g^i(x_k)$ , to identify the  $p$  phases of matter that minimize the Gibbs energy of the system subject to the constraints of mass balance and that the amount of a phase cannot be less than zero. Assuming that any energetic effects arising from interactions (e.g., surface tension) between phases are negligible, the Gibbs energy of the system is

$$G^{\text{system}} = \sum_{j=1}^{\Pi} \alpha^j g^j, \quad (11)$$

where the subscript  $j$  identifies a phase represented by one of the  $g^i(x_k)$  equations of state under consideration. Mass balance requires that the compositions of these phases satisfy

$$N_k^{\text{system}} = \sum_{j=1}^{\Pi} \alpha^j x_k^j, \quad k = 1, \dots, c-1, \quad (12)$$

and that the amounts of the phases satisfy

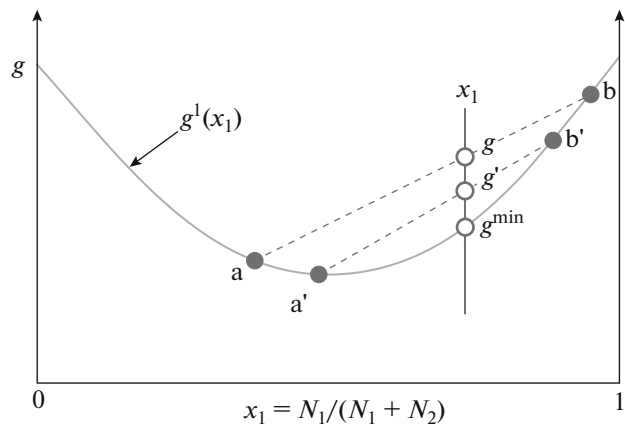
$$\alpha^j \geq 0, \quad j = 1, \dots, \Pi. \quad (13)$$

The solution to Eqs. (11)–(13) corresponds to the point on the convex hull in the  $c$ -dimensional  $g$ - $x$  space that bounds the various equations of state at the specified composition of the system. Provided the pressure and temperature of the system are arbitrarily specified, then the maximum number of phases in this solution is  $c$ . In this case, the convex hull must be linear at the composition of the system and the identities and compositions of the phases are given by the  $c$  points at which the hull is tangent to the equations of state. The minimum number of phases (i.e.,  $p = 1$ ) corresponds to the case that the hull is coincident with one equation of state at the composition of the system.

To make the foregoing expression of the phase equilibrium problem less abstract consider a two-component system. If the minimum Gibbs energy constraint is discounted, the system may be composed of any positive linear combination of the phase states defined by the equations of state that satisfy mass balance (Eq. (12)). In a system in which all states of matter are described by a single equation of state (Fig. 2), if two such phases exist, then from Eq. (11) the Gibbs energy of the system is given by the  $g$ -coordinate of the chord connecting the  $g$ - $x$  coordinates of the phases at the  $x$ -coordinate of the system. Provided the equation of state is convex with respect to the  $g$ -coordinate, the Gibbs energy of the system is lowered as the compositions of the phases are made to approach each other. Thus, in this case, the stable state of the system will always consist of a single phase. In contrast, if the equation of state is concave over a compositional interval (Fig. 3), then the convex hull of minimum Gibbs energy states must be simultaneously tangent to two compositions on either side of the concave interval. The Gibbs energy of any homogeneous state within this larger interval is greater than the Gibbs energy of a mixture of the two states that bound the interval. Since no state on a concave interval can be stable, it is natural to ask whether concave functions need be considered at all. The reason such functions must, in general, be considered is that geometry of the surface is a function of pressure and temperature therefore not known a priori. For example, at high temperatures plagioclase is a continuous stable solution between albite and anorthite, whereas at low temperature intermediate plagioclase compositions are unstable with respect to a mixture of albite- and anorthite-rich compositions.

### NON-LINEAR GIBBS ENERGY MINIMIZATION STRATEGIES

Gibbs energy minimization strategies used for earth science applications (e.g., Ghiorso et al., 1983; Saxena and Eriksson, 1983; Wood and Holloway, 1984; Karpov et al. 1997; Bina, 1998; Asimow and Ghiorso, 1998; Tirone et al., 2009; Stixrude and Lithgow-Bertelloni, 2011) that solve the true non-linear formulation of the phase equilibrium problem



**Fig. 2.** Schematic  $g$ - $x$  space of a binary ( $c=2$ ), isobaric-isothermal, system in which all possible states of matter are described by a single convex equation of state  $g^l(x_1)$ . If the equilibrium constraint is discounted, then the possible states of the system are any positive linear combination of states represented by  $g^l(x_1)$  that spans  $x^{\text{system}}$ . For example, if the system is made up of matter in the states indicated by points  $a$  and  $b$ , then  $g^{\text{system}}$  is the  $g$ -coordinate of the chord connecting these states at  $x^{\text{system}}$ . From this construction it is apparent that the  $g^{\text{system}}$  is lowered as the compositions of states  $a$  and  $b$  approach  $x_1^{\text{system}}$ , and that  $g^{\text{system}}$  is minimized when all parts of the system are in the same state. The construction also illustrates that no more than one state of matter represented by a convex  $g(x)$  function can be present in a stable system.

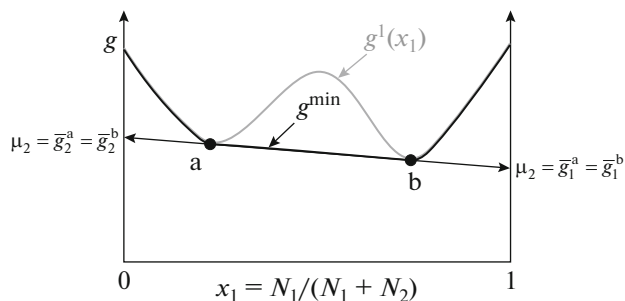
do not express the Gibbs energy of a system as a direct function of the energy of its phases, rather the Gibbs energy function of any phase with variable composition is expressed in terms of the properties of an arbitrarily defined set of “endmembers” or “species” of fixed composition. In this formulation, the specific Gibbs energy of a phase is

$$g^j = \sum_{l=1}^s y_l^j \bar{g}_l^j, \quad (14)$$

where  $y_l^j$  is the molar fraction of species  $l$  in phase  $j$  and

$$\bar{g}_l^j \equiv \frac{\partial G^j}{\partial N_l} \quad (15)$$

is the partial molar Gibbs energy of the species. In this paper the variables held constant during partial differentiation of a function are not indicated if the variables correspond to the natural variables of the function (Callen, 1960); thus in Eq. (15), it is implicit that differentiation is done at constant  $P$ ,  $T$ , and  $N_{k \neq l}$ . The distinction between components and species may merit clarification by example. Consider the  $\text{H}_2\text{O}$  system, all the phases (various ices, water, and steam) that may form in this system are essentially stoichiometric  $\text{H}_2\text{O}$ , thus the system has only one component.



**Fig. 3.** Schematic  $g$ - $x$  space of a binary ( $c=2$ ), isobaric-isothermal, system in which all possible states of matter are described by the equation of state  $g^1(x_1)$ , which has two inflections. The convex hull bounding  $g^1(x_1)$  defines the stable states of the system as a function of its composition and is linear between points  $a$  and  $b$ . For any composition of the system in that interval, the homogeneous state of the system represented by  $g^1(x_1)$  is metastable with respect to a mixture of the phases represented by points  $a$  and  $b$ . This behavior is referred to as phase separation or immiscibility. Although schematic, the shape of  $g^1(x_1)$  is characteristic of condensed phase solution behavior and reflects the relative contributions of the stabilizing configurational and destabilizing strain energy terms (Hillert, 2008). In the limit  $x \rightarrow 0$  at finite temperature,  $g^1(x_1)$  is always convex because the configurational term varies as  $\ln x$ , whereas the strain term typically varies as  $x$ . The destabilizing strain term is weakly dependent on pressure and temperature, whereas the stabilizing configurational term varies as  $T$ . Consequently, in the limit  $T \rightarrow 0$ ,  $g^1(x_1)$  is concave and there is no stable chemical mixing, whereas in the limit  $T \rightarrow \infty$ ,  $g^1(x_1)$  must be convex. The transition from a uniformly to partly convex  $g^1(x_1)$  function with falling temperature is the origin of critical phenomena. The  $g$ -coordinate of tangent to the minimum Gibbs energy surface of the system extrapolated to the composition of either component, i.e.,  $N_2$  at  $x_1 = 0$  and  $N_1$  at  $x_1 = 1$ , is identical to the chemical potential of the component and the partial molar free energies of the component in the stable phases of the system.

However, particularly at high temperature, it is known that steam is a mixture of, at least, three molecular species,  $\text{H}_2\text{O}$ ,  $\text{H}_2$ , and  $\text{O}_2$ . Likewise, the electrolytic properties of water cannot be explained without acknowledging the existence of  $\text{H}^+$  and  $\text{OH}^-$  ions. From a purely thermodynamic perspective, the existence of microscopic species is irrelevant, but acknowledging their existence may facilitate construction of equations of state. An equation of state in terms of  $s > c$  endmembers, implies  $s - c$  auxiliary constraints (e.g., mass and charge balance, closure, and internal equilibrium).

In simple equations of state the species may be identified as chemically pure species, but more generally species may represent hypothetical states that are chosen for convenience. The equations of state of these species,  $g_l^0(P, T)$ , are compiled in thermody-

namic data bases, while the functions that describe how these equations of state are to be combined to define  $g^i(P, T, x_k)$ , the equation of state of an impure phase, are referred to as solution models.

In terms of partial molar Gibbs energies, the Gibbs energy of the system can be expressed

$$g^{\text{system}} = \sum_{m=1}^t z_m \bar{g}_m^{j(m)}, \quad (16)$$

where  $z_m$  is the molar amount of species  $m$  in the system, present as a constituent of phase  $j(m)$ , and  $t$  is the total number of species needed to describe the possible phases of the system. Eq. (16) is then minimized by varying the amounts of the species subject to the linear constraints

$$x_k^{\text{system}} = \sum_{m=1}^t z_m x_m^{j(m)}, \quad k = 1, \dots, c - 1 \quad (17)$$

and

$$z_m^{\text{min}} \leq z_m, \quad m = 1, \dots, t. \quad (18)$$

Although the mass of a phase cannot be negative, solution models may be formulated in such a way that the relative amounts of all the species need not be positive. Thus, the bounds on the optimization variables, Eq. (18), cannot be specified without knowledge of the specific formulations of the solution models under consideration.

The use of Eq. (16) as an objective function poses two major difficulties. The first is that unless all the  $g^i(x_k)$  functions of interest are convex, the same species may occur more than once in the stable phases of the system. In such circumstances, the partial molar Gibbs energy of the species are identical in the coexisting phases, but the concentration of the species differ (Fig. 3). Treatment of this problem requires that the species, as counted in Eqs. (16)–(18), must be distinguished on the basis of their concentrations as well as their formal identity. However, knowledge of the concentrations of the species implies knowledge of the stable phases, which are, of course, not known a priori. While strategies have been developed to resolve this problem (e.g., Karpov et al., 1997), in general, non-linear optimization strategies are unsuited or poorly suited to applications where phase separation, a common phenomenon in minerals, is possible.

Even when it can be assumed that all  $g^i(x_k)$  functions of interest are convex, a generic difficulty in minimizing Eq. (16) is that the  $\bar{g}_m^{j(m)}$  functions involve logarithmic terms that are undefined at the lower bound on  $z_m$ . Thus in practice a species must be eliminated from the minimization procedure if its concentration approaches this limit. Once the minimization converges with a reduced set of the species, some criterion must be applied to decide whether any endmembers



eliminated in this way should be restored. The fallibility of such criteria complicates non-linear optimization and increases the probability of convergence to a local minimum; thus as a group these non-linear optimization strategies require expertise.

The THERIAK algorithm (DeCapitani and Brown, 1987), which has proven particularly effective for solid-earth applications (Sobolev and Babeyko, 1994; Gerya et al., 2001), is unique among non-linear minimization strategies in that the Gibbs energy of the system is expressed as direct function of the Gibbs energies of its constituent phases. In the initial step of the THERIAK algorithm the  $\Pi$  possible pure phases are considered. The  $c$  stable phases under this constraint are found by minimizing

$$G^{\text{system}} = \sum_{j=1}^p \alpha^j g^j, \quad (19)$$

subject to

$$N_k^{\text{system}} = \sum_{j=1}^p \alpha^j x_k^j, \quad k = 1, \dots, c-1 \quad (20)$$

and

$$\alpha^j \geq 0, \quad j = 1, \dots, p \quad (21)$$

by linear programming. This initial solution defines the  $g$ - $x$  plane (Fig. 4a)

$$g = \mu_c + \sum_{j=1}^{c-1} x_j (\mu_j - \mu_c). \quad (22)$$

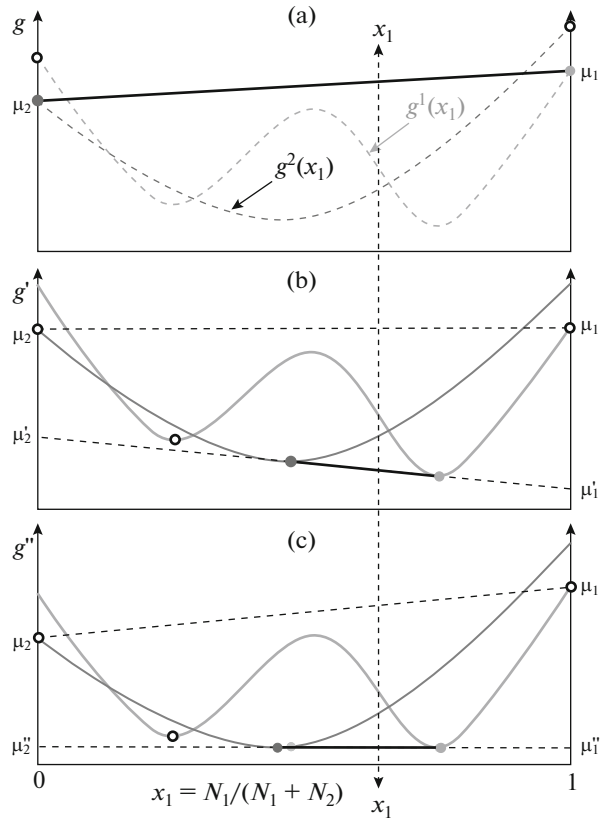
The complete set of  $g^i(x_k)$  functions of interest are then transformed as

$$g^{i'} = g^i - g \quad (23)$$

so that in the transformed  $g$ - $x$  space the plane of the initial solution is horizontal (Fig. 4b). Non-linear programming is then used to locate the minima of the individual  $g^{i'}$  functions and the linear programming step is repeated considering these minima and the phases of the initial solution. These two steps are repeated iteratively until the solution is judged to have converged to the global minimum. The virtue of THERIAK is it provides a general solution to the immiscibility problem. However, this solution is subject to the caveat that the location of all local minima during the non-linear programming step is essential to assure convergence to the global minimum and is not algorithmically certain.

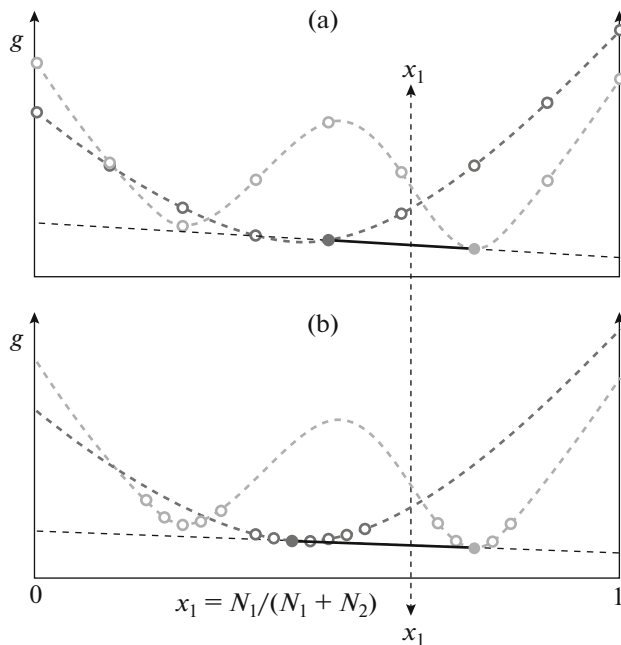
### LINEARIZED GIBBS ENERGY MINIMIZATION

The THERIAK algorithm is a partially linearized solution to the phase equilibrium problem in that the global minimum in Gibbs energy is determined considering only phases with specified compositions, but non-linear methods are used to derive these specified



**Fig. 4.** Schematic illustration of the THERIAK algorithm (DeCapitani and Brown, 1987) for a binary ( $c = 2$ ), isobaric-isothermal, system with composition  $x_1^{\text{system}}$  in which all possible states of matter are described equations of state  $g^1(x_1)$  and  $g^2(x_1)$ . The initial solution is obtained by linear programming considering only the limiting compositions of  $g^1(x_1)$  and  $g^2(x_1)$  (circular symbols in a). This solution, the filled symbols, defines a  $g$ - $x$  plane and chemical potentials  $\mu_1$  and  $\mu_2$ . Given these chemical potentials the  $g$ -coordinates of  $g^1(x_1)$  and  $g^2(x_1)$  are transformed according to Eq. (23), so that the  $g$ - $x$  plane of the original solution is horizontal (b). The minima in the transformed functions  $g^{i'}(x_1)$  and  $g^{j'}(x_1)$  are then located by non-linear programming. A new solution (filled circles in b) is obtained from these minima and the previous solution by linear programming, which defines the  $g$ - $x$  plane with chemical potentials  $\mu_1'$  and  $\mu_2'$ , the transformation (Eq. (23)), the minima relocated, and linear programming used to identify the new solution (filled circles in b, gray circles indicate the previous solution). These steps are repeated iteratively until the phase compositions converge within the desired tolerance. Note that in b, the resolution of the drawing is inadequate to clearly show that the line connecting the filled symbols is not identical to the common tangent between  $g^1(x_1)$  and  $g^2(x_1)$ , from c it is evident that the common tangent must lie at slightly lower values of  $x_1$  for any given value of  $g$ .

compositions. An extraordinarily simple alternative to non-linear methods originally proposed by White et al. (1958), and implemented in various incarnations of the `Perple_X` computer program (e.g., Connolly



**Fig. 5.** Schematic illustration of the linearized formulation (White et al., 1958, Connolly and Kerrick, 1987) of the phase equilibrium problem for a binary ( $c = 2$ ), isobaric-isothermal, system with composition  $x_1^{\text{system}}$  in which all possible states of matter are described by two equations of state (dashed curves). Each equation of state is represented by a finite set of points (circular symbols) and the solution (filled circles in a) is obtained by linear programming. If desired, the solution can be iteratively refined by increasing the resolution of the discretization around a solution obtained at lower resolution (filled circles in b). To avoid convergence to local minima during iterative refinement it is necessary to increase the resolution around metastable states that are close to the  $g$ - $x$  plane of the previous solution.

and Kerrick, 1987; Connolly, 2005), is to completely linearize the problem by approximating the continuous spectrum of states defined by each  $g^i(x_k)$  function by a finite number of discrete phase states (Fig. 5a). The stable assemblage is then found without iteration by minimizing the Gibbs energy of the system (Eq. (19)) subject to mass balance (Eq. (20)) and non-negativity (Eq. (21)) constraints, where  $\Pi$  is now the number of discrete states. For an arbitrarily specified state of the system, the stable discretized assemblage consists of  $c$  discrete phase states. If more than one discrete state of a phase is stable, then within the resolution of the discretization the states that are compositionally adjacent correspond to a single phase in the real problem; whereas discrete states that are separated by unstable states of the same equation of state represent distinct states in the real problem (e.g., immiscible states). The virtues of the linearized formulation are its extraordinary simplicity and that an optimization algorithm (Simplex, White et al., 1958) can be selected that assures convergence to a global minimum.

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 consider that the discretization of a  $c - 1$  dimensional function on a uniform Cartesian grid with spacing  $\delta$  generates

$$\Pi \approx \frac{1}{2} \times \left( \sum_{i=c-2}^{c-1} \frac{(1/\delta + 1)^i}{(i-1)!} + c - 1 + \sum_{i=1}^{c-1} \frac{(1/\delta - 1)^i (c-1)!}{(i!)^2 (c-1-i)!} \right) \quad (24)$$

phase states. Thus discretization 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.,  $\sim 2$  Gb of addressable memory). In such cases, iterative refinement of the linearization can be used to achieve resolution that is limited by machine precision rather than memory (White et al., 1958). Within the inherent limitations of a method with finite resolution, the non-iterative solution of the linearized problem is algorithmically certain. In contrast, the iterative solution suffers from the possibility of convergence to a local minimum. The origin of this weakness is that a low resolution optimization may not identify the phases that would be stable at higher resolution. To minimize this risk it is essential to refine the discretization of phases that are nearly stable as well as those that are stable. While the strategy implemented for this purpose in *Perple\_X* (Connolly, 2009) has proven robust it, in common with all non-linear optimization strategies, is not algorithmically certain.

## PHYSICAL PROPERTIES

Given the equations of state  $g^i(P, T, x_k)$  for the possible phases of a system, Gibbs energy minimization yields the amounts and compositions of the stable phases of the system as function of its pressure, temperature and composition. While the notion of using  $g^i(P, T, x_k)$  as the equation of state of a phase may seem unduly complex in comparison to the simple  $P$ - $v$ - $T$  relations such as the Birch-Murnaghan or Vinet often discussed in mineral physics for pure phases, it offers a consistent and compact means of summarizing the information contained separately in the caloric, mechanical and compositional equations of state used to describe impure phases. This information is trivially recovered from the thermodynamic identities that relate the Gibbs energy to internal energy, enthalpy and the Helmholtz energy

$$u = g + Ts - Pv, \quad (25)$$

$$h = g + Ts, \quad (26)$$

$$f = g - Pv, \quad (27)$$

and various partial derivatives. From Eq. (8), the first order derivatives of  $g$  yield

$$s = -\partial g / \partial T, \quad (28)$$

$$v = \partial g / \partial P. \quad (29)$$

Second order properties such the isothermal bulk modulus, isobaric expansivity, and the isobaric heat capacity are then

$$K_T \equiv -v / (\partial v / \partial P)_T = -\frac{\partial g / \partial P}{\partial^2 g / \partial P^2}, \quad (30)$$

$$\alpha_P \equiv \frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_P = \frac{1}{\partial g / \partial P} \frac{\partial^2 g}{\partial P \partial T}, \quad (31)$$

$$c_P \equiv \frac{\partial h}{\partial T} = \frac{\partial(g + Ts)}{\partial T} = -T \frac{\partial^2 g}{\partial T^2}. \quad (32)$$

In geophysics it is generally assumed that the time-scale for seismic wave propagation is short compared to the time-scale for thermal relaxation and therefore that the associated deformation is better described by adiabatic rather than isothermal elastic moduli. The additional arithmetic necessary to express adiabatic or isochoric derivatives in terms of  $g(P, T)$  follows assuming two zeroth-order homogeneous functions  $f(x, y)$  and  $z(x, y)$ , such as  $s(P, T)$  and  $v(P, T)$  from Eqs. (28) and (29). Taking the total differential of  $f(x, y)$

$$df = (\partial f / \partial x)_y dx + (\partial f / \partial y)_x dy \quad (33)$$

and differentiating with respect to  $x$  at constant  $z$  yields

$$(\partial f / \partial x)_z = (\partial f / \partial x)_y + (\partial f / \partial y)_x / (\partial y / \partial x)_z. \quad (34)$$

From Euler's chain rule for differentiation

$$(\partial y / \partial x)_z = -(\partial z / \partial x)_y / (\partial z / \partial y)_x \quad (35)$$

and substituting Eq. (35) into Eq. (34)

$$\begin{aligned} (\partial f / \partial x)_z &= (\partial f / \partial x)_y \\ &- (\partial f / \partial y)_x (\partial z / \partial x)_y / (\partial z / \partial y)_x. \end{aligned} \quad (36)$$

The utility of Eq. (36) is apparent if a property such as the adiabatic bulk modulus

$$K_S = -v / (\partial v / \partial P)_S \quad (37)$$

is required. Mapping  $\{s, v, P, T\} \rightarrow \{z, f, x, y\}$  in Eq. (36) yields

$$\begin{aligned} (\partial v / \partial P)_S &= (\partial v / \partial P)_T \\ &- (\partial v / \partial T)_P (\partial s / \partial P)_T / (\partial s / \partial T)_P \end{aligned} \quad (38)$$

and substituting Eq. (38) into Eq. (37) and expressing  $s$  and  $v$  in terms of  $g$

$$K_S = -\frac{\partial g}{\partial P} / \left[ \frac{\partial^2 g}{\partial P^2} - \left( \frac{\partial^2 g}{\partial P \partial T} \right)^2 / \frac{\partial^2 g}{\partial T^2} \right]. \quad (39)$$

For generality, it is expedient to approximate the partial derivatives of the Gibbs energy needed to estimate physical properties by finite difference operators.

Through manipulations of the type outlined above it is possible to obtain all thermodynamic properties with the exception of elastic shear moduli. This exception is a consequence of the fact that current thermodynamic equations of state for phase equilibrium models discount the minor energetic effect attributable to non-hydrostatic stress (Dahlen, 1992; Connolly, 2009). To date, shear moduli are computed from ad-hoc empirical functions (e.g., Bina and Helffrich, 1992; Sobolev and Babeyko, 1994; Hacker and Abers, 2004) or from explicit formulations of the Helmholtz energy as a function of the strain tensor (Stixrude and Lithgow-Bertelloni, 2005). It is of course possible to express the Gibbs energy of a non-hydrostatically stressed solid as a function of its stress tensor components (Callen, 1960). In such a formulation the shear modulus can be expressed analogously to Eq. (39) in terms of partial derivatives of the Gibbs energy with respect to the six stress tensor components and temperature.

The partial derivatives of the equations of state of individual phases of a system do not account for processes of inter-phase chemical equilibration that occur in response to changing pressure and temperature. Given that the time-scale for inter-phase equilibration is orders of magnitude greater than that for thermal equilibration, the use of such derivatives, designated "isomorphous" derivatives (Stixrude and Lithgow-Bertelloni, 2011), is appropriate for the evaluation of properties relevant to seismic studies. In contrast, for the longer time scales typical of geodynamic processes such as mantle convection, it is reasonable to assume inter-phase equilibrium is maintained, in which case the physical properties of the system are best estimated by differentiation of the Gibbs energy of the system, rather than from the isomorphous derivatives of its constituent phases. Elsewhere (Connolly et al., 2009) it has been remarked that because the derivatives of the Gibbs energy are singular during low order phase transformations ( $p > c$ ), the formulation of governing equations in terms of the natural variables ( $s, v, x_k$ ) of the internal energy may be preferable to the natural variables of the Gibbs energy ( $P, T, x_k$ ). Such a reformulation does not necessarily require direct optimization of the internal energy.

## CONCLUDING REMARKS

Gibbs energy minimization yields a numeric equation of state from which it is possible to recover all thermodynamic properties of an equilibrium thermodynamic system. An unfortunate consequence of the non-linear character of the optimization problem is that there is no means of propagating the uncertainties in the equations of state of individual phases short of expensive Monte Carlo methods (Connolly and Khan, 2016). This difficulty has contributed to the false perception that simple parameterizations of experimentally determined phase relations and prop-



erties are more reliable than thermodynamic methods. Thermodynamic data bases and simple parameterizations are ultimately based on the same underlying data, but, in practice, thermodynamic data bases are, invariably, derived by sampling a broader spectrum of experimental data. Thus a pragmatic solution to the problem of assessing the uncertainty of properties derived by Gibbs energy minimization is to rely on parameterizations of that uncertainty.

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