

# Thermodynamic coupling of phase and chemical boundaries in planetary interiors

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## ABSTRACT

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Mass-transfer equilibrium in multi-component closed systems at thermal and mechanical equilibrium requires that the chemical potential of each component be uniform over all phases in the system, yielding the classical Gibbs phase rule relating the number of independent components (i.e. chemical species), the number of externally unconstrained state variables (i.e. 'degrees of freedom'), and the number of coexisting phases at equilibrium. More general closed systems, however, may be subject to thermal or mechanical disequilibrium (e.g. non-zero temperature gradients), giving rise to non-zero chemical potential gradients. Such systems require 'intra-phase' equilibrium conditions upon the chemical potential gradients in addition to the usual 'interphase' conditions upon the chemical potentials themselves, yielding a modified phase rule restricting the stability of regions of multi-phase coexistence. The attainment of mass-transfer equilibrium under such conditions requires that isochemical multi-phase systems break down into chemically distinct juxtaposed single-phase regions, thermodynamically coupling multivariant phase transitions to chemical discontinuities.

Hence, for example, phase change and chemical change hypotheses for seismic velocity discontinuities in the Earth's interior need not be mutually exclusive. The kinetic hindrance by slow diffusion of phase-transition-coupled chemical differentiation in the Earth may be alleviated by high temperatures, the presence of fluids or melts, convective mass flow, negative Clapeyron slopes, or stratification due to earlier episodes of differentiation. Radial mass-transfer equilibrium across the spinel–perovskite transition for an upper mantle with  $X_{\text{Mg}} \approx 0.89$ , for example, yields a stable contrast in Fe/Mg composition with  $X_{\text{Mg}} \approx 0.86$  in the lower mantle.

## 1. Introduction

The characterization of internal stratification is an important part of the study of planetary interiors. For example, rapid changes in seismic velocity in the Earth, such as those which occur at approximately 400 and 670 km depth, are indicative of radial variations in the material properties of the planet's interior. Such changes in material

properties have been ascribed either to phase transitions in material of constant bulk composition (e.g. Bernal, 1936; Ringwood, 1970) or to changes in bulk chemical composition (e.g. Bullen, 1937; Anderson and Bass, 1986). The question of whether such seismic velocity variations represent changes in phase or changes in chemical composition is of fundamental importance to understanding the composition, structure and dynamics of the Earth's interior (see Silver et al., 1985, 1988). By comparing the seismologically determined properties of the Earth's interior with the experi-

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mentally determined properties of various mineral assemblages, numerous studies have attempted to distinguish between such phase change and chemical change hypotheses (see Lees et al., 1983; Jeanloz and Thompson, 1983). One purpose of this article, however, is to point out that such phase and chemical change hypotheses need not be mutually exclusive (Kumazawa et al., 1974). Indeed, we demonstrate that chemical discontinuities may be expected to accompany multivariant phase transitions in planetary interiors.

The usual procedure for estimating the equilibrium composition and distribution of phases in the Earth's interior (e.g. Jeanloz and Thompson, 1983; Lees et al., 1983; Bina and Wood, 1984, 1987; Navrotsky and Akaogi, 1984) is to conceptually divide the region under consideration into a large number of concentric spherical 'shells'. Each of these shells is assumed to be internally in thermal and mechanical equilibrium, and it is assumed that no radial mass transfer occurs between shells. Thus, each shell is characterized by a given pressure, temperature and fixed bulk composition, so that the classical thermodynamics of closed systems may be applied to each shell individually.

Standard thermodynamic treatments of mass-transfer equilibrium in multi-component closed systems at thermal and mechanical equilibrium (e.g. Guggenheim, 1950; Denbigh, 1981) follow the classical approach of Gibbs, defining 'chemical potential' functions and deriving the conditions for equilibrium with respect to mass transfer between phases in terms of these chemical potentials. This gives rise to the usual requirement that the chemical potential of each component be uniform over all phases in the system, yielding the classical 'Gibbs phase rule' (see Callen, 1960, pp. 163–167) specifying the relationship between the number of independent components (i.e. chemical species), the number of externally unconstrained state variables (i.e. 'degrees of freedom'), and the number of coexisting phases at equilibrium. Thus, this phase rule describes the systems for which solutions exist — i.e. the physically realizable equilibrium states.

Implicit in this usual approach is the assumption that mass transfer between adjacent shells

does not occur. Given that a planet is characterized by non-zero radial pressure and temperature gradients, the consequence of this assumption is that such a planetary model is in radial disequilibrium with respect to mass transfer. In other words, adjacent shells at different temperatures and pressures are not in mass-transfer equilibrium with each other. It is a straightforward matter to remove this common assumption and to solve for the state of radial equilibrium with respect to mass transfer.

In general closed systems, the conditions of thermal and/or mechanical equilibrium may not hold (e.g. non-zero temperature gradients). In such systems, the usual 'inter-phase' conditions upon the chemical potentials are not sufficient to describe the equilibrium state with respect to mass transfer. Because the individual phases are no longer homogeneous in terms of their state variables, they must each be considered as a continuous sequence of infinitesimally differing phases (see Guggenheim, 1950, p. 355). Thus, additional 'intra-phase' conditions upon the chemical potential gradients are required in order to specify mass-transfer equilibrium states. These conditions lead to a modified form of the phase rule characterizing the physically realizable equilibrium states.

We find that this extended phase rule effectively restricts the stability of regions of multi-phase coexistence, so that attainment of mass-transfer equilibrium under conditions of thermal or mechanical disequilibrium requires that isochemical multi-phase systems break down into chemically distinct juxtaposed single-phase regions. The prominent feature in the case of radial disequilibrium, in which it is assumed that mass transfer cannot occur between shells, is the existence of broad multivariant regions in which multiple phases coexist in inter-phase equilibrium; the compositions and relative proportions of these phases vary in a continuous manner throughout the multivariant region, but the bulk composition does not vary. In the case of radial equilibrium, however, in which mass transfer is allowed to occur between shells, the multivariant region is replaced by a univariant boundary separating regions of single-phase stability; the bulk composi-

tion changes discontinuously across this univariant boundary. Thus, radial mass-transfer equilibrium in planetary interiors entails the thermodynamic coupling of chemical discontinuities to multivariant phase transitions. Hence, for example, the attainment of radial mass-transfer equilibrium should give rise to sharp, discontinuous changes in material properties, rather than the gradual, continuous changes usually associated with isochemical multivariant phase transitions (see Bina and Wood, 1987).

Here we review the derivation of the classical conditions for inter-phase mass-transfer equilibrium. We summarize the derivation of the Gibbs phase rule from these conditions and its implications in terms of stable phase assemblages. We then derive the additional conditions required for intra-phase mass-transfer equilibrium, and we derive an extended form of the phase rule as required by these additional conditions. Subsequently, we examine the consequences of this extended phase rule with regard to stable phase assemblages, and we discuss its relationship to the classical Gibbs phase rule. Finally, we comment upon some kinetic and dynamic considerations in the attainment of mass-transfer equilibrium in planetary interiors.

## 2. Inter-phase mass transfer equilibrium

Thermodynamic equilibrium is the state, characterized completely by the extensive parameters  $S$  (entropy),  $V$  (volume) and  $N_i$  (number of moles of component  $i$ ), in which these parameters, in the absence of internal constraints, assume values which minimize the function  $U$  (internal energy) for a given value of the total entropy (see Callen, 1960, p. 88).

$$dU = \left( \frac{\partial U}{\partial S} \right)_{V, N_i} dS + \left( \frac{\partial U}{\partial V} \right)_{S, N_i} dV + \sum_i \left( \frac{\partial U}{\partial N_i} \right)_{S, V, N_j} dN_i = 0 \quad (1)$$

Upon employing the definitions

$$P \equiv - \left( \frac{\partial U}{\partial V} \right)_{S, N_i} \quad T \equiv \left( \frac{\partial U}{\partial S} \right)_{V, N_i} \quad (2)$$

$$\mu_i \equiv \left( \frac{\partial U}{\partial N_i} \right)_{S, V, N_j}$$

where  $P$  is pressure,  $T$  temperature, and  $\mu_i$  the 'chemical potential' of component  $i$ , we can express the 'energy minimum principle' eqn. (1) as

$$dU = T dS - P dV + \sum_i \mu_i dN_i = 0 \quad (3)$$

(Strictly, this is an 'extremum principle'; the actual 'minimum principle' includes an additional  $d^2U > 0$  stability requirement (see Callen, 1960, pp. 27–28).) Upon considering an internally unconstrained closed system of multiple phases  $\phi$ , eqn. (3) describing thermodynamic equilibrium becomes

$$dU = \sum_{\phi} dU^{\phi} = \sum_{\phi} T^{\phi} dS^{\phi} - \sum_{\phi} P^{\phi} dV^{\phi} + \sum_{i, \phi} \mu_i^{\phi} dN_i^{\phi} = 0 \quad (4)$$

The energy minimum principle applies to closed systems of fixed volume, bulk composition and total entropy, giving the closure conditions

$$\sum_{\phi} dS^{\phi} = 0 \quad \sum_{\phi} dV^{\phi} = 0$$

$$\sum_{\phi} dN_i^{\phi} = 0 \quad \text{for all components } i \quad (5)$$

Upon solving eqn. (4) subject to eqns. (5), we obtain the standard description of the equilibrium state. In particular, thermal equilibrium between phases requires uniformity of temperature:

$$T^{\phi} = T^{\psi} \quad \text{for all phases } \phi \text{ and } \psi \quad (6)$$

mechanical equilibrium between phases requires uniformity of pressure:

$$P^{\phi} = P^{\psi} \quad \text{for all phases } \phi \text{ and } \psi \quad (7)$$

and mass-transfer equilibrium between phases requires uniformity of chemical potential for each component:

$$\mu_i^{\phi} = \mu_i^{\psi} \quad \text{for all components } i$$

$$\text{in all phases } \phi \text{ and } \psi \quad (8)$$

General thermodynamic equilibrium ( $dU = 0$ ) thus requires simultaneous thermal, mechanical and mass-transfer equilibrium.

To extend this analysis to systems which may be subject to external potential fields, we replace the chemical potentials  $\mu_i^\phi$  in the above equations by the 'generalized chemical potentials'  $\eta_i^\phi$

$$\eta_i^\phi \equiv \mu_i^\phi + E_i^\phi \quad (9)$$

where  $E_i^\phi$  is the molar potential energy of component  $i$  in phase  $\phi$  due to external potential fields. Thus, in the presence of external potential fields (e.g. gravity), eqs. (8) describing inter-phase mass-transfer equilibrium become

$$\eta_i^\phi = \eta_i^\psi \quad \text{for all components } i \quad (10)$$

in all phases  $\phi$  and  $\psi$

requiring uniformity of generalized chemical potential across all phases for each component.

### 3. The Gibbs phase rule

Consider a closed multi-phase system of several components, characterized by some uniform pressure  $P$  and temperature  $T$ . At equilibrium with respect to mass transfer between phases, the generalized chemical potential of each component must be the same in all phases, as indicated in eqn. (10) above. For a system of  $N$  components in  $R$  phases, we thus have

$$\eta_i^{\phi_1} = \eta_i^{\phi_2} = \dots = \eta_i^{\phi_R} \quad \text{for all components } i \quad (11)$$

giving  $R - 1$  equations for each component, or  $(R - 1)N$  equations in all. Since the generalized chemical potentials are functions of pressure, temperature and composition, the unknown quantities in these equations are  $P$ ,  $T$  and the mole fractions  $X_i^\phi$  of each component  $i$  in each phase  $\phi$ , given by

$$X_i^\phi \equiv \frac{N_i^\phi}{\sum_i N_i^\phi} \quad (12)$$

Since  $\sum_i X_i^\phi$  is unity, we have  $N - 1$  independent mole fractions for each phase, giving a total of

$2 + R(N - 1)$  unknowns. The number of undetermined variables, or 'degrees of freedom'  $F$ , is given by the number of unknowns less the number of constraining equations. Hence, we obtain the usual 'Gibbs phase rule' (see Callen, 1960, pp. 163-167)

$$F = N + 2 - R \quad (13)$$

Thus, for example, single-component ( $N = 1$ ) systems have  $3 - R$  degrees of freedom in their equilibrium state. For two phases ( $R = 2$ ) to coexist in equilibrium, we may freely vary one ( $F = 1$ ) parameter (e.g. pressure), but the other (e.g. temperature) will be determined by the equilibrium conditions. Two-component ( $N = 2$ ) systems have  $4 - R$  degrees of freedom. For two phases ( $R = 2$ ) to coexist in equilibrium, we may freely vary two ( $F = 2$ ) parameters (e.g. pressure and temperature), but the others (e.g. the compositions of the two phases) will be determined by the equilibrium conditions.

Consider, for example, a simple binary (i.e. two-component) system A-B in which two phases,  $\alpha$  and  $\beta$ , may coexist. At equilibrium with respect to mass transfer between the phases, the generalized chemical potential of component A must be the same in both phases, and the generalized chemical potential of component B must be the same in both phases, as stipulated in eqns. (10). Hence, we have

$$\begin{aligned} \eta_A^\alpha(P, T, X_B^\alpha) &= \eta_A^\beta(P, T, X_B^\beta) \\ \eta_B^\alpha(P, T, X_B^\alpha) &= \eta_B^\beta(P, T, X_B^\beta) \end{aligned} \quad (14)$$

where we have indicated the functional dependence of the generalized chemical potentials upon pressure, temperature and phase composition. The Gibbs phase rule eqn. (13) indicates that this system possesses two degrees of freedom. Thus, we may freely vary any two of the unknowns (e.g.  $P$  and  $T$ ), and the remaining variables (e.g.  $X_B^\alpha$  and  $X_B^\beta$ ) will be fully determined by the constraining equations. Hence, at any fixed pressure and temperature we have two equations (eqns. (14)) in two unknowns,  $X_B^\alpha$  and  $X_B^\beta$ , so that we may solve for the equilibrium compositions of the two phases. Such solutions are depicted in the phase diagram of Fig. 1, where equilibrium phase

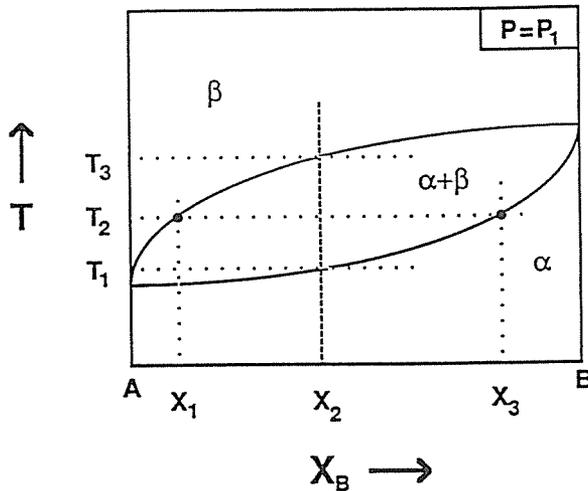


Fig. 1. Equilibrium binary phase diagram in isobaric temperature-composition space for A-B join. Lines indicate single-phase  $\alpha$  and  $\beta$  stability fields of coexisting phases in the divariant  $\alpha + \beta$  region.

assemblages and compositions are given as functions of temperature for a given fixed pressure  $P_1$ . Given a sample of bulk composition  $X_2$ , its stable state will be pure  $\alpha$  phase of composition  $X_2$  at any temperature below  $T_1$ . At any temperature above  $T_3$ , its stable state will be pure  $\beta$  phase of composition  $X_2$ . Between  $T_1$  and  $T_3$  there lies a 'divariant' region in which, at any given pressure, the stable state is a mixture of coexisting  $\alpha$  and  $\beta$  phases of various compositions. For example, at temperature  $T_2$  the stable state consists of a mixture of  $\alpha$  phase of composition  $X_3$  and  $\beta$  phase of composition  $X_1$ . The phase diagram of Fig. 1 thus yields a profile of equilibrium phase composition as a function of temperature at pressure  $P_1$ . The relative proportions of the  $\alpha$  and  $\beta$  phases in the equilibrium phase assemblage can be determined by applying the mass-balance conditions known as the 'lever rule' (see Callen, 1960, pp. 154–156).

$$X_{\alpha}^{\text{equil}} = \frac{X_{\text{B}}^{\text{bulk}} - X_{\text{B}}^{\beta}}{X_{\text{B}}^{\alpha} - X_{\text{B}}^{\beta}} \quad (15)$$

where  $X_{\text{B}}^{\text{bulk}}$  is the mole fraction of component B in the bulk composition of the system, and  $X_{\alpha}^{\text{equil}}$  is the mole fraction of phase  $\alpha$  in the system at equilibrium.

While such phase diagrams yield equilibrium phase compositions as functions of temperature and pressure, they can only be used to infer the state of mass-transfer equilibrium in a planetary interior if the planet can be represented as a number of layers or 'shells' each characterized by a given fixed pressure, temperature and bulk chemical composition. However, if the planet's interior is subject to non-zero pressure, temperature or compositional gradients, such a characterization is equivalent to the assumption that no mass transfer occurs between adjacent shells.

#### 4. Intra-phase mass transfer equilibrium

Let us now expand the systems under consideration to include those subject to non-zero gradients in pressure or temperature. In eqns. (8)–(10) above, we considered equilibrium with respect to mass transfer due to chemical potential differences between phases, where each phase was homogeneously characterized by a given pressure, temperature and composition. Since individual phases no longer need be homogeneous in state, we must now address the issue of equilibrium with respect to mass transfer due to chemical potential gradients within each phase, effectively considering each phase to be a continuous sequence of infinitesimally differing phases (see Guggenheim, 1950, p. 355).

Mass-transfer processes are driven by chemical potential gradients (see Denbigh, 1981, pp. 86–87). The flux  ${}_n J_i^{\phi}$  of component  $i$  in phase  $\phi$  in some (e.g. 'barycentric' or ' $n$ th-component velocity') reference frame  $n$  (see DeGroot and Mazur, 1962, pp. 240–241) can be expressed by a generalized diffusion equation

$${}_n J_i^{\phi} = D_{in}^{\phi} (\nabla \mu_i^{\phi} - \nabla \mu_n^{\phi})$$

for all components  $i$  in all phases  $\phi$  (16)

where the  $D_{in}^{\phi}$  are transport coefficients (in the reference frame  $n$ ) for each component  $i$  in phase  $\phi$  (see Appendix A). At equilibrium with respect to mass transfer, the fluxes must vanish (see DeGroot and Mazur, 1962, p. 267).

$${}_n J_i^\phi = 0 \quad \text{for all components } i \text{ in all phases } \phi \quad (17)$$

Since the  $D_{in}^\phi$  are in general non-zero, from eqns. (16) and (17) we obtain

$$\nabla \mu_i^\phi = \nabla \mu_n^\phi \quad \text{for all components } i \text{ in all phases } \phi \quad (18)$$

Thus, at mass-transfer equilibrium, the chemical potential gradients must be uniform across all components in a given phase.

$$\nabla \mu_i^\phi = \nabla \mu_j^\phi \quad \text{for all components } i \text{ and } j \quad (19)$$

in all phases  $\phi$

To extend this discussion to systems which may be subject to external potential fields, we proceed in the manner of eqn. (9), replacing the chemical potentials  $\mu_i^\phi$  in the above equations by the generalized chemical potentials  $\eta_i^\phi$ .

$$\nabla \eta_i^\phi = \nabla \mu_i^\phi - F_i^\phi \quad (20)$$

where  $F_i^\phi = -\nabla E_i^\phi$  is the molar force acting upon component  $i$  in phase  $\phi$  due to external potential fields (e.g. gravity). Equations (19) for intra-phase mass-transfer equilibrium now become

$$\nabla \eta_i^\phi = \nabla \eta_j^\phi \quad \text{for all components } i \text{ and } j \quad (21)$$

in all phases  $\phi$

requiring uniformity of generalized chemical potential gradients across all components in each phase.

### 5. An extended phase rule

For systems subject to gradients in pressure or temperature, individual phases are no longer homogeneous in their state variables. Therefore, we need to consider the requirements of intra-phase mass-transfer equilibrium (eqns. (21)) in addition to the inter-phase mass-transfer equilibrium conditions (eqns. (10)) used to derive the Gibbs phase rule; eqn. (13) above. Consider a general system of  $N$  components in  $R$  phases. As independent unknown functions, we have  $P(\mathbf{r})$ ,  $T(\mathbf{r})$  and  $R(N-1)$  functions  $X_i^\phi(\mathbf{r})$ , where  $\mathbf{r}$  is a vector denoting position within the system, giving a total of

$2 + RN - R$  unknown functions. As constraining equations, we have the  $N(R-1)$  inter-phase equilibrium equations (eqns. (10)),

$$\eta_i^\phi(\mathbf{r}) = \eta_i^\psi(\mathbf{r}) \quad \text{for all components } i \quad (22)$$

in all phases  $\phi$  and  $\psi$

and  $R(N-1)$  intra-phase equilibrium equations (eqns. (21)),

$$\nabla \eta_i^\phi = \nabla \eta_j^\phi \quad \text{for all components } i \text{ and } j \quad (23)$$

in all phases  $\phi$

giving a total of  $2RN - R - N$  equations. The number of unknowns less the number of equations determines the number of degrees of freedom,  $F$ , giving

$$F = 2 + N - RN \quad (24)$$

Thus, all single-phase systems ( $R = 1$ ) have two degrees of freedom in their equilibrium state: choosing two functions (e.g. the temperature and pressure profiles) determines the others (e.g. the compositional profiles). A two-phase, single-component system ( $R = 2$ ,  $N = 1$ ) has one degree of freedom: choosing one function (e.g. the pressure profile) determines the other (e.g. the temperature profile). A two-phase, two-component system ( $R = 2$ ,  $N = 2$ ) has zero degrees of freedom, but the only solutions are non-physical in that  $X_i^\phi \geq 1$  or  $X_i^\phi \leq 0$ . A three-phase, single-component system ( $R = 3$ ,  $N = 1$ ) also has zero degrees of freedom, but there is no solution unless  $\nabla T = 0$  and  $\nabla P = 0$ . All other multi-phase systems ( $R > 1$ ) are overdetermined ( $F < 0$ ) and have no equilibrium state (i.e. the number of phases present must decrease in order for equilibrium to be attained).

For those systems which do have an equilibrium state, the integration of eqns. (23) gives an additional  $2 + R(N-1)$  surface functions  $P(\mathbf{r}_0)$ ,  $T(\mathbf{r}_0)$  and  $X_i^\phi(\mathbf{r}_0)$  which are subject to an additional two boundary conditions:

$$P(\mathbf{r}_0) = \text{given}, \quad T(\mathbf{r}_0) = \text{given}, \quad (25)$$

where  $\mathbf{r}_0$  describes the surface of the volume under consideration. We also have an additional  $R-1$  unknown phase distribution functions

$X_\phi(\mathbf{r})$ , which are subject to an additional  $N - 1$  independent mass-balance constraints.

$$\int_{\text{volume}} \sum_{\phi} X_{\phi} X_i^{\phi} dv = X_i^{\text{sys}} \int_{\text{volume}} dv \quad \text{for all components } i \quad (26)$$

where  $X_i^{\text{sys}}$  is the mole fraction of component  $i$  in the bulk composition of the entire system. These additional  $1 + RN$  unknown functions and  $1 + N$  constraining equations give an additional  $RN - N$  degrees of freedom, so that eqn. (24) becomes

$$F = 2 \quad (27)$$

If we further assume that mechanical (e.g. hydrostatic) equilibrium is maintained, we introduce the additional constraining equation

$$\nabla P = \frac{\sum_{i,\phi} X_{\phi} X_i^{\phi} \mathbf{F}_i^{\phi}}{\sum_{i,\phi} X_{\phi} X_i^{\phi} \hat{V}_i^{\phi}} \quad (28)$$

(e.g.  $\nabla P = -\rho \mathbf{g}$  for gravity), so that eqn. (27) becomes

$$F = 1 \quad (29)$$

Thus, choosing one function (e.g. the temperature profile) determines the others (e.g. the pressure and compositional profiles).

Consider, for example, a multi-component system containing a single phase  $\alpha$  in a gravitational field. The generalized chemical potential of eqn. (9) becomes (see Denbigh, 1981, pp. 87–88)

$$\eta_i^{\alpha} = \mu_i^{\alpha} - m_i \mathbf{g} \cdot \mathbf{r} \quad (30)$$

where  $m_i$  is the molar mass of component  $i$ ,  $\mathbf{g}$  is gravitational acceleration, and  $\mathbf{r}$  is position in the gravitational field. Our extended phase rule (eqn. (24)) indicates that such a system possesses two degrees of freedom; choosing two of the unknown functions (e.g.  $P(\mathbf{r})$  and  $T(\mathbf{r})$ ) determines the remaining functions (e.g. the  $X_i(\mathbf{r})$ ). Thus, we may choose temperature and pressure profiles which satisfy thermal ( $\nabla T = 0$ ) and mechanical ( $\nabla P = -\rho \mathbf{g}$ ) equilibria (see Appendix B). Under such conditions, solution of the equilibrium equations (eqns. (21)) gives rise to the familiar ‘sedi-

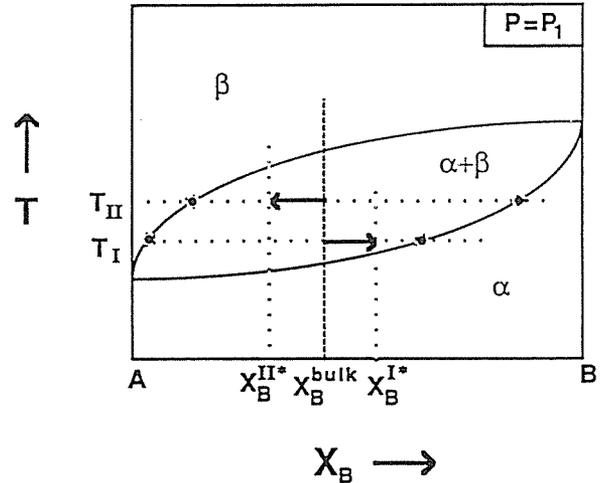


Fig. 2. Equilibrium binary phase diagram in isobaric temperature-composition space for A–B join. Arrows illustrate compositional migration is the discrete case of two adjacent shells as the system, which is subject to non-zero temperature gradients and is initially in inter-phase mass-transfer equilibrium (dotted line), evolves toward intra-phase equilibrium.

mentation equilibrium’ (see DeGroot and Mazur, 1962, pp. 267–269) in which the proportion of denser components increases with depth at the expense of the lighter components.

$$\mathbf{g}(m_i - \rho \hat{V}_i) = \sum_j^{N-1} \left( \frac{\partial \mu_i}{\partial X_j} \right)_{T,P,X_k \neq j} \frac{dX_j}{dr} \quad \text{for all components } i \quad (31)$$

where  $\rho$  is the density of the system.

As another example, consider the binary system A–B of Fig. 1 in which two phases,  $\alpha$  and  $\beta$ , may coexist. According to our extended phase rule (eqn. (24)), such a system is overdetermined in the absence of either mechanical or thermal equilibrium and must break down into single-phase regions in order to attain an equilibrium state with respect to mass transfer. For simplicity, we consider first the discrete case of two adjacent ‘shells’ I and II, both at pressure  $P_1$  (i.e. mechanical equilibrium), where  $T_{II}$  is greater than  $T_I$  (i.e. thermal disequilibrium); this case is depicted in Fig. 2. We shall assume that these two shells are initially of the same bulk composition, so that both  $X_B^I$  and  $X_B^{II}$  are initially equal to  $X_B^{\text{bulk}}$ , and

that each shell is initially in a state of inter-phase equilibrium, as given by eqns. (14). The initial stable phase assemblages can be read from the equilibrium phase diagram of Fig. 2. We see, by application of the lever rule of eqn. (15), that shell II will contain a larger proportion of phase  $\beta$  than shell I. Moreover, the compositions of both the  $\alpha$  and  $\beta$  phases in shell II will be richer in component B than the corresponding phases in shell I. These differences in phase composition will give rise to corresponding generalized chemical potential differences, so that component B will tend to migrate from the  $\alpha$  phase in shell II to the  $\beta$  phase in shell I, and from the  $\beta$  phase in shell II to the  $\alpha$  phase in shell I, a situation indicated by the arrows in Fig. 2. The immediate result of this mass transfer is that the two shells no longer have the same bulk composition: shell I has become richer in component B than shell II. If we now determine the equilibrium phase assemblages of the two shells for their new bulk compositions  $X_B^{I*}$  and  $X_B^{II*}$ , we find that the proportion of  $\alpha$  phase in shell I has increased while that of  $\alpha$  phase in shell II has decreased. The compositions of both the  $\alpha$  and  $\beta$  phases in shell II, however, are still individually richer in component B than the corresponding phases in shell I, so the mass transfer will continue. Thus we see that the trend of the mass-transfer processes is for shell II to become simultaneously depleted in component B and dominated by phase  $\beta$ , while shell I becomes enriched in component B and dominated by phase  $\alpha$ .

This result may be extended to the continuous case in a straightforward manner. Consider again a phase transition from  $\alpha$  to  $\beta$  in the simple binary system A-B at a given pressure  $P_1$ . If the initial bulk composition is given uniformly by  $X_B^{\text{bulk}}$ , then the subsequent compositional migration is shown by the arrows in Fig. 3. The higher temperature systems become depleted in component B while becoming dominated by phase  $\beta$ ; the lower temperature systems become enriched in component B while becoming dominated by phase  $\alpha$ . The trend is toward a state in which  $\alpha$  phase vanishes from the higher temperature systems while  $\beta$  phase vanishes from the lower temperature systems. The higher temperature

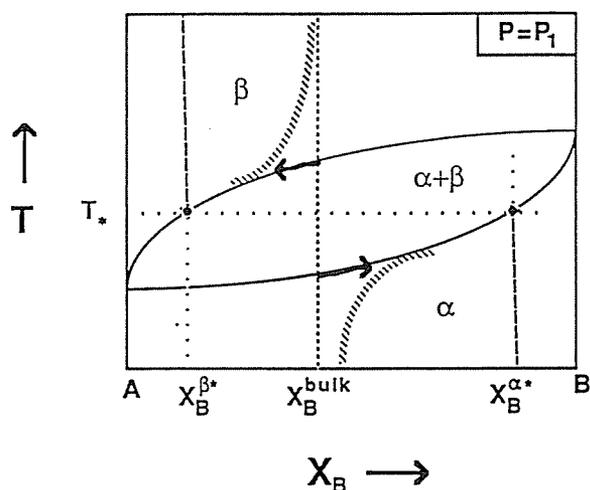


Fig. 3. Equilibrium binary phase diagram in isobaric temperature-composition space for A-B join. Arrows illustrate compositional migration as the continuous system, which is subject to non-zero temperature gradients and is initially in inter-phase mass-transfer equilibrium (dotted line), evolves toward intra-phase equilibrium (dashed line). The hatched line indicates the intermediate compositional profile, with degree of mass transfer decreasing away from phase transition.

systems then will consist of pure  $\beta$  phase of some B-poor composition  $X_B^{\beta*}$ , and the lower temperature systems will consist of pure  $\alpha$  phase of some B-rich composition  $X_B^{\alpha*}$ . At the boundary between these two regions, the  $\alpha$  and  $\beta$  phases will coexist at compositions dictated by the usual inter-phase equilibrium conditions (eqns. (10)). The location of the boundary is constrained by the global mass-balance conditions

$$\int_{\text{volume 1}} X_B^{\alpha}(\mathbf{r}) \, dV + \int_{\text{volume 2}} X_B^{\beta}(\mathbf{r}) \, dV = X_B^{\text{glob}} \int_{\text{volumes 1+2}} dV \quad (32)$$

where  $X_B^{\text{glob}}$  is the total bulk composition of the regions. Such trends will produce a compositional contrast across the phase transition boundary, attaining an equilibrium state when the differential generalized chemical potential gradients have vanished in accordance with eqns. (21). The compositional profile for this state is indicated by the dashed line in Fig. 3. (If, however, the kinetics of the mass-transfer mechanisms are favorable only in the region of phase transition, the actual de-

gree of mass transfer may decrease with distance from the phase change; the compositional profile for such an intermediate non-equilibrium state is indicated by the hatched profiles in Fig. 3.)

## 6. Discussion

Thus, for systems whose phases are homogeneous in their state variables (i.e. where the gradients of  $P$ ,  $T$ ,  $N_i$  and  $E_i$  are zero) we obtain the mass-transfer equilibrium conditions (eqns. (10)). For more general systems characterized by phases which are not homogeneous in their state variables (i.e. where there exist non-zero gradients) we obtain the larger set of mass-transfer equilibrium conditions (eqns. (10) and (21)). Equations (21) do not contribute to analysis of the homogeneous case, since all of the chemical potential gradients are trivially zero. From the  $N(R-1)$  equations (eqns. (10)), we obtain the usual Gibbs phase rule (eqn. (13)) for the homogeneous case. For the inhomogeneous case, we have the additional  $R(N-1)$  equations (21), transforming rule (13) into rule (24). In general, we have

$$F = N + 2 - R - \chi R(N - 1) \quad (33)$$

where  $\chi$  is zero when all of the chemical potential gradients are zero — giving eqn. (13) — and is unity otherwise — giving eqn. (24).

It is important to note, however, that it is possible for all of the chemical potential gradients to be zero — giving  $\chi = 0$  and rule (13) — even in the inhomogeneous case. In particular, as derived in Appendix B by application of the Gibbs–Duhem equation, we obtain

$$\nabla \eta_i^\phi = 0 \quad \text{for all components } i \text{ in all phases } \phi \quad (34)$$

and hence  $\chi = 0$  whenever the system is in both mechanical and thermal equilibrium. Thus, for example, we may have non-zero pressure gradients in mechanical equilibrium with non-zero potential gradients, along with the thermal equilibrium of a zero temperature gradient, and still obtain eqn. (34). This is the usual situation in isothermal laboratory experiments, where the potential field is gravitational (eqn. (30)), giving rise

to the common applicability of eqn. (34) and the Gibbs phase rule (eqn. (13)). Thermal disequilibrium ( $\nabla T \neq 0$ ), on the other hand, yields  $\chi = 1$  and rule (24), giving rise to such phenomena as distillation through the resulting eqn. (29).

Thus, for planetary interiors characterized by non-zero temperature gradients, the ‘shell’ hypothesis of radial disequilibrium across regions of phase transformation implies the existence of multivariant regions of finite depth-extent over which phase proportions and elastic properties vary continuously. On the other hand, for such non-isothermal planetary interiors, the attainment of radial mass-transfer equilibrium across regions of phase transformation requires that such multivariant regions break down into juxtaposed single-phase regions separated by discontinuities in bulk composition and elastic properties. However, the degree to which such radial mass-transfer equilibrium can be attained is dependent upon the kinetics of the mass-transfer mechanisms (e.g. diffusion). While the attainment of equilibrium elemental partitioning between coexisting phases requires only inter-phase diffusion over distances comparable in scale to mineral grain sizes, evolution toward the chemically distinct juxtaposed single-phase regions characteristic of radial mass-transfer equilibrium requires inter-phase diffusion over much larger distance scales. Hence, the usual justification for applying the ‘shell’ radial disequilibrium model to the Earth is the observation that rates of solid-state diffusion are generally so slow (e.g. Wuensch, 1975) as to prohibit significant levels of gross chemical differentiation of initially homogeneous material over the lifetime of the planet.

However, such a justification in terms of prohibitively slow mass-transfer mechanisms is certainly not applicable to all planets, with their varied internal states. Furthermore, an approach to radial mass-transfer equilibrium in the Earth itself might be facilitated by significantly accelerated rates of solid-state diffusion at depth, perhaps due to elevated temperatures (see Putnis and McConnell, 1980, pp. 138–139), or by the action of more efficient mass-transfer processes at depth, such as advective transport by fluids or partial melts.

In addition, the occurrence of thermal convection in planetary interiors affects the stability of any chemical differentiation accompanying the approach to radial mass-transfer equilibrium. The effect of phase transitions upon convection in the Earth's interior is a function of the Clapeyron slope of the phase transition (see Christensen and Yuen, 1984). Upper mantle phase transitions, such as the  $\alpha$ - $\beta$  transitions (see Akaogi et al., 1984; Bina and Wood, 1987) and the eclogite-garnetite transitions (see Bina and Wood, 1984; Akaogi et al., 1987) which occur near 400 km depth, are characterized by positive Clapeyron slopes. Hence, any chemical differentiation developed across such phase transitions would not be stable with respect to convective remixing. Lower mantle phase transitions, however, such as the transformations to silicate perovskite and magnesiowüstite (see Navrotsky, 1980; Ito and Takahashi, 1989) which occur near 670 km depth, are characterized by negative Clapeyron slopes. Since such phase transitions constitute impediments to convection, associated phase-transition-coupled chemical discontinuities would be stable with respect to chemical rehomogenization through convective mixing. Moreover, convective material

flow above and below such a Clapeyron-negative phase transition would actually enhance any chemical differentiation across it, effectively decreasing the distance scale over which radial diffusion must operate by continuously bringing new material into the zone immediately adjacent to the evolving chemical discontinuity.

Alternatively, if the Earth's interior experienced a significant degree of chemical differentiation early in its history (e.g. Anderson and Jordan, 1970; Anderson, 1981), then discontinuities in bulk composition across regions of phase transition would remain as stable radial equilibrium states, obviating the need for substantial chemical differentiation of initially homogeneous material by diffusion.

Finally, as an example, we illustrate in Fig. 4 the radial mass-transfer equilibrium state associated with the spinel-perovskite transition in olivine. Assuming an upper mantle composition characterized by a magnesium content  $X_{\text{Mg}}$  of 0.89 (Ringwood, 1975), the phase diagram of Ito and Takahashi (1989) implies that the lower mantle should ultimately be enriched in iron (Kumazawa et al., 1974) to an  $X_{\text{Mg}}$  of approximately 0.86.

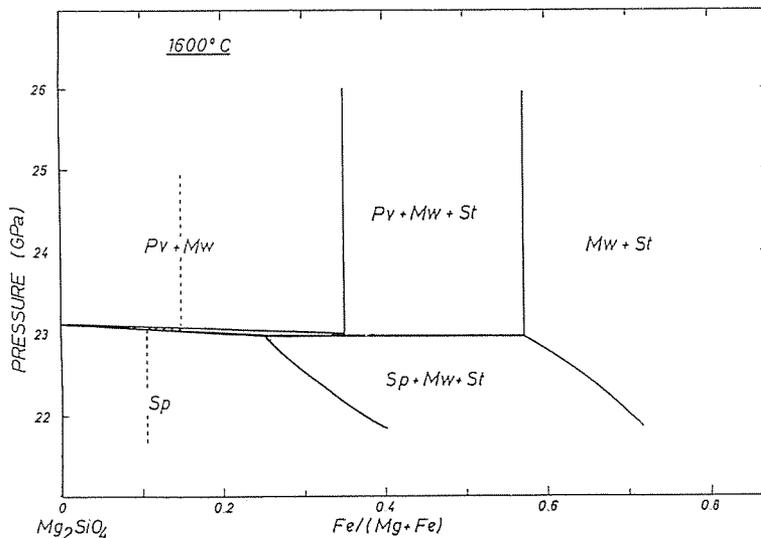


Fig. 4. Phase diagram for the system  $\text{Mg}_2\text{SiO}_4$ - $\text{Fe}_2\text{SiO}_4$  at  $1600^\circ\text{C}$  (from Ito and Takahashi, 1989). Dashed line depicts the direction and magnitude of compositional discontinuity attendant upon radial mass-transfer equilibrium across phase transition of  $\gamma$ -spinel (Sp) to perovskite (Pv) and magnesiowüstite (Mw).

## 7. Conclusions

The mass-transfer equilibrium state of simple multi-component systems, characterized by thermal and mechanical equilibrium, can be found from the standard inter-phase equilibrium requirement of uniform chemical potential of each component across all phases. Intra-phase chemical potential gradients in such systems are trivially zero, although all state variable gradients need not be so. These equilibrium requirements give rise to the usual Gibbs phase rule, specifying the relationship between the number of independent components, the number of externally unconstrained state variables, and the number of coexisting phases at equilibrium.

However, more general systems, which may be subject to thermal and/or mechanical disequilibrium, require consideration of additional intra-phase mass-transfer equilibrium conditions. These conditions stipulate that the (non-zero) chemical potential gradients be uniform across all components within each phase, and they allow the derivation of an extended phase rule. For systems of more than one component, subject to thermal or mechanical disequilibrium, this extended phase rule indicates that only single-phase regions possess an equilibrium state with respect to mass transfer.

Thus, the mass-transfer equilibrium state for multi-component systems subject to thermal or mechanical disequilibrium consists of single-phase domains separated by discontinuities in bulk chemical composition. Multi-phase assemblages are not stable with respect to mass transfer in the case of thermal or mechanical disequilibrium, and there exist driving forces, in the form of generalized chemical potential gradients, for the evolution of isochemical multi-phase systems toward the mass-transfer equilibrium state of chemically distinct juxtaposed single-phase regions. Hence, radial mass-transfer equilibrium in planetary interiors entails the thermodynamic coupling of chemical discontinuities to multivariant phase transitions.

Attainment of radial equilibrium with respect to mass transfer is constrained by the kinetics of the active mass-transfer mechanisms. While such

chemical differentiation in the Earth may be hindered by sluggish solid-state diffusion, factors such as high temperatures and the presence of fluids or melts may act to enhance the development of phase-transition-coupled chemical discontinuities. While compositional contrasts developed across phase transitions of positive Clapeyron slope would be subject to convective remixing, those associated with Clapeyron-negative phase transitions would remain stable against such remixing, enhancing the rate of chemical differentiation through convective mass flow. Alternatively, the development of gross chemical stratification early in the Earth's history would give rise to thermodynamically stable contrasts in bulk composition across regions of phase transition, with a corresponding sharpening of elasticity contrasts. As an example, the development of radial mass-transfer equilibrium across the spinel-perovskite transition would result in a sharp 670 km discontinuity supporting a stable contrast in Fe/Mg composition of  $X_{\text{Mg}} \approx 0.89$  in the upper mantle versus  $X_{\text{Mg}} \approx 0.86$  in the lower mantle.

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## Appendix A: Simple mass transfer equilibrium

Consider a single-phase system of two components (1 and 2) in the absence of external potential fields. The generalized diffusion equation (eqn. (16))

$${}_n J_i = D_{in}(\nabla\mu_i - \nabla\mu_n) \quad \text{for all components } i \quad (\text{A1})$$

becomes, for the case of two-component diffusion,

$${}_2 J_1 = D_{12}(\nabla\mu_1 - \nabla\mu_2) \quad (\text{A2})$$

where  ${}_2 J_1$  is the flux of component 1 in the 2nd-component velocity reference frame (see DeGroot and Mazur, 1962, pp. 240–241). At equilibrium the flux must vanish. Since  $D_{12}$  is in general non-zero, this requires that the chemical potential gradients be equal, thus,

$${}_2 J_1 = 0 \rightarrow \nabla\mu_1 = \nabla\mu_2 \quad (\text{A3})$$

Upon applying the Gibbs–Duhem equation,

$$X_1 \left( \frac{\partial\mu_1}{\partial X_1} \right)_{P,T} \nabla X_1 + (1 - X_1) \left( \frac{\partial\mu_2}{\partial X_1} \right)_{P,T} \nabla X_1 = 0 \quad (\text{A4})$$

to eqn. (A2), we obtain

$${}_2 J_1 = D_{12} \left[ \left( \frac{1}{1 - X_1} \right) \left( \frac{\partial\mu_1}{\partial X_1} \right)_{P,T} \nabla X_1 + \nabla P (\hat{V}_1 - \hat{V}_2) - \nabla T (\hat{S}_1 - \hat{S}_2) \right] \quad (\text{A5})$$

where the  $\hat{S}_i$  and  $\hat{V}_i$  are the partial molar entropies and volumes, respectively. It is apparent that in the special case of  $\nabla T = 0$  (thermal equilibrium) and  $\nabla P = 0$  (mechanical equilibrium), eqn. (A5) reduces to the more familiar form of the diffusion equation

$${}_2 J_1 = d_1 \nabla X_1 \quad (\text{A6})$$

where  $d_1$ , a diffusion coefficient describing the diffusivity of component 1, is given by

$$d_1 = \frac{D_{12}}{1 - X_1} \left( \frac{\partial \mu_1}{\partial X_1} \right)_{P,T} \quad (\text{A7})$$

At equilibrium the flux  ${}_2J_1$  must vanish. Since  $d_1$  is in general non-zero, eqn. (A6) requires that the compositional gradient vanishes.

$${}_2J_1 = 0 \rightarrow \nabla X_1 = 0 \quad (\text{A8})$$

which is the usual result for simple diffusive equilibrium.

### Appendix B: Application of the Gibbs–Duhem equation

Consider a general multi-component, multi-phase system. At equilibrium with respect to mass transfer, eqns. (10) and (21) give a uniform chemical potential gradient across all components in all phases, so that we have

$$c = \nabla \eta_i^\phi \quad \text{for all components } i \text{ in all phases } \phi \quad (\text{B1})$$

where  $c$  is some constant vector. To find the general value of  $c$ , we expand the total differential in terms of  $P$ ,  $T$ , the  $X_j^\phi$ , and the molar forces  $F_i^\phi$  due to the external potential fields, so the eqns. (B1) become

$$c = \hat{V}_i^\phi \nabla P - \hat{S}_i^\phi \nabla T - F_i^\phi + \sum_j^{N-1} \left( \frac{\partial \eta_i^\phi}{\partial X_j^\phi} \right)_{P,T,X_k \neq j} \nabla X_j^\phi \quad (\text{B2})$$

for all components  $i$  in all phases  $\phi$ , where  $\hat{S}_i^\phi$  and  $\hat{V}_i^\phi$  are the partial molar entropy and volume, respectively, of component  $i$  in phase  $\phi$ .

We then multiply eqn. (B2) by  $X_i^\phi$  and sum over all components  $i$ , giving

$$c = \nabla P \sum_i X_i^\phi \hat{V}_i^\phi - \nabla T \sum_i X_i^\phi \hat{S}_i^\phi - \sum_i X_i^\phi F_i^\phi + \sum_i^N X_i^\phi \sum_j^{N-1} \left( \frac{\partial \eta_i^\phi}{\partial X_j^\phi} \right) \nabla X_j^\phi \quad (\text{B3})$$

for all phases  $\phi$ . However, according to the Gibbs–Duhem equation (see Callen, 1960, pp. 48–50)

$$\sum_i^N X_i^\phi \sum_j^{N-1} \left( \frac{\partial \eta_i^\phi}{\partial X_j^\phi} \right) \nabla X_j^\phi = 0 \quad \text{for all phases } \phi \quad (\text{B4})$$

the last term in eqn. (B3) is zero, thus giving

$$c = \nabla P \sum_i X_i^\phi \hat{V}_i^\phi - \nabla T \sum_i X_i^\phi \hat{S}_i^\phi - \sum_i X_i^\phi F_i^\phi \quad \text{for all phases } \phi \quad (\text{B5})$$

Finally, we multiply eqns. (B5) by  $X_\phi$  and sum over all phases  $\phi$ , giving

$$c = \nabla P \sum_{i,\phi} X_\phi X_i^\phi \hat{V}_i^\phi - \nabla T \sum_{i,\phi} X_\phi X_i^\phi \hat{S}_i^\phi - \sum_{i,\phi} X_\phi X_i^\phi F_i^\phi \quad (\text{B6})$$

For the case of mechanical equilibrium

$$\nabla P = \frac{\sum_{i,\phi} X_\phi X_i^\phi F_i^\phi}{\sum_{i,\phi} X_\phi X_i^\phi \hat{V}_i^\phi} \quad (\text{B7})$$

eqn. (B6) reduces to

$$c = -\nabla T \sum_{i,\phi} X_\phi X_i^\phi \hat{S}_i^\phi \quad (\text{B8})$$

Finally, for simultaneous thermal equilibrium ( $\nabla T = 0$ ) we have  $c = 0$ .