[AMERICAN JOURNAL OF SCIENCE, VOL. 292, MARCH, 1992, P. 184–198]

METAMORPHISM OF NONHYDROSTATICALLY STRESSED ROCKS

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ABSTRACT. The condition for metamorphic phase equilibrium within a fluid-saturated porous rock subject to a macroscopic nonhydrostatic stress depends upon the reaction site and mechanism. In most cases the local equilibrium condition depends explicitly on the microscopic state of stress within the solid phases; this precludes finding an approximate condition that depends only on the macroscopic thermodynamic parameters. If the reaction occurs by means of dissolution of the solid reactants followed by precipitation of the solid reaction products at the fluid-solid interface, the macroscopic condition is $\Delta_r G(P_f, T) \approx 0$ where $\Delta_r G(P_f, T)$ is the change in the Gibbs free energy of reaction at the pore fluid pressure P_f and temperature T. Alternative approximate equilibrium conditions that depend upon the mean solid stress or other macroscopic parameters in addition to P_f and T are difficult to justify.

INTRODUCTION

Pore fluid pressure is commonly observed to be less than the stress due to the lithostatic overburden in the Earth's upper crust. In addition, the maximum and minimum regional horizontal stresses may differ significantly from the lithostatic vertical stress, particularly in regions of active compressional or extensional tectonics. Thompson (1955) and Bruton and Helgeson (1983) have considered the effect of these phenomena on metamorphic phase equilibria, with differing conclusions; this tutorial paper clarifies the difference between their two approaches. Using elementary arguments, we determine the local equilibrium condition for a metamorphic reaction in a fluid-saturated, nonhydrostatically stressed rock. The equilibrium condition for a reaction that occurs within the solid phases depends explicitly on the microscopic solid stress; because of this it is not possible to find an approximate condition that depends only on the macroscopic thermodynamic parameters. Bruton and Helgeson's macroscopic equilibrium condition, which depends only on the pore fluid pressure and temperature, is a good approximation, provided that the reaction occurs by means of dissolution of the solid reactants followed by precipitation of the solid reaction products at the fluid-solid interface.

MICROSCOPIC VERSUS MACROSCOPIC STRESS

We model the upper crust as a solid skeleton or matrix honeycombed with an interconnecting network of voids, microcracks, and fractures completely filled with a fluid phase. For brevity we call the space not occupied by the solid grains the pore space. Viscous shear stress and microscopic heterogeneity within the pore fluid can be justifiably ignored because of the low permeabilities of crustal rocks; we denote the pore fluid pressure by P_f. The state of stress within the solid is in contrast

nonhydrostatic and highly heterogeneous on the scale of individual solid grains. We denote the heterogeneous microscopic solid stress by $\boldsymbol{\sigma}_s$.

A geophysicist who speaks of "the state of stress in the Earth's crust" is (usually) not referring to $\boldsymbol{\sigma}_s$ but rather to a macroscopic aggregate stress we denote by $\bar{\boldsymbol{\sigma}}$. Let V be an averaging volume centered on a point $\mathbf{x}$ within the crust, let V_s be the volume within V occupied by the solid, and let $V_f = V - V_s$ be the volume within V occupied by the fluid. The average of the microscopic solid stress in V_s is

$$\bar{\boldsymbol{\sigma}}_s = \frac{1}{V_s} \int_{V_s} \boldsymbol{\sigma}_s \, dV. \tag{1}$$

The geophysicist's stress $\bar{\boldsymbol{\sigma}}$ is related to the macroscopic solid stress $\bar{\boldsymbol{\sigma}}_s$ and the pore fluid pressure P_f by

$$\bar{\boldsymbol{\sigma}} = (1 - \phi)\bar{\boldsymbol{\sigma}}_s - \phi P_f \mathbf{I}, \tag{2}$$

where

$$\phi = V_f / V \tag{3}$$

is the porosity, and $\mathbf{I}$ is the identity tensor. Physically, $\bar{\boldsymbol{\sigma}}$ is the average stress in the fluid-solid aggregate (Hubbert and Rubey, 1959). The sign convention in eq (2) and elsewhere in this paper is that a compressive stress is negative.

If such an averaging process is carried out at every point in the Earth's crust, we may regard the macroscopic quantities $\bar{\boldsymbol{\sigma}}_s$, $\bar{\boldsymbol{\sigma}}$, and ϕ as continuous functions of the position vector $\mathbf{x}$. In order for this procedure to be meaningful, the size of the averaging volume must be much smaller than a typical macroscopic scale length but large enough to average over many grains and many pore spaces. The macroscopic stresses $\bar{\boldsymbol{\sigma}}_s$ and $\bar{\boldsymbol{\sigma}}$ will then vary negligibly on the grain scale, but they may vary appreciably on the outcrop or regional scale of interest to a structural geologist or geophysicist. A petrologist seeks to interpret a local or regional isograd pattern in terms of the macroscopic stress exerted on the rocks at the time of metamorphism; however, metamorphic reactions involve individual solid grains subject to $\boldsymbol{\sigma}_s$ rather than $\bar{\boldsymbol{\sigma}}_s$ or $\bar{\boldsymbol{\sigma}}$. It is important to distinguish between the microscopic and macroscopic solid stress in considering the condition for metamorphic phase equilibrium.

IDEALIZED MODEL SYSTEM

The problem is most clearly posed in the context of an idealized laboratory thought experiment. Consider a fluid-saturated, porous rock situated in a triaxial pressure vessel as shown in figure 1. Uniform tractions $-\bar{\sigma}_1$, $-\bar{\sigma}_2$, $-\bar{\sigma}_3$ are applied to the walls of the pressure vessel; the walls are assumed to be rigid and diathermal. The pore space is completely filled with a fluid at pressure P_f; for the purpose at hand it is permissible to ignore gravity and assume that P_f is constant. The entire apparatus is maintained in thermal equilibrium with a heat bath at

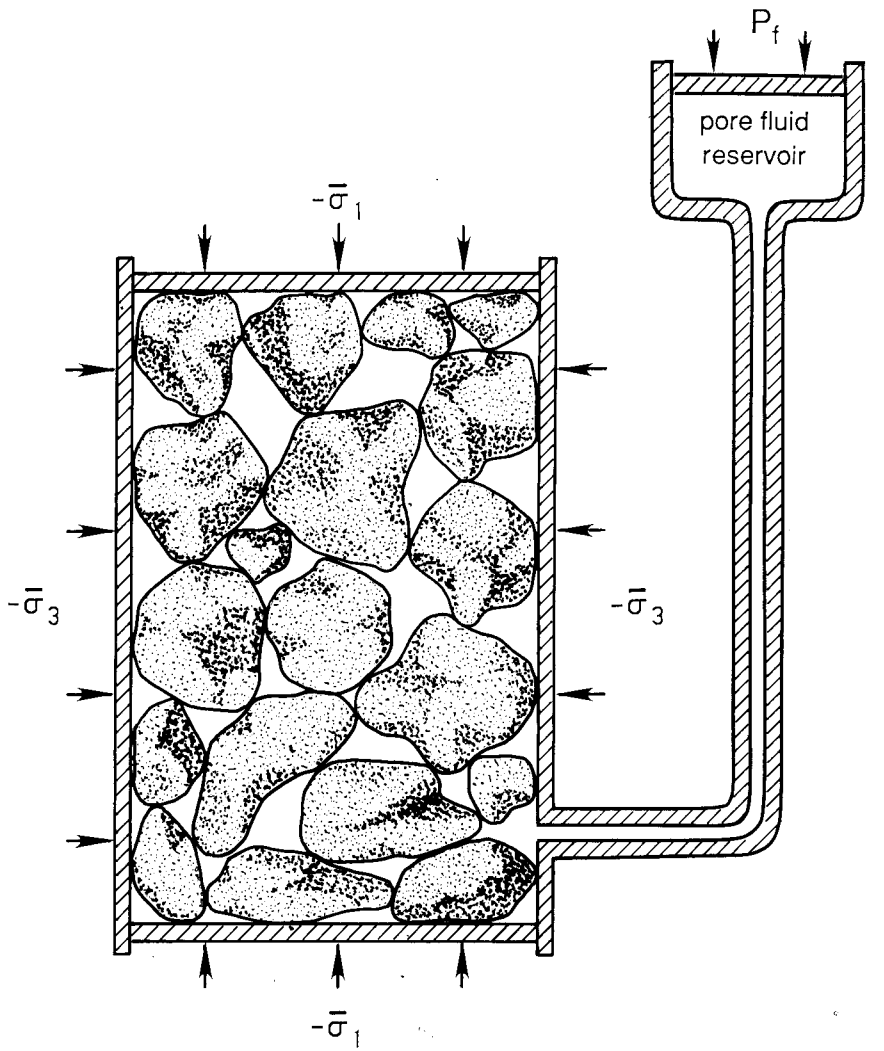

Fig. 1. Schematic diagram of an idealized laboratory thought experiment. A fluid-saturated, porous rock is subject to three unequal orthogonal tractions $-\bar{\sigma}_1$, $-\bar{\sigma}_2$, (in and out of page), and $-\bar{\sigma}_3$. The walls surrounding the rock are rigid and diathermal. The entire system is in thermal equilibrium at temperature T. A uniform hydrostatic pressure P_f is maintained in the pore fluid by a moveable piston.

temperature T. Denote the interface between the solid and the fluid by Σ_{fs} and let $\hat{\mathbf{n}}$ be the unit normal on Σ_{fs} pointing out of the solid grains into the fluid. The heterogeneous microscopic solid stress $\boldsymbol{\sigma}_s$ must satisfy

$$\nabla \cdot \boldsymbol{\sigma}_s = \mathbf{0} \text{ in } V_s \text{ and } \hat{\mathbf{n}} \cdot \sigma_s = -\hat{\mathbf{n}} P_f \text{ on } \Sigma_{fs} \tag{4}$$

in order for the solid and the fluid to be in mechanical equilibrium. The macroscopic solid stress $\overline{\boldsymbol{\sigma}}_s$ can be regarded as homogeneous; the averaging volume V in this case is the interior volume of the pressure vessel. The principal macroscopic stresses $\overline{\sigma}_{1s}$, $\overline{\sigma}_{2s}$, $\overline{\sigma}_{3s}$ in the solid are given in terms of the experimentally applied tractions by

$$\overline{\sigma}_{1s} = (1 - \phi)^{-1}(\overline{\sigma}_1 + \phi P_f), \tag{5}$$

$$\overline{\sigma}_{2s} = (1 - \phi)^{-1}(\overline{\sigma}_2 + \phi P_f), \tag{6}$$

$$\overline{\sigma}_{3s} = (1 - \phi)^{-1}(\overline{\sigma}_3 + \phi P_f), \tag{7}$$

where ϕ is the porosity of the sample.

To begin with, we consider the solid to be composed of a number of pure mineral phases Φ_1, Φ_2, . . ., and we consider the fluid to be pure H_2O. We seek the chemical equilibrium condition for a dehydration reaction of the form

$$0 \rightleftarrows \sum_{\alpha} \nu_\alpha \Phi_\alpha + \nu_{H_2O} H_2O, \tag{8}$$

where ν_1, ν_2, . . ., and ν_{H_2O} are integer stoichiometric coefficients considered to be positive for the reaction products and negative for the reactants. If possible, we would like to find a condition that depends only on the macroscopic thermodynamic parameters: the temperature T, the pore fluid pressure $P_f = P_{H_2O}$, and either the principal solid stresses $\overline{\sigma}_{1s}$, $\overline{\sigma}_{2s}$, $\overline{\sigma}_{3s}$, or the principal aggregate stresses $\overline{\sigma}_1$, $\overline{\sigma}_2$, $\overline{\sigma}_3$. Any equilibrium condition that depends on the microscopic solid stress $\boldsymbol{\sigma}_s$ rather than on $\overline{\boldsymbol{\sigma}}_s$ or $\overline{\boldsymbol{\sigma}}$ will not be useful to a petrologist seeking to infer the macroscopic conditions of metamorphism from observed phase assemblages.

OSMOTIC EQUILIBRIUM

If the experimentally applied tractions are equal,

$$\overline{\sigma}_1 = \overline{\sigma}_2 = \overline{\sigma}_3 = -\overline{P}, \tag{9}$$

then the macroscopic solid stress is a homogeneous hydrostatic pressure:

$$\overline{P}_s = (1 - \phi)^{-1}(\overline{P} - \phi P_f). \tag{10}$$

In the treatment of Thompson (1955), the solid phases are regarded as subject to this macroscopic solid pressure $\overline{P}_s$ whereas the fluid is subject to the pore fluid pressure P_f. The equilibrium condition for reaction (8) is in that case

$$\sum_{\alpha} \nu_\alpha G_\alpha(\overline{P}_s, T) + \nu_{H_2O} G_{H_2O}(P_f, T) = 0, \tag{11}$$

where $G_\alpha(\overline{P}_s, T)$ is the molar Gibbs free energy of Φ_α at pressure $\overline{P}_s$ and temperature T, and $G_{H_2O}(P_f, T)$ is the molar Gibbs free energy of H_2O at pressure P_f and temperature T.

There are two difficulties with this argument. The first is that it cannot be generalized to the case of unequal macroscopic solid stresses $\overline{\sigma}_{1s} \neq \overline{\sigma}_{2s} \neq \overline{\sigma}_{3s}$, since the Gibbs free energy of a nonhydrostatically stressed

solid cannot be defined, even if the stress is homogeneous. A number of workers, including Verhoogen (1951) and Thompson (1955), have sought to incorporate the effect of nonhydrostatic stress in eq (11) by utilizing the mean solid stress $-\frac{1}{3}(\bar{\sigma}_{1s} + \bar{\sigma}_{2s} + \bar{\sigma}_{3s})$ in place of $\bar{P}_s$, but that cannot be rigorously justified (Kamb, 1961; Paterson, 1973). Even more fundamentally, the above argument disregards the distinction between the microscopic and macroscopic solid stresses $\boldsymbol{\sigma}_s$ and $\bar{\boldsymbol{\sigma}}_s$; in particular, the condition $\hat{\mathbf{n}} \cdot \boldsymbol{\sigma}_s = -\hat{\mathbf{n}} P_f$ that guarantees microscopic mechanical equilibrium along the fluid-solid interface Σ_{fs} has been ignored. The result (11) would be correct if every solid grain were covered with a membrane capable of maintaining the grain in a state of homogeneous hydrostatic stress $\bar{\boldsymbol{\sigma}}_s = -\bar{P}_s \mathbf{I}$. If the membrane were permeable to H_2O then the solid and the fluid would be in osmotic equilibrium with $P_f \leq \bar{P}_s$. Thompson (1955) argued that such an osmotic equilibrium model might be appropriate if the fluid phase were present only in occasional macroscopic fissures, and the reaction occurred within the solid phases at a macroscopic distance from these fissures; the intervening rock between the fissures and the reacting phases might then serve as a semipermeable membrane. This leaves open the question of how to generalize to the case $\bar{\sigma}_{1s} \neq \bar{\sigma}_{2s} \neq \bar{\sigma}_{3s}$; moreover, even if the solid phases that engage in the reaction are not in contact with the pore fluid, they are still subject to $\boldsymbol{\sigma}_s$, not to $\bar{\boldsymbol{\sigma}}_s$.

In fact, there is no exact global equilibrium condition that depends only on the macroscopic principal stresses $\bar{\sigma}_{1s}$, $\bar{\sigma}_{2s}$, $\bar{\sigma}_{3s}$, or $\bar{\sigma}_1$, $\bar{\sigma}_2$, $\bar{\sigma}_3$ in addition to the pore fluid pressure P_f and the temperature T. Local equilibrium on the scale of individual solid grains is the only equilibrium possible, and it depends on the microscopic solid stress $\boldsymbol{\sigma}_s$. In what follows we consider several forms of the local microscopic equilibrium condition and ask whether there are circumstances in which a condition that depends only on the macroscopic parameters may be approximately valid.

EQUILIBRIUM CONDITION FOR A REACTION WITHIN THE SOLID PHASES

We suppose first that reaction (8) occurs entirely within the solid phases, out of contact with the fluid phase, as envisaged by Thompson (1955). The local equilibrium condition in that case can be obtained by considering a sequence of imaginary cutting and welding operations analogous to those considered by Eshelby (1957) in his classic analysis of the transformation of an elastic inclusion. For simplicity we suppose that every solid grain is a continuous mixture of the various mineral phases; we use n_α to denote the number of moles per unit volume of Φ_α at a point $\mathbf{x}$ within V_s.

The Gibbs free energy of the nonhydrostatically stressed solid cannot be defined, but its Helmholtz free energy can (Kamb, 1961; Paterson, 1973). An applicable general form of the thermodynamic equilibrium condition is that the variation in the Helmholtz free energy vanish:

$$\Delta F_{\text{total}} = \Delta F_s + \Delta F_f = 0, \tag{12}$$

subject to the constraints

$$\Delta V_{\text{total}} = \Delta V_s + \Delta V_f = 0 \text{ and } \Delta T = 0. \tag{13}$$

In applying condition (12) we must be careful to include all the changes in the Helmholtz free energy of the system produced by an infinitesimal change in the amounts of the various phases. Without loss of generality, we consider a variation in which H_2O is released rather than absorbed. It is convenient to regard the variation as a four-step process; we use Roman numeral superscripts I, II, III, and IV to distinguish changes in the system during each of the four steps.

In the first step we cut out and remove a portion of the solid and allow the species within it to react; we refer to the portion of the solid that is removed as the reaction volume. Let Δn_α be the infinitesimal virtual change in the number of moles per unit volume of Φ_α at a point $\mathbf{x}$ within the reaction volume; the local stoichiometric balance condition is

$$\Delta n_\alpha = \nu_\alpha \Delta n, \tag{14}$$

where Δn is a normalized common variation. It is convenient to define Δn to be zero outside the reaction volume; the number of moles of H_2O released by the virtual reaction is then

$$\Delta N_{H_2O} = \nu_{H_2O} \int_{V_s} \Delta n \, dV. \tag{15}$$

To maintain mechanical equilibrium during the cutting and removing, we must impose tractions $\hat{\mathbf{n}} \cdot \boldsymbol{\sigma}_s$ on the outer surface of the reaction volume and $-\hat{\mathbf{n}} \cdot \boldsymbol{\sigma}_s$ on the interior surface of the cavity left behind. The virtual reaction is presumed to occur at constant $\hat{\mathbf{n}} \cdot \boldsymbol{\sigma}_s$ and T; the H_2O released is added to the pore fluid reservoir at constant P_f and T. The infinitesimal changes in Helmholtz free energy and volume of the system during the first step are

$$\Delta F^{\text{I}} = \int_{V_s} \Delta n \sum_\alpha \nu_\alpha F_\alpha \, dV + \Delta N_{H_2O} F_{H_2O}, \tag{16}$$

$$\Delta V^{\text{I}} = \int_{V_s} \Delta n \sum_\alpha \nu_\alpha V_\alpha \, dV + \Delta N_{H_2O} V_{H_2O}. \tag{17}$$

The quantities F_α and V_α are the molar Helmholtz free energy and volume of Φ_α at a point x within the nonhydrostatically stressed solid, and the quantities F_{H_2O} and V_{H_2O} are the molar Helmholtz free energy and volume of H_2O at pressure P_f and temperature T.

Following Eshelby (1957) we suppose that the change in the shape of the reaction volume as a result of the change in the phase of the solid can be described by a transformational strain $\boldsymbol{\epsilon}$. We define $\boldsymbol{\epsilon}$ to be the strain that would occur at a point $\mathbf{x}$ if the material there consisted initially of the solid reactants in stoichiometric proportions and the reaction were complete. The actual strain that accompanies the infinitesimal virtual

reaction is $\Delta n V \boldsymbol{\epsilon}$, where

$$V = \frac{1}{\sum_{\alpha} n_{\alpha}} \tag{18}$$

is the molar volume of the solid at $\mathbf{x}$.

In the second step we apply incremental tractions to the boundary of the reaction volume to return it to its original shape, replace it in the original cavity, and reweld the cut. The incremental tractions must be those that give rise to an isothermal strain $-\Delta n V \boldsymbol{\epsilon}$. The infinitesimal changes in the Helmholtz free energy and volume of the system due to the imposition of these tractions are

$$\Delta F^{\mathrm{II}} = -\int_{V_s} \Delta n V(\boldsymbol{\sigma}_s : \boldsymbol{\epsilon})\, \mathrm{d}V, \tag{19}$$

$$\Delta V^{\mathrm{II}} = -\int_{V_s} \Delta n V(\mathrm{tr}\, \boldsymbol{\epsilon})\, \mathrm{d}V, \tag{20}$$

where tr denotes the trace.

After the rewelding, the incremental tractions required to restore the transformed inclusion to its original shape are still present as a layer of body force spread over the interface between the matrix and the inclusion. In the third step this unwanted layer of body force is relaxed. The transformed inclusion cannot return to the shape it had prior to reinsertion because of the constraining effect of the surrounding matrix. Instead both the inclusion and the matrix undergo an infinitesimal deformation in response to the relaxation of the body force. Suppose that a particle at $\mathbf{x}$ moves to $\mathbf{x} + \mathbf{u}$ during this isothermal deformation. The resulting changes in the Helmholz free energy and volume of the system, correct to first order in $\mathbf{u}$, are given by

$$\Delta F^{\mathrm{III}} = \int_{V_s} \boldsymbol{\sigma}_s : \nabla \mathbf{u}\, \mathrm{d}V, \tag{21}$$

$$\Delta V^{\mathrm{III}} = \int_{V_s} \nabla \cdot \mathbf{u}\, \mathrm{d}V \tag{22}$$

An application of Gauss' theorem to eq (21) yields

$$\Delta F^{\mathrm{III}} = \int_{\partial V_s} \hat{\mathbf{n}} \cdot \boldsymbol{\sigma}_s \cdot \mathbf{u}\, \mathrm{d}A - \int_{V_s} \mathbf{u} \cdot (\nabla \cdot \boldsymbol{\sigma}_s)\, \mathrm{d}V \tag{23}$$

where ∂V_s is the boundary V_s and $\hat{\mathbf{n}}$ is the outward unit normal. The volume integral in (23) vanishes because $\nabla \cdot \boldsymbol{\sigma}_s = \mathbf{0}$ in V_s, and the surface integral is only over the fluid-solid interface Σ_{fs} because $\mathbf{u} = \mathbf{0}$ on the walls of the rigid pressure vessel. On Σ_{fs}, however, $\hat{\mathbf{n}} \cdot \boldsymbol{\sigma}_s = -\hat{\mathbf{n}} P_f$; thus

$$\Delta F^{\mathrm{III}} = -P_f \int_{\Sigma_{fs}} \hat{\mathbf{n}} \cdot \mathbf{u}\, \mathrm{d}A. \tag{24}$$

Applying Gauss' theorem to eq (22) and invoking the rigidity of the pressure vessel again, we find that the change in volume due to the deformation is

$$\Delta V^{\mathrm{III}} = \int_{\Sigma_{fs}} \hat{\mathbf{n}} \cdot \mathbf{u}\, \mathrm{d}A. \tag{25}$$

Comparing (24) and (25) we see that ΔF^{III} can be written in the simple form

$$\Delta F^{\mathrm{III}} = -P_f \Delta V^{\mathrm{III}}. \tag{26}$$

The first three steps have, by assumption, been carried out at constant P_f and T. These changes have led to a change in the volume of the system given by $\Delta V^{\mathrm{I}} + \Delta V^{\mathrm{II}} + \Delta V^{\mathrm{III}}$. To accommodate this change the piston on the pore fluid reservoir (fig. 1) must have moved either up or down. The fourth and final step is to keep T constant and return the piston to its original position so that

$$\Delta V_{\mathrm{total}} = \Delta V^{\mathrm{I}} + \Delta V^{\mathrm{II}} + \Delta V^{\mathrm{III}} + \Delta V^{\mathrm{IV}} = 0. \tag{27}$$

The work we must do to move the piston changes the Helmoltz free energy of the system by an amount

$$\Delta F^{\mathrm{IV}} = -P_f \Delta V^{\mathrm{IV}} = P_f(\Delta V^{\mathrm{I}} + \Delta V^{\mathrm{II}} + \Delta V^{\mathrm{III}}). \tag{28}$$

Moving the piston changes the Helmholtz free energy of both the fluid and the solid; eq (28) accounts for both these changes correct to first order in the infinitesimal variations.

Adding eqs (16), (19), (26), and (28) we obtain the total change in the Helmholtz free energy:

$$\begin{aligned} \Delta F_{\mathrm{total}} &= \Delta F^{\mathrm{I}} + \Delta F^{\mathrm{II}} + \Delta F^{\mathrm{III}} + \Delta F^{\mathrm{IV}} \\ &= \int_{V_s} \Delta n \left[\sum_{\alpha} \nu_\alpha F_\alpha - V(\boldsymbol{\sigma}_s : \boldsymbol{\epsilon}) \right] \mathrm{d}V + \Delta N_{\mathrm{H_2O}}(F_{\mathrm{H_2O}} + P_f V_{\mathrm{H_2O}}). \end{aligned} \tag{29}$$

In writing (29) we have made use of the identity

$$V \operatorname{tr} \boldsymbol{\epsilon} = \sum_{\alpha} \nu_\alpha V_\alpha. \tag{30}$$

The quantity $F_{\mathrm{H_2O}} + P_f V_{\mathrm{H_2O}}$ is the molar Gibbs free energy of the fluid at pressure P_f and temperature T:

$$G_{\mathrm{H_2O}} = F_{\mathrm{H_2O}} + P_f V_{\mathrm{H_2O}}. \tag{31}$$

Since $G_{\mathrm{H_2O}}$ is independent of $\mathbf{x}$ we can rewrite (29) in the form

$$\Delta F_{\mathrm{total}} = \int_{V_s} \Delta n \left[\sum_{\alpha} \nu_\alpha F_\alpha - V(\boldsymbol{\sigma}_s : \boldsymbol{\epsilon}) + \nu_{\mathrm{H_2O}} G_{\mathrm{H_2O}} \right] \mathrm{d}V. \tag{32}$$

If ΔF_{total} is to vanish for an arbitrary virtual variation Δn we must have

$$\sum_{\alpha} \nu_{\alpha} F_{\alpha} - V(\boldsymbol{\sigma}_s : \boldsymbol{\epsilon}) + \nu_{H_2O} G_{H_2O} = 0. \tag{33}$$

Eq (33) is the local equilibrium condition for a reaction that occurs at a site $\mathbf{x}$ within the solid phases.

DISCUSSION

Suppose now that the microscopic solid stress is homogeneous and equal to the hydrostatic stress in the pore fluid:

$$\boldsymbol{\sigma}_s = -P_f \mathbf{I}. \tag{34}$$

Substituting (34) into (33) and invoking (30) we obtain in this case

$$\sum_{\alpha} \nu_{\alpha} [F_{\alpha} + P_f V_{\alpha}] + \nu_{H_2O} G_{H_2O} = 0. \tag{35}$$

The quantity $F_{\alpha} + P_f V_{\alpha}$ is the molar Gibbs free energy of Φ_{α} at pressure P_f and temperature T:

$$G_{\alpha} = F_{\alpha} + P_f V_{\alpha}. \tag{36}$$

This confirms that (33) reduces to the familiar global condition

$$\sum_{\alpha} \nu_{\alpha} G_{\alpha}(P_f, T) + \nu_{H_2O} G_{H_2O}(P_f, T) = 0 \tag{37}$$

if the stress in both the solid and fluid phases is homogeneous and hydrostatic.

It is clear that Thompson's (1955) equilibrium condition, eq (11), could likewise be "derived" by substituting $\boldsymbol{\sigma}_s = -\overline{P}_s \mathbf{I}$ rather than $\boldsymbol{\sigma}_s = -P_f \mathbf{I}$ into eq (33). The objections to this procedure are noted above: first, the thermodynamically appropriate mean solid stress $\overline{P}_s$ is not well determined except in the case of equal principal stresses $\overline{\sigma}_{1s} = \overline{\sigma}_{2s} = \overline{\sigma}_{3s}$; second, even in that case, the substitution $\boldsymbol{\sigma}_s = -\overline{P}_s \mathbf{I}$ is not well justified. The local equilibrium condition (33) for a reaction that occurs at a point $\mathbf{x}$ within the solid depends explicitly on the local microscopic solid stress $\boldsymbol{\sigma}_s$ via the term $V(\boldsymbol{\sigma}_s : \boldsymbol{\epsilon})$; this explicit dependence makes it impossible to find an approximate condition that depends only on the macroscopic thermodynamic parameters.

EQUILIBRIUM CONDITION FOR A REACTION ADJACENT TO THE FLUID-SOLID INTERFACE

The explicit dependence of the local equilibrium condition on $\boldsymbol{\sigma}_s$ persists if the reaction occurs in the immediate vicinity of the fluid-solid interface Σ_{fs}. In that limiting case the transformational strain $\boldsymbol{\epsilon}$ can be written in the form (Backus, 1967)

$$\boldsymbol{\epsilon} = \hat{\mathbf{n}}\hat{\mathbf{n}}\epsilon_{fs}^{nn} + \hat{\mathbf{n}}\boldsymbol{\epsilon}_{fs}^{\Sigma} + \boldsymbol{\epsilon}_{fs}^{\Sigma}\hat{\mathbf{n}} + \boldsymbol{\epsilon}_{fs}^{\Sigma\Sigma}. \tag{38}$$

The quantities ϵ_{fs}^{nn}, $\boldsymbol{\epsilon}_{fs}^{\Sigma}$, and $\boldsymbol{\epsilon}_{fs}^{\Sigma\Sigma}$ are, respectively, scalar, tangent vector, and symmetric second-order tangent tensor fields on Σ_{fs}; the latter two fields satisfy $\hat{\mathbf{n}} \cdot \boldsymbol{\epsilon}_{fs}^{\Sigma} = 0$, and $\hat{\mathbf{n}} \cdot \boldsymbol{\epsilon}_{fs}^{\Sigma\Sigma} = \boldsymbol{\epsilon}_{fs}^{\Sigma\Sigma} \cdot \hat{\mathbf{n}} = \mathbf{0}$. The microscopic solid stress on Σ_{fs} can likewise be written in the form

$$\boldsymbol{\sigma}_s = -\hat{\mathbf{n}}\hat{\mathbf{n}} P_f + \boldsymbol{\sigma}_s^{\Sigma\Sigma}, \tag{39}$$

where $\hat{\mathbf{n}} \cdot \boldsymbol{\sigma}_s^{\Sigma\Sigma} = \boldsymbol{\sigma}_s^{\Sigma\Sigma} \cdot \hat{\mathbf{n}} = \mathbf{0}$. The equilibrium condition (33) thus becomes

$$\sum_{\alpha} \nu_{\alpha} F_{\alpha} + P_f V \epsilon_{fs}^{nn} - V(\boldsymbol{\sigma}_s^{\Sigma\Sigma} : \boldsymbol{\epsilon}_{fs}^{\Sigma\Sigma}) + \nu_{H_2O} G_{H_2O} = 0. \tag{40}$$

This depends explicitly not only on P_f and T but also on the microscopic tangential solid stress $\boldsymbol{\sigma}_s^{\Sigma\Sigma}$.

EQUILIBRIUM CONDITION FOR A REACTION AT A COHERENT INTERFACE WITHIN THE SOLID

Thus far it has been assumed that the solid phases Φ_{α} are distributed continuously throughout the solid volume V_s. Suppose instead that the solid reactants and the solid reaction products are physically isolated from each other in distinct grains and that the reaction is confined to the interface Σ_{gb} separating the two phase mixtures. To find the local equilibrium condition in this case we return to the integral expression for the change in the Helmholtz free energy, eq (32), and consider a variation of the form

$$\Delta n = \Delta n_{gb} \delta_{\Sigma_{gb}}. \tag{41}$$

The quantity $\Delta n_{gb} \delta_{\Sigma_{gb}}$ is a weighted Dirac delta distribution on the grain boundary Σ_{gb}, with the replication property

$$\int_{V_s} \Delta n_{gb} Q \delta_{\Sigma_{gb}} \, dV = \int_{\Sigma_{gb}} \Delta n_{gb} Q \, dA \tag{42}$$

for an arbitrary continuous test function Q. The resulting integral

$$\Delta F_{\text{total}} = \int_{V_s} \Delta n_{gb} \left[\sum_{\alpha} \nu_{\alpha} F_{\alpha} - V(\boldsymbol{\sigma}_s : \boldsymbol{\epsilon}) + \nu_{H_2O} G_{H_2O} \right] \delta_{\Sigma_{gb}} \, dV \tag{43}$$

is undefined unless the transformational strain $\boldsymbol{\epsilon}$ is of the form

$$\boldsymbol{\epsilon} = \hat{\mathbf{n}}\hat{\mathbf{n}} \epsilon_{gb}^{nn} + \hat{\mathbf{n}} \boldsymbol{\epsilon}_{gb}^{\Sigma} + \boldsymbol{\epsilon}_{gb}^{\Sigma} \hat{\mathbf{n}}, \tag{44}$$

where $\hat{\mathbf{n}}$ is the unit normal to Σ_{gb}, and $\hat{\mathbf{n}} \cdot \boldsymbol{\epsilon}_{gb}^{\Sigma} = 0$. Eq (44) is the condition that the interface be coherent (Fletcher, 1973; Robin, 1974). The product $\boldsymbol{\sigma}_s : \boldsymbol{\epsilon}$ is continuous across a coherent interface Σ_{gb}; the change in the Helmholtz free energy becomes

$$\Delta F_{\text{total}} + \int_{\Sigma_{gb}} \Delta n_{gb} \left[\sum_{\alpha} \nu_{\alpha} F_{\alpha} - V(\sigma_s^{nn} \epsilon_{gb}^{nn} + 2\boldsymbol{\sigma}_s^{\Sigma} \cdot \boldsymbol{\epsilon}_{gb}^{\Sigma}) + \nu_{H_2O} G_{H_2O} \right] dA. \tag{45}$$

The quantities σ_s^{nn} and $\boldsymbol{\sigma}_s^{\Sigma}$ are the normal and tangential parts of the

microscopic solid traction on Σ_g:

$$\hat{\mathbf{n}} \cdot \boldsymbol{\sigma}_s = \hat{\mathbf{n}}\sigma_s^{nn} + \boldsymbol{\sigma}_s^{\Sigma}. \tag{46}$$

The requirement that ΔF_{total} vanish for an arbitrary virtual variation Δn_{gb} yields

$$\sum_{\alpha} \nu_\alpha F_\alpha - V(\sigma_s^{nn}\epsilon_{gb}^{nn} + 2\boldsymbol{\sigma}_s^{\Sigma} \cdot \boldsymbol{\epsilon}_{gb}^{\Sigma}) + \nu_{H_2O} G_{H_2O} = 0. \tag{47}$$

Eq (47) is the local equilibrium condition for a reaction that occurs at a point $\mathbf{x}$ on a coherent interface Σ_{gb} between two phase mixtures.

Coherency is unlikely except in the case of certain solid-solid phase transformations of the type

$$\Phi_A \rightleftarrows \Phi_B \tag{48}$$

Eq (47) reduces in the case of such transformations to the condition given by Fletcher (1973) and Robin (1974):

$$F_B - F_A - V(\sigma_s^{nn}\epsilon_{gb}^{nn} + 2\boldsymbol{\sigma}_s^{\Sigma} \cdot \boldsymbol{\epsilon}_{gb}^{\Sigma}) = 0. \tag{49}$$

The explicit dependence on the microscopic solid traction $\hat{\mathbf{n}} \cdot \boldsymbol{\sigma}_s$ precludes finding an approximate condition for a coherent interface that depends on the macroscopic parameters.

EQUILIBRIUM CONDITION FOR A DISSOLUTION-PRECIPITATION REACTION

Finally we consider a reaction that occurs by a process of dissolution of the solid reactants followed by precipitation of the solid reaction products at the fluid-solid interface. The argument used to obtain the local equilibrium condition in this case is essentially identical to the argument used by Gibbs (1878) to derive his famous solubility condition for a nonhydrostatically stressed solid phase. McLellan (1980) gives a particularly clear exposition of Gibbs' result; his treatment is followed closely here. We write the reaction, schematically, in the form

$$\sum_{\alpha}{}' \nu_\alpha \Phi_\alpha \rightleftarrows \sum_{\alpha}{}' \nu_\alpha \Phi_\alpha^* \tag{50}$$

$$0 \rightleftarrows \sum_{\alpha} \nu_\alpha \Phi_\alpha^* + \nu_{H_2O} H_2O, \tag{51}$$

$$\sum_{\alpha}{}'' \nu_\alpha \Phi_\alpha^* \rightleftarrows \sum_{\alpha}{}'' \nu_\alpha \Phi_\alpha. \tag{52}$$

The prime in (50) and double prime in (52) denote sums over the solid reactants and solid reaction products, respectively, and Φ_α^* denotes the component of Φ_α dissolved in the pore fluid. The dehydration reaction (51) is presumed to occur within the fluid at constant P_f and T. It is again convenient to regard the virtual variation as a four-step process and to

use Roman numeral superscripts I, II, III, and IV to distinguish changes in the system during each of the four steps.

In the first step the solid reactants are allowed to dissolve into the fluid; the number of moles per unit area of Φ_α that dissolve at a point $\mathbf{x}$ on Σ_{fs} is denoted by $\nu_\alpha \Delta n_{fs}$. The infinitesimal changes in the Helmholtz free energy and volume of the system during this step are

$$\Delta F^{\mathrm{I}} = \int_{\Sigma_{fs}} \Delta n_{fs} \sum_\alpha{}' \nu_\alpha F_\alpha \, dA - \Delta N_{fs} \sum_\alpha{}' \nu_\alpha F^*_\alpha, \tag{53}$$

$$\Delta V^{\mathrm{I}} = \int_{\Sigma_{fs}} \Delta n_{fs} \sum_\alpha{}' \nu_\alpha V_\alpha \, dA - \Delta N_{fs} \sum_\alpha{}' \nu_\alpha V^*_\alpha, \tag{54}$$

where F^*_α and V^*_α are the partial molar Helmholtz free energy and volume of Φ^*_α in solution at pressure P_f and temperature T. The quantity ΔN_{fs} is the normalized number of moles dissolved:

$$\Delta N_{fs} = \int_{\Sigma_{fs}} \Delta n_{fs} \, dA. \tag{55}$$

In the second step reaction (51) among the dissolved components is allowed to proceed within the fluid. The resulting changes in the Helmholtz free energy and volume of the system are

$$\Delta F^{\mathrm{II}} = \Delta N_{fs} \left[\sum_\alpha \nu_\alpha F^*_\alpha + \nu_{\mathrm{H_2O}} F_{\mathrm{H_2O}} \right], \tag{56}$$

$$\Delta V^{\mathrm{II}} = \Delta N_{fs} \left[\sum_\alpha \nu_\alpha V^*_\alpha + \nu_{\mathrm{H_2O}} V_{\mathrm{H_2O}} \right], \tag{57}$$

In the third step amounts $\nu_\alpha \Delta n_{fs}$ of the dissolved reaction products are allowed to precipitate onto the original dissolution sites $\mathbf{x}$ on Σ_{fs}. The changes in the Helmholtz free energy and volume of the system during this step are

$$\Delta F^{\mathrm{III}} = \int_{\Sigma_{fs}} \Delta n_{fs} \sum_\alpha{}'' \nu_\alpha F_\alpha \, dA - \Delta N_{fs} \sum_\alpha{}'' \nu_\alpha F^*_\alpha, \tag{58}$$

$$\Delta V^{\mathrm{III}} = \int_{\Sigma_{fs}} \Delta n_{fs} \sum_\alpha{}'' \nu_\alpha V_\alpha \, dA - \Delta N_{fs} \sum_\alpha{}'' \nu_\alpha V^*_\alpha, \tag{59}$$

The first three steps have led to a net change in the volume of the system given by

$$\begin{aligned} \Delta V^{\mathrm{I}} + \Delta V^{\mathrm{II}} + \Delta V^{\mathrm{III}} &= \int_{\Sigma_{fs}} \Delta n_{fs} \sum_\alpha \nu_\alpha V_\alpha \, dA + \Delta N_{fs} \, \nu_{\mathrm{H_2O}} \, V_{\mathrm{H_2O}} \\ &= \int_{\Sigma_{fs}} \Delta n_{fs} \left[\sum_\alpha \nu_\alpha \, V_\alpha + \nu_{\mathrm{H_2O}} \, V_{\mathrm{H_2O}} \right] dA. \end{aligned} \tag{60}$$

The fourth and final step, as before, is to return the piston on the pore fluid reservoir to its original position so that

$$\Delta V_{\text{total}} = \Delta V^{\text{I}} + \Delta V^{\text{II}} + \Delta V^{\text{III}} + \Delta V^{\text{IV}} = 0. \tag{61}$$

This final step changes the Helmholtz free energy of the system by an amount

$$\Delta F^{\text{IV}} = -P_f \Delta V^{\text{IV}} = P_f \int_{\Sigma_{fs}} \Delta n_{fs} \left[\sum_{\alpha} \nu_{\alpha} V_{\alpha} + \nu_{\text{H}_2\text{O}} V_{\text{H}_2\text{O}} \right] \mathrm{d}A. \tag{62}$$

Adding eqs (53), (56), (58), and (62), we obtain the total change in the Helmholtz free energy:

$$\Delta F_{\text{total}} = \int_{\Sigma_{fs}} \Delta n_{fs} \left[\sum_{\alpha} \nu_{\alpha} (F_{\alpha} + P_f V_{\alpha}) + \nu_{\text{H}_2\text{O}} G_{\text{H}_2\text{O}} \right] \mathrm{d}A. \tag{63}$$

This will vanish for an arbitrary virtual variation Δn_{fs} if and only if

$$\sum_{\alpha} \nu_{\alpha} (F_{\alpha} + P_f V_{\alpha}) + \nu_{\text{H}_2\text{O}} G_{\text{H}_2\text{O}} = 0. \tag{64}$$

Eq (64) is the local equilibrium condition for a reaction that proceeds by dissolution of the solid reactants followed by precipitation of the solid reaction products at a site $\mathbf{x}$ on the fluid-solid interface Σ_{fs}.

APPROXIMATE MACROSCOPIC EQUILIBRIUM CONDITION

It is noteworthy that the equilibrium condition for a dissolution-precipitation reaction does not depend explicitly on the microscopic solid stress $\boldsymbol{\sigma}_s$; the only dependence on $\boldsymbol{\sigma}_s$ is the implicit dependence of the quantities F_{α} and V_{α}. This feature distinguishes (64) from the previously derived conditions and makes it possible to obtain an approximate equilibrium condition in this case. We make two approximations that are known to be reasonable under the stress and temperature conditions that prevail in the upper crust: first, we ignore isothermal compressibility and account only for the effect of thermal expansion on V_{α}; second, we ignore strain energy contributions and account only for the contributions from thermal energy and entropy in calculating F_{α}. In that approximation both V_{α} and F_{α} can be regarded as functions only of temperature, and the quantity $F_{\alpha}(T) + P_f V_{\alpha}(T)$ can be regarded as the molar Gibbs free energy $G_{\alpha}(P_f, T)$ of Φ_{α}. The equilibrium condition (64) thus simplifies to

$$\sum_{\alpha} \nu_{\alpha} G_{\alpha}(P_f, T) + \nu_{\text{H}_2\text{O}} G_{\text{H}_2\text{O}}(P_f, T) \approx 0. \tag{65}$$

Eq (65) states that the solid phases in a dissolution-precipitation reaction can be treated as though they were in a hydrostatic state of stress at the pore fluid pressure P_f and temperature T, even though the microscopic solid stress $\boldsymbol{\sigma}_s$ at the fluid-solid interface is nonhydrostatic and highly heterogeneous. This is the conclusion reached by Bruton and Helgeson (1983).

The molar Gibbs free energy of Φ_α is given in the above approximation by

$$G_\alpha(P_f, T) = H^o_\alpha - T S^o_\alpha + \int_{T^o}^{T} c_{p,\alpha}(T)\, dT$$
$$-T \int_{T^o}^{T} \frac{c_{p,\alpha}(T)}{T}\, dT + (P_f - P^o)V_\alpha(T). \qquad (66)$$

The quantities H^o_α and S^o_α are the apparent molar enthalpy of formation from the elements and the molar third law entropy at the reference pressure P^o and temperature T^o, and $c_{p,\alpha}(T)$ is the molar heat capacity. The molar Gibbs free energy of H_2O is calculated in an analogous manner except that isothermal compressibility must be accounted for:

$$G_{H_2O}(P_f, T) = H^o_{H_2O} - T S^o_{H_2O} + \int_{T^o}^{T} c_{p,H_2O}(T)\, dT$$
$$-T \int_{T^o}^{T} \frac{c_{p,H_2O}(T)}{T}\, dT + \int_{P^o}^{P_f} V_{H_2O}(P, T)\, dP. \qquad (67)$$

Eq (65) assumes that all phases are pure. More generally, the phases $\Phi_1, \Phi_2, \ldots$ may be solid solutions, and the fluid phase may contain other species in addition to H_2O. The dissolved components of the solids must be present in the fluid if the reaction proceeds by means of dissolution and precipitation; there may also be other volatiles present, such as CO_2. The general approximate equilibrium condition for a dehydration reaction of the form (8) is

$$\Delta_r G(P_f, T) = \Delta_r G^o(P_f, T) + RT \ln \left[\prod_\alpha a_\alpha^{\nu_\alpha}\, a_{H_2O}(P_f, T)^{\nu_{H_2O}} \right] \approx 0. \qquad (68)$$

The quantity $\Delta_r G^o(P_f, T)$ is the change in the Gibbs free energy of the reaction among the pure phases, given by the left side of eq (65). The quantity a_α is the constant activity of the impure phase Φ_a in the solid, $a_{H_2O}(P_f, T)$ is the activity of H_2O in the fluid, and R is the gas constant.

CONCLUSION

In general, the chemical equilibrium condition for a metamorphic reaction in a fluid-saturated, nonhydrostatically stressed rock depends explicitly on the microscopic stress $\boldsymbol{\sigma}_s$ within the solid phases. There is, however, no explicit dependence on $\boldsymbol{\sigma}_s$ for a dissolution-precipitation reaction at the fluid-solid interface. The equilibrium condition for such a reaction is approximately $\Delta_r G(P_f, T) \approx 0$, where $\Delta_r G(P_f, T)$ is the change in the Gibbs free energy of the reaction evaluated at the pore fluid pressure P_f and temperature T. Alternative approximate equilibrium conditions that depend on the macroscopic principal stresses $\overline{\sigma}_{1s}, \overline{\sigma}_{2s}, \overline{\sigma}_{3s}$ or $\overline{\sigma}_1, \overline{\sigma}_2, \overline{\sigma}_3$ in addition to the pore fluid pressure P_f and temperature T are difficult to justify.

It is noteworthy that condition $\Delta_r G(P_f, T) \approx 0$ is applicable even in the case of a solid-solid metamorphic reaction ($\nu_{H_2O} = 0$). The only restriction is that the reaction must occur in a fluid-saturated rock, by means of dissolution of the solid reactants followed by precipitation of the solid reaction products at the fluid-solid interface Σ_{fs}. It is insufficient to stipulate simply that the reaction site is adjacent to the fluid-solid interface, since the local equilibrium condition for a reaction on Σ_{fs} depends upon the interfacial tangential solid stress $\boldsymbol{\sigma}_s^{\Sigma\Sigma}$.

To simplify the discussion in this paper, we have assumed throughout that the transformational strain $\boldsymbol{\epsilon}$ is infinitesimal. The derivation is more complicated in the case of a finite transformational strain; however, the result is substantially the same. Regardless of whether the transformational strain is infinitesimal or finite, the local equilibrium condition for a reaction within the nonhydrostatically stressed solid phases depends upon the microscopic rather than the macroscopic stress. In the case of a finite strain the condition depends upon the microscopic Piola-Kirchhoff stress (Malvern, 1969; Larché and Cahn, 1978) rather than upon $\boldsymbol{\sigma}_s$.

ACKNOWLEDGMENTS

I am grateful to an anonymous reviewer whose caustic but constructive criticism of an earlier version of this paper prompted me to reformulate the discussion substantially. This work was supported by the National Science Foundation under grants EAR-8804098 and EAR-9104477.

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