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THE EQUILIBRIUM BETWEEN A SPHERICAL NUCLEUS AND THE MATRIX

IN A SOLID-STATE TRANSFORMATION*

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The Gibbs approach [1] has been used [2] in considering the conditions for chemical equilibrium in a nonhydrostatically stressed solid phase in contact with solution or melt. A state of uniaxial stress may be characterized by two pressures P and p, and for this it has been shown that the equilibrium with liquid at pressure p can be considered as an example of a system with unequal pressures on the phases. The thermodynamic description of such a system, however, does not reduce to assigning different pressures to the phases and using standard formulas. Here we consider a further example of nonhydrostatic equilibrium where the phases are under different pressures. This situation occurs in homogeneous nucleation in a solid.**

**Recently, there has been a substantial elucidation (see [3] for example) of the conditions for equilibrium between nonhydrostatically stressed solid phases.

In a solid-state reaction accompanied by a nonzero volume change, nucleation of a new phase produces elastic stresses in the matrix, which are of substantially nonhydrostatic character. The elastic strain energy may be comparable with the heat of the transformation [4], and it introduces some special features into the description of the initial stages in solid-state reactions. Nucleation of a new phase produces stress concentrations, which decrease rapidly away from the inclusion. As a result, the pressure in the main volume of the matrix corresponding to heterogeneous equilibrium with the nucleus is different from that predicted from the hydrostatic $P-T$ curve for equilibrium at the given temperature.

The equilibrium between a nucleus and a matrix has been considered in [5-8], mainly in describing partial melting. Here we derive new formulas for estimating the degree of metastability that may be attained in the synthesis of high-pressure phases and during quenching. Numerical estimates are made for the transition of forsterite to the β-spinel structure.

We consider the equilibrium conditions for a spherical nucleus in an infinite elastic matrix under some general pressure P_0. The materials in both phases are considered as isotropic, and we assume that the solid-state reaction amounts to a homogeneous density change, so the symmetry in the boundary conditions makes it possible to define equilibrium configurations amongst the spherically symmetrical ones. We neglect the nonhydrostatic components of the stress tensor for the nucleus and assume that under equilibrium conditions there is a certain hydrostatic pressure P in the newly formed phase. We assume for definiteness that the transformation is accompanied by an increase in volume, so $P > P_0$. While the nonhydrostatic elastic deformations in the matrix are small, and one can use the classical linear theory of elasticity, a nonlinear approach may be required to describe the deformations occurring on the phase change. We use a quasiliquid (nonlinear) model for the internal problem in order to avoid the difficulties in the nonlinear theory of elasticity.*

The classical solution to the Lamé problem [4] allows us to describe the excess stresses and strains arising in an infinite matrix ($P_\infty = P_0$) containing a spherical hole of radius R, at which there is a pressure $P_R = P$:

$$U_r = \frac{P-P_0}{4\mu_1}\frac{R^3}{r^2}; \quad \sigma_{rr} = -(P-P_0)\cdot\frac{R^3}{r^3};$$
$$\sigma_{\theta\theta} = \sigma_{\varphi\varphi} = \frac{P-P_0}{2}\frac{R^3}{r^3}, \tag{1}$$

where the reference state is that of hydrostatic compression by pressure P_0, U_r is the radial displacement component, σ_{rr}, $\sigma_{\theta\theta}$, and $\sigma_{\varphi\varphi}$ are the nonzero stress-tensor components in a spherical coordinate system, and μ_1 is the shear modulus of the matrix material (phase 1). An infinite matrix in essence corresponds to the approximation $R/L \ll 1$, where L is the characteristic dimension in the initial problem, e.g., the distance between centers of nuclei. Therefore, in this formulation we can consider only the initial stage of the transformation, when the degree of transformation in the bulk is close to zero. Basic formulas are given in the appendix for the case where the size of the inclusion is comparable with that of the matrix.

We will consider the following simplified scheme in order to describe the phase transition. Out of the matrix we cut a spherical region of radius R_0 at $P = P_0$ (the temperature T_0 is fixed), and produce a pressure P_0 at the outer boundary of this cavity, thereby preventing the matrix from deforming. The equilibrium transformation of phase 1 into phase 2 at $P = P_0$ leads to an increase in radius, with $R_0^3 \rho_1(P_0, T_0) = \tilde{R}^3 \rho_2(P_0, T_0)$; $\Delta\rho = \rho_1(P_0, T_0) - \rho_2(P_0, T_0) > 0$ being the change in density in the phase transition. We set up a pressure P at the boundary of the removed region to get a sphere of radius R; the value of R can be determined from the condition $R^3\rho_2(P, T_0) = \tilde{R}^3\rho_2(P_0, T_0)$ where $\rho_2(P, T_0) = \rho_2(P_0, T_0)(1 + (P-P_0)/K_2)$; $K_2 = \rho_2(\partial P_2/\partial\rho_2)|_T$ is the bulk modulus of phase 2. We now produce a pressure P at the outer boundary of the cavity, which produces

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*For $\Delta\rho/\rho \to 0$, where $\Delta\rho$ is the density change in the phase transition, one can use a linearized formulation, which leads to homogeneity and a hydrostatic state of stress within the nucleus [5]. It seems that the regularity condition at the center in an isotropic phase will eliminate the nonhydrostatic components also in the nonlinear case.

radial displacements U_r in the matrix and the cavity acquires a radius R. The two phases can thus be conjugate; the difference between coherent and incoherent conjugation [3, 4, 8, 9] is eliminated because of the symmetry; the displacements have only a radial component, which is normal to the phase interface. The condition for continuity of the displacements $R = R_0 + U_r$ allows us to determine P. We use the approximate equation $\Delta\rho/\rho_2 = (1 + U_r/R)^3(1 + (P - P_0)/K_2) - 1$ to get

$$P = P_0 + \Delta P, \quad \Delta P = \frac{\Delta\rho}{\rho_2} \frac{4K_2\mu_1}{3K_2 + 4\mu_1} . \tag{2}$$

We neglect the pressure and temperature dependence of the moduli and refer them to the reference state of stress.

Let us make a simple estimate from (2). At $P_0 \sim 130$ kbar and $T_0 \sim 1000$ K, there is a solid-state transformation of forsterite to a modified spinel structure [10]: $\alpha\text{-Mg}_2\text{SiO}_4$ (phase 2) = $\beta\text{-Mg}_2\text{SiO}_4$ (phase 1), which is accompanied by a volume change $\Delta\rho/\rho_2 \sim 6.5\%$. The approximate values for the moduli are $\mu_1 \simeq 800$ kbar and $K_2 \simeq 1500$ kbar, so we get that $\Delta P \simeq 40$ kbar. Therefore, the pressure difference may be considerable.* This estimate also confirms that we were correct in using the approximation $\Delta P/K_2 \simeq 0.03 \ll 1$.

These mechanical equilibrium conditions do not enable us to derive the chemical equilibrium curve, i.e., to determine the relation between P_0 and T_0 for heterogeneous equilibrium (nucleation). Here we have to use the chemical-equilibrium condition [1-3, 9], which amounts to continuity in the Gibbs chemical potential at the interphase boundary. The Gibbs formula derived for equilibrium in a nonhydrostatically stressed solid phase in contact with a liquid [1] can be used here because of the assumption about the quasiliquid behavior of the nucleus.

We use (1) to calculate the density of the excess elastic energy in phase 1 at the interphase ($r = R$):

$$\rho_1(P_0, T_0)\Delta f_1(P_0, T_0) = \frac{1}{2}(\sigma_{rr}\varepsilon_{rr} + 2\sigma_{\theta\theta}\varepsilon_{\theta\theta})|_R = \frac{3(P - P_0)^2}{8\mu_1}, \tag{3}$$

where $\varepsilon_{rr} = \partial U_r/\partial r$, $\varepsilon_{\theta\theta} = \varepsilon_{\varphi\varphi} = U_r/r$ are the nonzero components of the strain tensor. We can then show readily that the equation for determining $P_0(T_0)$ is

$$f_2(P, T_0) + \frac{P}{\rho_2(P, T_0)} = f_1(P_0, T_0) + \frac{P}{\rho_1(P_0, T_0)} + \frac{3(P - P_0)^2}{8\mu_1\rho_1(P_0, T_0)}, \tag{4}$$

where P is the known function of P_0 and T_0 in (2) and $f_{1,2}(P, T)$ are the specific free energies of phases 1 and 2 in the state of hydrostatic compression by pressure P.

We introduce the pressure P_0^* corresponding to phase equilibrium under hydrostatic conditions.

Considerable interest for applications attaches to the difference $P_0 - P_0^*$ at a given T_0, since this determines the degree of metastability that may occur in a solid-state reaction. Retaining the quadratic terms in the expansion of f_1 and f_2 with respect to $P_0 - P_0^*$ and substituting the corresponding expressions into (4), we get a quadratic equation for $x = P_0 - P_0^*$, whose solution takes the form

$$x = a\Delta P[-1 + (1 - b/a)^{1/2}], \tag{5}$$

where

$$a = 1 + \left(1 + \frac{3K_2}{4\mu_1}\right)\Big/\varepsilon, \quad b = \left(2 - \frac{v_2}{v_1} + \frac{3K_2}{4\mu_1}\right)\Big/\left(1 + \varepsilon + \frac{3K_2}{4\mu_1}\right),$$

$$\varepsilon = K_2/K_1 - v_2/v_1, \quad v_1 = 1/\rho_1(P_0^*, T_0), \quad v_2 = 1/\rho_2(P_0^*, T_0),$$

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*If the strength of the material is exceeded, a plastic layer is formed in the interphase zone and stress relaxation occurs [4, 6]. These effects will not be considered here as the study is designed to provide upper bounds.

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and $K_{1,2}$ are the bulk moduli of the phases. In the case of practical importance where the bulk moduli of the two phases are similar ($\varepsilon \ll 1$), we get the simple relation

$$x = -\frac{\Delta P}{2} \frac{3K_2 + 4\mu_1 (2 - v_2/v_1)}{3K_2 + 4\mu_1 (1 + K_2/K_1 - v_2/v_1)} .$$ (6)

Similar arguments provide another important formula. Let the pressure in the matrix be fixed at P_0, while the standard equilibrium temperature at this pressure is T_0 (hydrostatic equilibrium). To obtain a nucleus of the less dense phase, we need a temperature rise $\Delta T = T_0^* - T_0$, where the pair T_0^*, P_0 satisfies (4). The estimate for ΔT takes the form ($\varepsilon \ll 1$):

$$\Delta T = \frac{dT}{dP} \frac{\Delta P}{2} \frac{3K_2 + 4\mu_1 (2 - v_2/v_1)}{3K_2 + 4\mu_1 [1 + (dT/dP)(\alpha_1 - (v_2/v_1)\alpha_2) K_2]} ,$$ (7)

where $dT/dP = \Delta v/\Delta s$ and $\alpha_{1,2}$ are the thermal-expansion coefficients of the phases. For the above transformation in forsterite we have [10]: $K_1 \simeq 2000$ kbar, $v_1 \simeq 38.5$ cm³/mol, $v_2 \simeq 41.0$ cm³/mol, $\alpha_1 \simeq \alpha_2 \simeq 3 \cdot 10^{-5}$ K^{-1}, and $dT/dP \simeq 29$ K/kbar. We substitute these values into (6) and (7) to get $x \simeq 30$ kbar and $\Delta T \approx 600$ K. This indicates that there may be considerable supercooling for high-pressure phases, which must be borne in mind in explaining quenching phenomena.

These inhomogeneous equilibrium states correspond to turning points in the over-all free energy at a given temperature (the Gibbs principle [1, 3, 9]). The radius of the nucleus is not determined in this approach, i.e., the equilibrium between the nucleus and the matrix is indifferent in relation to radial perturbations, because there is no quantity with the dimensions of length in the list of definitive parameters. In that sense, the results correspond to the asymptote $\xi \to 0$, where ξ is the degree of transformation. This equilibrium is not stable because the nonhydrostatic stress components relax in a finite time. Therefore, while the argument is applicable to laboratory results, the equilibria are to be taken as hydrostatic over geological times. Effects due to elastic stresses in the matrix in experiments may result in hysteresis in the synthesis of high-pressure phases. Therefore, the true monovariant equilibrium curve will be recorded with an uncertainty of the order of $2x$. These effects may produce a systematic narrowing in the phase coexistence region in the experimental determination of divariant phase-equilibrium fields for solutions.

Metastable states occur as a rule because the conversion rate is low, i.e., the explanation is in terms of kinetic factors. In the present case, the transformation is considered as occurring instantaneously when the equilibrium conditions are attained. Here the equilibrium curve itself is displaced because of the elastic stresses. It should be noted that stress relaxation enables one to characterize effects related to the nonhydrostatic conditions also as kinetic ones.

Appendix. This analysis is applicable in describing a nucleus whose characteristic dimension is much less than that of the matrix (or of the distance between nuclei). Now let the size of the converted region be comparable with the size of the initial specimen. In that case, one naturally considers the phase transition in a region of fixed volume [11].

For simplicity we retain the assumption of spherical symmetry and consider a region in the form of a sphere of fixed radius R (phase 1). When the nucleus of a new phase with radius $R > R_0$ ($\rho_2 < \rho_1$) appears at the center of symmetry, elastic stresses occur in the matrix, and

$$U_r = \frac{(P - P_0)\, r}{3K_1 \xi + 4\mu_1} \left(\frac{R^3}{r^3} - \xi \right) ,$$

where $\xi = (R/R_0)^3$ is the degree of transformation. It is readily seen that the strain does not amount to pure shear in this case. The pressure in phase 2 is

$$P = P_0 + \Delta P, \quad \Delta P = \frac{\Delta \rho}{\rho_2} \frac{4K_2\mu_1 + 3K_1 K_2 \xi}{3K_2 + 4\mu_1 + 3\xi (K_1 - K_2)} .$$

The condition for phase equilibrium can be put as

$$f_2(P, T_0) + \frac{P}{\rho_2(P, T_0)} = f_1(P_0, T_0) + \frac{3(P-P_0)\xi \cdot P_0}{(4\mu_1 + 3K_1\xi)\rho_1(P_0, T_0)} +$$
$$+ \frac{3}{2}\frac{(P-P_0)^2(4\mu_1 + 3K_1\xi^2)}{\rho_1(P_0, T_0)(4\mu_1 + 3K_1\xi)^2} + \left(1 - \frac{3(P-P_0)\xi}{3K_1\xi + 4\mu_1}\right)\frac{P}{\rho_1(P_0, T_0)}.$$

This equation allows us to determine the degree of conversion ξ for given P_0 and T_0, and therefore the size of the nucleus. The nucleus of the new phase occurs when $\xi = 0$; the pressure $P_0(T_0, \xi = 0)$ is calculated from (4). The transformation terminates at $R = R_0$; to calculate the corresponding pressure $P_0(T_0, \xi = 1)$, it is sufficient to put $\xi = 1$ in the phase-equilibrium condition. Simple arguments analogous to those given above indicate the degree of metastability attainable in experiment:

$$x = -\frac{\Delta P}{2} \cdot \frac{2(1 - \gamma\delta K_2) - \delta(v_2/v_1)}{1 - \delta(v_2/v_1 - K_2/K_1)},$$

$$\Delta T = \frac{dT}{dP}\frac{\Delta P}{2} \cdot \frac{2(1 - \gamma\delta K_2) - \delta(v_2/v_1)}{1 + \delta(dT/dP)K_2(\alpha_1 - (v_2/v_1)\alpha_2)},$$

where

$$\delta = \frac{4\mu_1 + 3K_1\xi}{4\mu_1 + 3K_1\xi + 3K_2(1-\xi)},$$

$$\gamma = \frac{3}{2}\frac{4\mu_1(1 - 2\xi) - 3K_1\xi^2}{(4\mu_1 + 3K_1\xi)^2}.$$

A direct check shows that for $\xi \to 0$, i.e., for sufficiently small nuclei, these formulas reduce to (6) and (7).

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