

## THE CHEMICAL-POTENTIAL TENSOR\*

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A study is made of the conditions for chemical equilibrium between solid phases in a state of nonhydrostatic stress. It is shown that transfer from a local Gibbs identity to the volume analog requires the introduction of a chemical-potential tensor. Three generalized models are discussed for phase boundaries in solid-state reactions: coherent, semicoherent, and incoherent. A model is proposed for semicoherent or incoherent surfaces. Gibbs method yields symmetrical conditions for chemical and mechanical equilibrium.

There is much evidence that there are nonhydrostatic conditions within the Earth. Examples are provided by tectonic processes such as mountain building, ocean floor spreading, and subduction, which are accompanied by considerable stresses in the crust, and these do not amount to hydrostatic ones, which means that they cannot be described by means of a single intensive parameter  $P$ . Seismology is also based on the concept of an elastic solid Earth. Shear strains occur at an earthquake focus, which generally do not involve volume change. On the other hand, nonhydrostatic stresses and strains are characteristic of solid-state reactions accompanied by volume changes. For example, the deposition of a nucleus of a new phase in the decomposition of a solid solution causes nonhydrostatic stresses to concentrate around it, and these may greatly exceed the average pressure in the specimen. In the initial stages, the new phase is coherently related to the matrix, which results in excess elastic energy and ultimately in displacement of the equilibrium curve. Similar phenomena occur in partial melting.

States of nonhydrostatic stress are also evidently typical of metamorphism. Reactions occurring via a fluid freely migrating in the system must be considered on the basis of differences in pressure on the liquid and on the solid phases. A characteristic example is provided by the reactions in an open natural system, where the pressure (fugacity) of the fluid is controlled by the external reservoir (buffer), while the solid phases are subject to the basic lithostatic pressure.

Particular consideration is required for chemical equilibria involving real anisotropic crystals, which deform nonhydrostatically even if a single pressure is applied. In that case, one gets specific orientation recrystallization effects, i.e., directional transport in the stress field. In general, the equilibrium between a nonhydrostatically stressed solid and a liquid is metastable and is accompanied by recrystallization, as Gibbs himself noted. For example, one gets macroscopic creep in a polycrystalline aggregate by dissolution at the grain boundaries, where the stresses concentrate (pressure solution).

These examples do not exhaust the variety of situations in which nonhydrostatic systems have to be considered; there are also the instances of deep-focus earthquakes, where there is relaxation of nonhydrostatic stresses as a polymorphic conversion front migrates, while nonhydrostatic states of stress are invoked to explain the orientations and shapes of magmatic chambers, and so on.

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The above thus indicates the importance of a correct thermodynamic consideration of nonhydrostatically stressed systems.

Considerable attention has been given recently [1 - 12] to general problems in the thermodynamics of chemical and phase equilibria involving nonhydrostatically stressed solids, because there are many applications in geochemistry, geophysics, geology, metallurgy, and the mechanics of materials. Thompson in 1862 formulated and tested the basic principles involved in the dissolution of crystals under conditions of differential loading. Within a year, Sorby [13] recognized the importance of these principles for geology, and he explained the changes in crystal shape in the formation of banding by solution under pressure, and he noted "Mechanical force is involved in a chemical process." Gibbs [14] laid the basis of the thermodynamic theory. He examined the equilibrium between a nonhydrostatically stressed solid and a liquid, and he formulated the conditions at the phase boundary and in essence demonstrated the tensor character of the chemical potential. There were major difficulties in transferring to equilibria between solid phases, and evidence for this comes from the discussions over the last 30 years [15 - 18]. There are several reviews dealing with critical analysis of the points of view [1, 2, 8, 19]. The difficulties are probably related to lack of clarity over the following three points.

1. There are no unified principles for deriving the thermodynamic conditions for chemical and phase equilibrium at the boundaries of solid phases in complex states of strain. Along with Gibbs's classical method [14], use has been made of the method of thermodynamic cycles [2, 20], the absolute chemical potential method [2, 21 - 23], and various semiempirical approaches [2].

2. When one considers solid-state reactions accompanied by finite strain, one must make proper use of the nonlinear theory of elasticity [6, 7, 12, 14, 24 - 28], transferring where possible to the correct linear approximation.

3. One must distinguish coherent, semicoherent, and incoherent phase boundaries in solid phases [2 - 7]. The concepts used in the model must be clearly stated. The differences in the conditions of equilibrium are often associated with inexplicit assumptions about the nature of the transition.

There are many papers [27 - 34] on the chemical thermodynamics of nonhydrostatically stressed solids. Grinfel'd's papers [6, 7] have played a decisive part, as he performed a rigorous mathematical study of some models for solid-state reactions. Ostapenko [2] has given an extensive survey and presented an original view on the problem.

Here unified concepts are used in an analysis of the conditions for chemical and phase equilibrium between solid phases. The discussion is within the framework of Gibbs's method and is a direct extension of the approach used in [6, 7, 12, 14, 28]. It is shown to be necessary to introduce the chemical-potential tensor  $\mu^{ij}$  (the Bowen-Grinfel'd tensor [7, 35 - 37]). It is shown that  $\mu^{ij}$  arises naturally in transferring from a local Gibbs identity to the volume analog under conditions of a nonhydrostatically stressed state, and it characterizes the change in energy of the body associated with mass transfer through the interphase surface. In terms of the macroscopic approach used in the theory of elasticity, a model is formulated for a semicoherent (incoherent) phase boundary, which enables us to derive the conditions for phase (chemical) and mechanical equilibrium with semicoherent (incoherent) phase conjugation, which differ from the corresponding conditions for a coherent boundary [6, 7, 28]. The conditions can be used in describing nucleation and growth in the solid state.

This study is a continuation of [12], so we use the definitions introduced there without detailed discussion. No assumptions are made about the smallness of the strains. The observer's Euler coordinate system is considered as cartesian. Summation with respect to the repeating subscripts is assumed in the tensor formulas.

#### GIBBS IDENTITY

In classical equilibrium thermodynamics, one considers homogeneous systems (ones consisting of homogeneous parts), within which the thermodynamic parameters are independent of the spatial coordinates. The local-equilibrium



hypothesis [38] represents a simple generalization to the case where there are gradients in the thermodynamic functions. According to this approach, the thermodynamic state in each physically very small element is described by a set of standard parameters:  $P$ , pressure;  $T$ , temperature,  $\rho$ , density, and  $u$  and  $s$ , specific internal energy and entropy, while the Gibbs identity\* applies locally:

$$du = Tds - Pd(1/\rho). \quad (1)$$

In essence, there is averaging here over scales less than some specified one  $\xi$ . The latter is chosen from the condition that at distances of the order of  $\xi$  the system may be considered as homogeneous; it is also assumed that local equilibrium is established in a time much less than the observation time.

For a homogeneous system, one can pass from the local identity (1) to the relation for a finite volume  $V$ :

$$dU = TdS - PdV + \mu dM, \quad (2)$$

where  $U = uM$ ,  $S = sM$ , and  $M = \rho V$ ; the intensive quantity

$$\mu = u - Ts + P/\rho \quad (3)$$

is called the chemical potential of a phase (necessarily one-component). Equation (2) enables one to distinguish the independent extensive degrees of freedom. Note that the parameter  $\mu(P, T)$  is absent in the local description and arises on passing to the volume relation (2).

Additional characteristics are required [24 - 26] to describe the strains in the solid phases, which in general do not amount to isotropic expansion or compression. Let  $\xi^\alpha$ ,  $\alpha = 1, 2, 3$  be Lagrange coordinates with  $x^i(\xi^\alpha)$  the law of motion (deformation) for points in the medium from the reference state  $x^i(\xi^\alpha) = \xi^i$  ( $i = 1, 2, 3$ ) to the actual one;  $x_\alpha^i = \partial x^i / \partial \xi^\alpha$  is the distortion tensor, which characterizes the distortion of an infinitely small cube as a result of the strain, with  $\epsilon_{\alpha\beta} = (1/2)(x_\alpha^i x_\beta^i - \delta_{\alpha\beta})$  the deformation tensor and  $\delta_{\alpha\beta}$  the Kronecker symbol (unit matrix). The fundamental equation of state for an elastic body takes the form [24 - 26]:

$$u = u(x_\alpha^i, s). \quad (4)$$

Arguments known as the principle of material independence lead to the requirement that the function  $u$  is dependent on the components of the tensor  $x_\alpha^i$  via the components of the tensor  $\epsilon_{\alpha\beta}$  [24 - 26]. The density change clearly does not characterize the strain completely, since a purely shear part remains. By definition

$$\rho = \rho_0 / \det(x_\alpha^i),$$

where  $\rho_0(\xi)$  is the density in the reference state and  $\rho$  is that in the actual state. For a liquid we have instead of (4) that

$$u = u(\rho, s), \quad (5)$$

which leads to (1) if we use the definitions  $T = \partial u / \partial s$ ,  $P = \rho^2 \partial u / \partial \rho$ . The equation of state (5) is a particular case of (4) characterized by an extremely special form of the function  $u(x_\alpha^i, s)$ . When we introduce the Cauchy stress tensor [24 - 26]  $P^{\alpha\beta} = \rho \partial u / \partial \epsilon_{\alpha\beta}$ , we can obtain the local Gibbs identity for an elastic body:

$$du = Tds + \frac{1}{\rho} P^{\alpha\beta} d\epsilon_{\alpha\beta}. \quad (6)$$

Equation (6) is an exact analog of (1).

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\*The phases are taken as of single-component type for simplicity.

As we have already noted, the extension of the chemical-potential concept for a solid phase to the nonhydrostatic case has been widely discussed in the literature. Researches in this area have been concerned mainly with generalizing (3) on the one hand and (2) on the other. We adopt the first approach and use (6) in a Lagrange transformation with respect to  $\epsilon_{\alpha\beta}$  and  $T$ , which gives us the concept of a scalar chemical potential:

$$g = u - Ts - \frac{1}{\rho} P^{\alpha\beta} \epsilon_{\alpha\beta}. \quad (7)$$

An obvious disadvantage of this definition is that  $g$  does not amount to  $\mu$  in the case of a liquid, as many authors have pointed out [2]. Also, the clear physical meaning of  $\mu$  is lost, since the equation analogous to (2) with  $\mu$  replaced by  $g$  obviously does not apply.

Generalization of (2) on the other hand leads to the significant concept of the chemical potential as becoming a tensor quantity, by analogy with the way in which the scalar pressure  $P$  becomes the stress tensor  $P^{\alpha\beta}$ . Gibbs [14] arrived at this concept in considering the equilibrium between a nonhydrostatically stressed solid and a liquid, although his paper lacks the concept of the chemical-potential tensor itself. Before we transfer to the general case, let us consider in more detail a very simple example first examined by Gibbs.

#### GIBBS'S EXAMPLE

Consider an isotropic solid in the form of a rectangular parallelepiped compressed on pairs of parallel faces by noncontacting liquids with pressures  $P_1$ ,  $P_2$ , and  $P_3$ . One then gets homogeneous strain, and the state of stress is characterized for the entire volume by the numbers  $P_1$ ,  $P_2$ , and  $P_3$ . Instead of the single intensive parameter  $P$  we have a stress tensor, which in the present case is diagonal:

$$P_{ij} = \begin{pmatrix} P_{11} & P_{12} & P_{13} \\ P_{21} & P_{22} & P_{23} \\ P_{31} & P_{32} & P_{33} \end{pmatrix} = \begin{pmatrix} -P_1 & 0 & 0 \\ 0 & -P_2 & 0 \\ 0 & 0 & -P_3 \end{pmatrix}. \quad (8)$$

If we consider a unit area with normal  $n_i$ , the resultant surface force acting on this area takes the form

$$F^i = P^{ij} n_j,$$

and the normal component  $F^i n_i$  amounts to a pressure in the case of a liquid, whereas the tangential component is related to the presence of tangential stresses and is absent for a liquid (in the static case). The minus sign in (8) is traditional and characterizes the compressive character of the pressure ( $P_1 > 0$ ,  $P_2 > 0$ , and  $P_3 > 0$ ).

The condition for mechanical equilibrium at the surface of the parallelepiped is that the pressures in the liquids are equal to the corresponding normal stresses  $P_{11} = -P_1$ ,  $P_{22} = -P_2$ ,  $P_{33} = -P_3$ ,  $P_{ij} = 0$ ,  $i \neq j$ . Gibbs showed that the chemical-equilibrium condition, i.e., equilibrium with respect to dissolution, phase transformation, and so on, is equality of the chemical potentials for a component of the solid phase in the liquids to the chemical potentials  $\mu_1$ ,  $\mu_2$ , and  $\mu_3$  defined at each face by means of the formula

$$\mu_i = u - Ts + P_i/\rho, \quad (9)$$

where  $P_i$  is the pressure on the given face.

Therefore, there are at once three chemical potentials, each of which is defined on one of the faces and characterizes the energy increment associated with mass transfer (chemical reaction) at that face. It is readily shown that



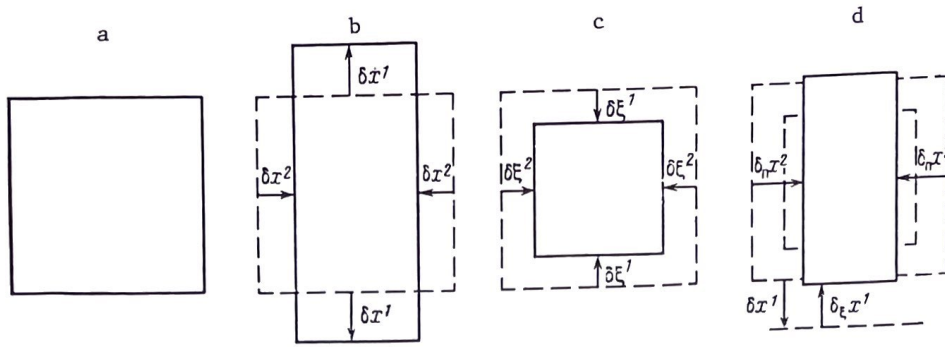


Fig. 1. Schematic representation of variations: a) initial state, b) small deformation, which amounts to compression along the  $x^2$  axis and stretching along the  $x^1$  axis, c) displacement of the boundary over particles of the material not accompanied by pure deformation but leading to change in mass, d) result of joint variation (b and c); the variations  $\delta x^i$  and  $\delta_{\xi} x^i$  are independent,  $\delta_t x^i = \delta x^i + \delta_{\xi} x^i$ .

we have

$$dU = TdS - P_1 \Sigma_1 \delta_t x_1 - P_2 \Sigma_2 \delta_t x_2 - P_3 \Sigma_3 \delta_t x_3 + \mu_1 \delta m_1 + \mu_2 \delta m_2 + \mu_3 \delta m_3, \quad (10)$$

where  $U = uM$  is the over-all internal energy,  $M$  the total mass,  $S = sM$  the entropy, and  $\Sigma_1, \Sigma_2, \Sigma_3$  the areas of the phases in the actual (deformed) state. By  $\delta_t x_i$  ( $i = 1, 2, 3$ ) we denote the total variations (coordinate increments) in the surface positions (Fig. 1). However, apart from these variations there are independent variations in the surface positions related to the mass change arising for example by chemical reaction. If we introduce the variations in surface position on the Lagrange coordinates  $\delta \xi^1, \delta \xi^2$ , and  $\delta \xi^3$  (Fig. 1), we get

$$\delta m_1 = \rho_0 \Sigma_{01} \delta \xi^1, \delta m_2 = \rho_0 \Sigma_{02} \delta \xi^2, \delta m_3 = \rho_0 \Sigma_{03} \delta \xi^3, \quad (11)$$

where  $\Sigma_{01}, \Sigma_{02}$ , and  $\Sigma_{03}$  are the face areas in the undeformed state. Let the deformation be given by the following formulas (law of motion):

$$x^i = k_i \xi^i, \quad x^2 = k_2 \xi^2, \quad x^3 = k_3 \xi^3, \quad (12)$$

where  $\xi^i = x^i$  are the coordinates of the points in the reference state ( $k_i = 1$ ). We use (11) and (12) to rewrite (10) as

$$dU = TdS - P_1 \Sigma_1 \delta(k_1 \xi^1) - P_2 \Sigma_2 \delta(k_2 \xi^2) - P_3 \Sigma_3 \delta(k_3 \xi^3) + \mu_1 \rho \Sigma_1 \delta_{\xi} x^1 + \mu_2 \rho \Sigma_2 \delta_{\xi} x^2 + \mu_3 \rho \Sigma_3 \delta_{\xi} x^3, \quad (13)$$

where  $\delta x^i = \xi^i \delta k_i$  are the variations for given Lagrange variables;  $\delta_{\xi} x^i = k_i \delta_{\xi} \xi^i$  are the variations associated with the mass transfer (there is no summation on the repeated subscripts,  $i = 1, 2, 3$ ). Therefore, Gibbs's generalization of the chemical potential for a one-component phase consists of the following: the chemical potential appears on passing from the local relation between the differentials of the thermodynamic parameters (Gibbs identity) to the relation between the variations in the mass extensive quantities and characterizes the energy increment associated with mass change.

#### GENERAL CASE

There is an obvious similarity between the conditions for chemical and mechanical equilibrium in this example, which indicates a natural generalization of the chemical potential concept, as does the symmetry in relation to  $P_i$  and  $\mu_i$  in (13). By analogy with the stress tensor, we introduce the chemical-potential tensor for a one-component solid phase (the Bowen-Grinfel'd tensor):



$$\mu_{ij} = (u - Ts) \delta_{ij} - \frac{1}{\rho} P_{ij}, \quad (14)$$

which in a liquid is spherical:

$$\mu_{ij} = \begin{pmatrix} \mu_{11} & \mu_{12} & \mu_{13} \\ \mu_{21} & \mu_{22} & \mu_{23} \\ \mu_{31} & \mu_{32} & \mu_{33} \end{pmatrix} = \begin{pmatrix} \mu & 0 & 0 \\ 0 & \mu & 0 \\ 0 & 0 & \mu \end{pmatrix},$$

with  $\mu = u - Ts + P/\rho$ , and  $P$  the pressure in the liquid, while for triaxial compression it is diagonal:

$$\mu_{ij} = \begin{pmatrix} \mu_1 & 0 & 0 \\ 0 & \mu_2 & 0 \\ 0 & 0 & \mu_3 \end{pmatrix}.$$

Expression (14) first appeared in papers by Bowen [35, 36] dealing with the theory of mixtures. Then the chemical-potential tensor was used in [37] in describing semipermeable membranes. In [7], a study was made of the equilibrium conditions at interphase surfaces within the framework of the theory of elasticity, and (14) was first used there in the present context for writing the conditions at a phase discontinuity in symmetrical form.

We will now show that Gibbs's method leads uniquely to the concept of (14) for the case of a nonhydrostatically stressed solid.

Consider the change in over-all internal energy of a nonhydrostatically stressed solid  $U = \int_V \rho u dV$ , occupying a volume  $V$  (Fig. 2) bounded by the interface  $\Sigma = \partial V$ . This change is related to:

a) variations in the law of motion in the volume:

$$\delta x^i = x^{i'}(\xi^\alpha) - x^i(\xi^\alpha),$$

i.e., to small deformation of the continuous medium (analog of the density change  $d\rho$ );

b) variations in the entropy in the volume:

$$\delta s = s'(\xi^\alpha) - s(\xi^\alpha);$$

c) variations in the position of the phase interface with respect to the Lagrange coordinates, namely the analog of  $dM$  in (2):\*

$$\delta \xi^\alpha = \tilde{\xi}^{\alpha'}(u^1, u^2) - \tilde{\xi}^\alpha(u^1, u^2),$$

where  $\tilde{\xi}^\alpha = \tilde{\xi}^\alpha(u^1, u^2)$  is the equation for the interphase surface in Lagrange coordinates and  $u^1$  and  $u^2$  are certain coordinates on surface  $\Sigma$ .

Standard transformations based on Stokes's theorem lead to the following (see Appendix 1):

$$\delta U = T \delta S + \oint_{\Sigma} P_i^k n_k \delta x^i d\sigma + \oint_{\Sigma} \rho \mu_i^k n_k \delta \xi^i d\sigma, \quad (15)$$

where  $S = \int_V \rho s dV$  is the overall entropy,  $T = \partial u / \partial s$  is the temperature, which is assumed independent of the spatial coordinates,  $P_i^k$  are the stress-tensor components, and  $n_k$  are the components of the unit normal vector to the surface  $\Sigma$ .

\*It is assumed that there is no difference between the phases in the reference (undeformed) state.



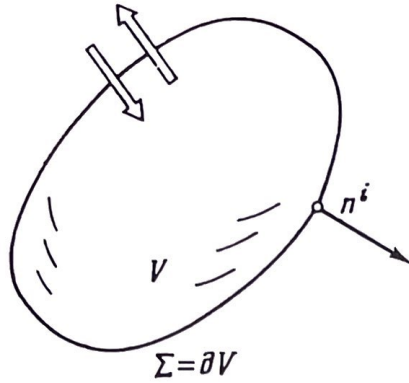


Fig. 2

Fig. 2. Representation of a volume element  $V$  bounded by the surface  $\Sigma = \partial V$  with normal  $n^i$ . Mass transfer can occur through the interface surface  $\Sigma$ .

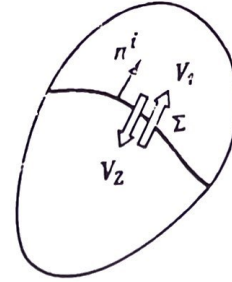


Fig. 3

Fig. 3. Representation of coexisting phases. At the interface surface separating phases 1 and 2, the conditions for thermal, mechanical, and chemical equilibrium should be obeyed.

By  $\delta_t x^i$  we denote the total variation in the coordinates of surface  $\Sigma$ :

$$\delta_t x^i = \delta x^i + \delta_\xi x^i,$$

which consists of the pure deformation  $\delta x^i$  and the variation  $\delta_\xi x^i = x_\alpha^i \delta \xi^\alpha$ , related to displacement of the surface along the Lagrange coordinates, i.e., with mass transfer through surface  $\Sigma$ . In deriving (15), we have used the conditions for mechanical equilibrium in volume  $V$ , i.e., we assumed that the stress tensor satisfies the following equation [24 - 26]:

$$\frac{\partial}{\partial x^l} P^{il} = 0. \quad (16)$$

The variational identity (15) may be called the fundamental Gibbs equation for volume  $V$  occupied by a nonhydrostatically stressed solid, and it is a direct generalization of (2). In fact, in the case of a liquid

$$P_i^k = -P\delta_i^k; \quad \mu_i^k = \mu\delta_i^k$$

and (15) simplifies to

$$\delta U = T\delta S - \oint_{\Sigma} P(\delta_t x^i n_i) d\sigma + \oint_{\Sigma} \rho\mu(\delta_\xi x^i n_i) d\sigma.$$

In the case of a homogeneous state  $P = \text{constant}$  and  $\mu = \text{constant}$ , we use the identities

$$\delta V = \oint_{\Sigma} (\delta_t x^i n_i) d\sigma;$$

$$\delta M = \rho \oint_{\Sigma} (\delta_\xi x^i n_i) d\sigma,$$

to arrive at (2).

Note that the work associated with volume change is expressed as an integral over the surface, since the surface forces arising from the surface position variations in actual space do work. The stress tensor is defined for all points within volume  $V$ ; on the other hand, the chemical-potential tensor (in our context) is defined only for points at the interphase surface.



Expression (15) explains why all attempts have been unsuccessful in the discussion of fairly general situations [17] to introduce chemical potential for a nonhydrostatically stressed solid as the partial derivative with respect to the mass for some characteristic function. However, essentially correct results have been obtained for very simple states of stress in this way [2].

### CONDITIONS FOR CHEMICAL (PHASE) EQUILIBRIUM

Consider the phase boundary  $\Sigma$  separating two elastic phases occupying volumes  $V_1$  and  $V_2$  (Fig. 3). From (15) we obtain for the two-phase system that

$$\delta(U_1 + U_2) = T\delta(S_1 + S_2) + \int_{\Sigma} [P_j^i \delta_\epsilon x^j]_1^2 n_i d\sigma + \int_{\Sigma} [\rho \mu_j^i \delta_\epsilon x^j]_1^2 n_i d\sigma. \quad (17)$$

The expression  $[f]_1^2 = f^2 - f^1$  denotes the discontinuity in  $f$  at the sides of the phase interface.\* In deriving (17), all variations have been taken as zero on parts of the surface  $\partial V_1 + \partial V_2$ , not representing a phase surface.

A first-order phase transition in a solid is accompanied by a discontinuity in the strain tensor, and in particular in the density. The states of stress on two sides of an interface are in general different. In the case of equilibrium, the discontinuities in the stresses and strains at a given temperature are not arbitrary but satisfy the conditions for mechanical and chemical equilibrium. g

Gibbs [14] derived the equilibrium conditions at the contact between a nonlinearly elastic solid and its melt or solution by the use of a variational principle, which amounts to seeking a turning point in the over-all internal energy  $U_1 + U_2$  for a given entropy  $S_1 + S_2$  of the variations described above. By using Gibbs's principle\*\* we get from (17) an equation known in variational calculus as the condition of transversality [39]: )

$$[P_j^i \delta_\epsilon x^j + \rho \mu_j^i \delta_\epsilon x^j]_1^2 n_i = 0. \quad (18)$$

We isolate the independent ones from the 12 variations  $\delta_\epsilon x_{1,2}^i, \delta_\epsilon x_{1,2}^i$  to get the conditions at the discontinuity. The differences in the physical mechanisms involved in the various transformations result ultimately in differences in the equilibrium conditions. Therefore, we first consider the classification of solid-state transformations from experimental data. -  
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### CLASSIFICATION OF SOLID-STATE REACTIONS

In this context we need to consider the existence of two essentially different classes of phase transitions in solids: coherent and incoherent [2-5].

In a coherent transition, the initial phase is converted to the final one in such a way that the latter has a strictly definite crystallographic orientation identical throughout the volume, which is determined by the state of the initial phase. In that case, the Euler coordinates are continuous at the interphase boundary, i.e., there is no slip of the phase relative to one another. Physically, this means continuous (coherent) conjugation of the lattices, which undergo marked deformation because of their crystallographic discrepancy (Fig. 4). In a coherent transition, the continuity of the material is not disrupted, and a Burgers contour intersecting the phase surface is always closed. An example of a completely coherent surface is provided by the planar boundary between two twins, namely the twin plane. The coherence arising from elastic strain can occur on nucleation or at early stages of growth, and the elastic strains near the interface may substantially exceed the usual elastic limit. )

\*Note that for a point  $x' = x_1'(\xi_1) = x_2'(\xi_2)$  on the phase interface we have in general  $\xi_1 \neq \xi_2$  for incoherent contact.

\*\*We omit consideration of the entropy variation, which leads to a condition for temperature homogeneity at the internal points and continuity of this at the phase boundary, since it is exactly analogous to that given by Gibbs [14].

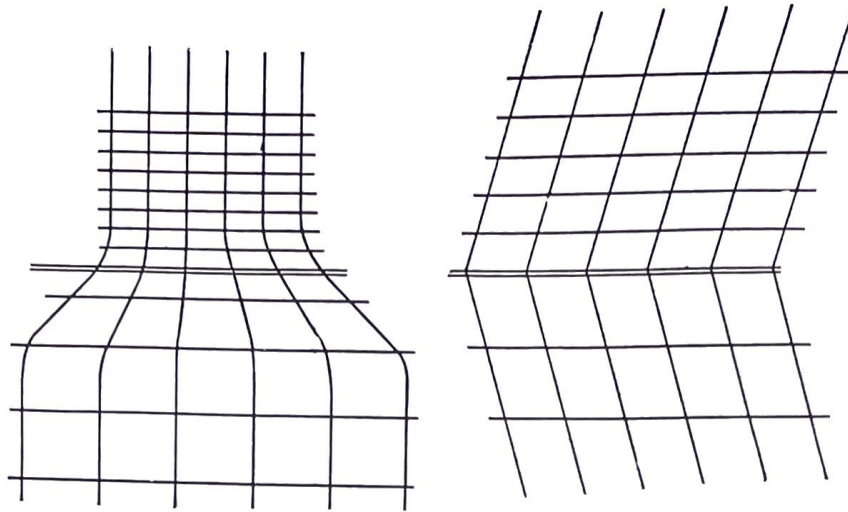


Fig. 4. Examples of coherent phase linking.

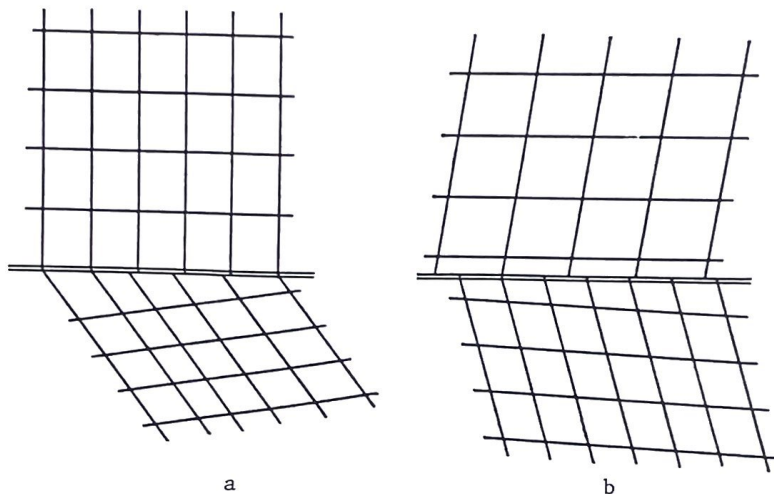


Fig. 5. Examples of semicoherent (a) and incoherent (b) phase linking.

The passage of particles of the medium through such a surface is a collective process and occurs simultaneously in a certain area.

The elastic displacements and consequently the internal stresses may be reduced if there is some other mechanism for compensating the lattice discrepancies. This mechanism is associated with dislocations. Phase linking in which the level of the internal stresses is reduced by discrepancy dislocations is called partially coherent or semicoherent. The prototype of such a boundary is a small-angle grain boundary. The surface may then be represented by parts with complete coherence attained by elastic lattice distortion separated by discrepancy regions.

An incoherent boundary is analogous to a large-angle grain boundary. The structure of such a boundary is relatively disordered, and the surface does not meet the conditions for continuity in the lattice vectors and planes on passage through it. Although this surface can be described formally in terms of dislocation theory, the description does not have a physical meaning, and lattice correspondence is not observed when the interface moves (Fig. 5).

A heterogeneous transformation with a coherent boundary can occur only in the solid state and involves the joint motion of many atoms, not the independent displacements of individual ones. Most of the atoms have the same nearest



neighbors before and after the transformation, although they are disposed in different ways, and the resultant displacement is such that a series of elementary cells in the initial phase is as it were homogeneously deformed in a sufficiently small region to become the corresponding series of cells in the new phase. Processes of this type are often called diffusion-free or shear transformations, but in recent years it has become usual to consider them as martensitic transformations.

In a typical incoherent transformation, the new phase grows at the expense of the old one by relatively slow migration of the interphase boundary, and growth occurs by successive passage of the atoms through the boundary [2]. The atoms move independently and their speeds vary appreciably with temperature. Such a transformation in the main is controlled by thermal excitation, and the elementary processes resemble chemical reactions.

A good example of a coherent transition is the  $\alpha$ - $\beta$  transition in quartz [28, 31, 40]. The same class covers twinning in crystals [3, 4], coherent deposition of a fluid component [28], and so on. The incoherent or semicoherent class includes most polymorphic transitions and solid-state reactions [2-4], weak crystallization of anisotropic crystals in stress fields [2], and so on.

### INTERPHASE BOUNDARY MODELS

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In the study of various structural transformations, the discussion is usually conducted at the microscopic level (atomic or molecular), and therefore boundary models are formulated in terms of the matching or otherwise of lattices, the presence or absence of dislocations, and so on. There are advantages in the macroscopic and in part phenomenological approach to describing a solid as a continuous medium as used in the theory of elasticity and deriving from Cauchy's studies, since it is possible to give an average description while retaining essential concepts on continuity, anisotropy, and elasticity. The stress distribution in a solid may be described on that approach, and therefore the character of the thermodynamic state. It is necessary to formulate equilibrium conditions whose form is dependent on the transformation model in order to solve some problems in the formation and propagation of interphase boundaries in solids.

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Grinfel'd [6] led the first rigorous mathematical discussion of coherent interphase boundaries. He used Gibbs's method and assumed continuity in the displacements at the phase boundary:

$$[x'(\xi^\alpha)]_1 = 0, \quad (19)$$

from which he derived equilibrium conditions for coherent phase linkup (Appendix 2).<sup>\*</sup> The extension to sufficiently slow movement of coherent boundaries was given in [41, 42]. It is not generally accepted to use Gibbs's method based on the assumption of locality for the equilibrium conditions in describing coherent transformations, and therefore some workers have devised alternative theories based on the absolute chemical potential [2, 4, 43].

Let us now consider incoherent and semicoherent transitions, which are simulated within the framework of the Gibbs approach. Here the condition (19) on the displacements must be weakened by allowing some slip of the phases relative to one another in the tangential plane, i.e., we allow discontinuities in the displacements. The following condition of the variations is necessary, since it forbids the formation of cavities between the phases and guarantees continuity conservation:

$$[\delta_t x^i]_1 n_i = 0. \quad (20)$$

If we adopt a single constraint on the variations of (20) as in [7], we get the following equilibrium conditions (see Appendix 3):

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<sup>\*</sup>Robin [28] has considered coherent phase transitions in a nonlinearly elastic medium within the framework of the present approach, but the paper contains some obscurities in describing the transformation kinematics.



$$\begin{aligned}
[P_j^i]_i^2 n_i &= 0, \quad P_{j_1, 2}^i n_i = -P n_j, \\
[u - Ts + P/\rho]_i^2 &= 0.
\end{aligned}
\tag{21}$$

The corresponding transitions have been called [7] slip transitions, since the presence of even infinitely small discontinuities in the tangential stresses at the phase interface leads to slip and disturbance of the equilibrium. The model is applicable when one of the phases is a liquid and also in the description of incoherent boundaries when there is no adhesion between the phases [5].

Now let the phases interact, with slip allowed only during the transformation, which is due to the impossibility of compensating the discrepancy between the lattices by means of elastic stresses alone. At equilibrium, when the phase boundary is at rest, the link between the lattices is partially coherent, and the application of a tangential force does not lead to slip. However, during the transformation, i.e., when the interphase surface moves, the partial coherence may be disrupted.

Condition (20) enables us to put

$$[\delta x^i]_i^2 n_i = -[x_\alpha^i \delta \xi_\alpha^i]_i^2 n_i \neq 0.$$

A very simple mathematical formulation of the above assumptions amounts to combining (20) with an additional nonholonomic conditions on the variations, which may be called the minimal-compensation condition. This takes the form

$$[\delta x^i \tau_i]_i^2 = 0, \tag{22}$$

where  $\tau^i$  is a vector tangential to the interphase surface and  $n^i \tau_i = 0$ . Formula (22) states that on the one hand there is a difference from a coherent transformation in that the tangential discrepancies are not compensated, while on the other there is no arbitrary element in relation to the slip along the interphase surface. From (22) we readily get analogs for the Gibbs conditions for mechanical and chemical equilibrium (see Appendix 3):

$$[P_j^i]_i^2 n_i = 0, \tag{23}$$

$$[\mu_j^i]_i^2 n_i n^j = 0, \tag{24}$$

where  $\mu_j^i$  is the chemical-potential tensor of (14). This model is intended to describe semicoherent and possibly incoherent boundaries. An advantage of conditions (23) and (24) is that they are formulated in terms of the Euler approach and can be applied directly as boundary conditions for the equations of elastostatics of (16). The sufficiency of these conditions is guaranteed by the variational mode of derivation. For example, condition (23) is conditional and denotes continuity in the force vector at the surface, while condition (24) characterizes the boundary as an equilibrium one and serves to define its position in space. Note that (24) may serve as an independent definition of the chemical-potential tensor.

## CONCLUSIONS

1. Basic concepts have been formulated in the thermodynamics of heterogeneous equilibria for nonhydrostatically stressed elastic solids. The Gibbs identity has been written for a finite volume containing the solid phase. It is necessary to use the chemical-potential tensor concept, which characterizes the energy increment on chemical transformations.

2. A model has been proposed for the semicoherent (incoherent) interface surface and Gibbs's method then provides symmetrical conditions for chemical and mechanical equilibrium, which enable one to consider the nucleation and growth of solid phases correctly for semicoherent (incoherent) linking.

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APPENDIX 1

We calculate the total variation in the overall internal energy:

$$\begin{aligned} \delta U \equiv & \delta \int_V \rho u(x'_\alpha, s) dV = \int_V \frac{\partial(\rho u)}{\partial x'_\alpha} \frac{\partial}{\partial \xi^\alpha} (\delta x') dV + \int_V \rho \frac{\partial u}{\partial s} ds dV + \\ & + \int_V \rho u \frac{\partial}{\partial x'^i} (\delta_t x^i) dV + \int_V \frac{\partial}{\partial x'^i} (\rho u) \delta_t x^i dV = - \int_V \left( \frac{\partial}{\partial x'^k} P_i^k \right) \delta x^i dV + \\ & + \oint_{\partial V} P_i^k n_k \delta_n x^i d\sigma + \oint_{\partial V} \rho \tilde{\mu}_i^k n_k \delta_\xi x^i d\sigma, \end{aligned} \quad (A1)$$

where

$$\begin{aligned} P_i^k &= \frac{\partial(\rho u)}{\partial x'_\alpha} x'_\alpha{}^k + \rho u \delta_i^k, \\ \rho \tilde{\mu}_i^k &= \rho \frac{\partial(\rho u)}{\partial x'_\alpha} x'_\alpha{}^k. \end{aligned}$$

Similarly, we have the variation in the overall entropy:

$$\delta S \equiv \delta \int_V \rho s(\xi) dV = \int_V \rho \delta s dV + \oint_{\partial V} \rho s \delta_\xi x^i n_i d\sigma. \quad (A2)$$

We combine (A1) and (A2) and use the constancy of the temperature in the system  $T = \partial u / \partial s = \text{constant}$  to get from (15) that

$$\delta U = T \delta S + \oint_{\partial V} P_i^k n_k \delta_t x^i d\sigma + \oint_{\partial V} \rho \mu_i^k n_k \delta_\xi x^i d\sigma,$$

where

$$\rho \mu_i^k = - \frac{\partial(\rho f)}{\partial x'_\alpha} x'_\alpha{}^k,$$

and  $f = u - Ts$  is the specific free energy.

APPENDIX 2

We derive the equilibrium conditions at a coherent interphase surface, which are obtained by using Gibbs's method. The coherence condition (19) gives the following equations, the latter of which is the Hademard compatibility relation:

$$\begin{aligned} [\delta_t x^i]_1^2 &= 0, \\ [x'_\alpha]_1^2 &= \lambda^i n_\alpha, \end{aligned} \quad (A3)$$

where  $n_\alpha = \rho x'_\alpha{}^i n_i$ , and  $\lambda^i$  is a certain vector called a characteristic one in crystallography. There is continuity in the Lagrange coordinates  $[\delta \xi^\alpha]_1^2 = 0$ , and the variations  $\delta_t x^i$  and  $\delta \xi^\alpha$  are independent, so we get

$$[P_j^i]_1^2 n_i = 0, \quad [\rho \mu_j^i x'_\alpha{}^j]_1^2 n_i = 0. \quad (A4)$$

The latter condition can be rewritten by using (A3) as

$$[\mu - Ts]_1^2 - P_j^i n_i \lambda^j = 0,$$

and therefore only one of the three conditions in (A4) is independent. If we introduce the vector  $n^\alpha = g^{\alpha\beta} n_\beta$ , where  $g^{\alpha\beta}$  is a metrical tensor in the reference configuration, while  $g_{\alpha\beta} = x'_\alpha{}^i x'_\beta{}^j g_{ij}$ ;  $n_\alpha = n_\alpha d\sigma / \rho_0 d\sigma_0$ ; and  $d\sigma$ , and  $d\sigma$  are elements of

area in the reference and actual states, we get

$$\lambda^i = [x_\alpha^i]_1^2 n_\alpha^0 \frac{d\sigma}{\rho_0 d\sigma},$$

from which follows the condition for chemical equilibrium found in [6]:

$$\left[ u - Ts - \frac{1}{\rho} P_\beta^\alpha n_\beta n_\alpha \right]_1^2 = 0.$$

Here

$$P_\beta^\alpha = x_\beta^i P_i^j \xi_j^\alpha, \quad \xi_j^\alpha = (x_\beta^i)^{-1},$$

while  $( )^{-1}$  is the operation of taking the reciprocal matrix.

### APPENDIX 3

Condition (20) enables one to rewrite (18) as

$$[P_i^k]_1^2 n_k \delta x_2^i + \left( P_i^k n_k - \frac{[u - Ts]_1^2}{[1/\rho]_1^2} n_i \right) [\delta x^i]_1^2 = 0.$$

For a transition with slip [7], we equate the coefficients to the independent variations to zero to get the six conditions (21). If we impose two additional constraints on the variations of (22), we get four equilibrium conditions:

$$[P_i^k]_1^2 n_k = 0, \quad P_i^k n_k n^i - \frac{[u - Ts]_1^2}{[1/\rho]_1^2} = 0,$$

which are readily reduced to (23) and (24). We see that relative displacement between adjacent points ( $[\delta x^i] \neq 0$ ) is possible only when the phase boundary moves along the Lagrange coordinates, i.e., when  $\delta \xi^\alpha n_\alpha \neq 0$ . In fact, we calculate  $\lambda = [\delta x^i]_1^2 n_i$ , to get

$$\lambda = - [x_\alpha^i \delta \xi^\alpha]_1^2 n_i = - \left[ \frac{1}{\rho} \right]_1^2 \frac{\rho_0 d\sigma}{d\sigma} (n_\alpha \delta \xi^\alpha),$$

where the equation  $\delta \xi^\alpha n_\alpha = 0$  denotes absence of reaction, since in that case one can produce  $\delta \xi^\alpha = 0$  by appropriate redefinition of the coordinates on the surface.

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## HIGH-TEMPERATURE SOLUTION CALORIMETRY FOR DETERMINING THE ENTHALPIES OF FORMATION FOR HYDROXYL-CONTAINING MINERALS SUCH AS TALC AND TREMOLITE \*

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The heats of solution have been determined for brucite, talc, and tremolite by high-temperature microcalorimetry both by direct solution and by the use of a  $2\text{PbO}\cdot\text{B}_2\text{O}_3$  melt as solvent. The values are in good agreement, which shows that it is possible to apply the high-temperature solution method to hydroxyl-containing minerals. The enthalpies of formation for talc and tremolite have been derived from that for brucite, which has been very reliably determined by various workers by acid calorimetry. The enthalpy of formation of tremolite is  $\Delta H_f^0, 298.15 = -2951.1 \pm 2.6$  kcal/mol, and an estimate has been made of the heat of solution of water in the calorimetric melt. These data have been used in calculating the upper temperature limit to the stability of tremolite in association with quartz and calcite. The displacement of the temperature limit is considered in relation to the total pressure on the mineral  $P_S$ , the fluid pressure  $P_{f1}$ , and the composition of the fluids (molar proportion of  $\text{CO}_2$ ).

During the last decade, there have been considerable advances in thermochemistry applied in mineralogy, with a considerable extension of the range of minerals examined, which indicates that current methods in high-temperature calorimetry as devised in the 1960's by Yokokawa and Kleppa [1] are highly effective. Although high-temperature solution calorimetry has many advantages over traditional acid calorimetry, there have up to now been some major constraints on its use: 1) to minerals that oxidize during high-temperature experiments and 2) to minerals containing volatile components ( $\text{OH}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ , etc.) and which decompose under the working conditions. The first constraint is largely eliminated by additional shielding measures (use of inert-gas atmospheres), as is evident from recent studies by Kleppa et al. [2]. A start has

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