

## CHEMICAL EQUILIBRIA IN A NONHYDROSTATIC SYSTEM\*

L.M. Truskinovskiy and O.L. Kuskov

Institute of Geochemistry and Analytical Chemistry,  
Academy of Sciences of the USSR, Moscow

Various geodynamic processes are accompanied by states of stress in the solid phases that do not amount to hydrostatic compression. Calculations of chemical and phase equilibria in such a system must make allowance for this. Here the theory of finite strains is used in considering the chemical and phase equilibria in an open system with nonhydrostatically stressed solid phases, in which the fluid pressure is controlled by an external reservoir. The following are the independent equilibrium factors for the simple state of strain: liquid pressure, temperature, and differential pressure on the solid phase. Analogs of the Clausius-Clapeyron equation are derived that differ from those used in the theory of systems with unequal pressures on the phases.

It is usual to take the state of stress as hydrostatic in considering chemical and phase equilibria, i.e., the state of stress is described by a single intensive characteristic, the pressure  $P$ . On the other hand, extensive studies have been made on systems with unequal pressures on the phases in chemical thermodynamics, e.g., osmotic systems and systems containing inert gases. The corresponding thermodynamic theories give good agreement with experiment [1, 2].

In applications, however, we encounter situations where the solid phases involved in a reaction are in a complex state of strain, which is not described by a single pressure. The chemical equilibria in an open system between nonhydrostatically stressed solid phases on the one hand and a gas or liquid on the other may involve, for example, reactions in which a volatile is released or absorbed. In that case, we cannot apply directly the standard concept of chemical potential (specific Gibbs energy) for a hydrostatically stressed single-component solid phase as used in calculations on chemical equilibria, because we cannot identify an intensive characteristic that acts as the pressure and that is the equilibrium factor. It is clear that solid phases in complex states of strain that are in contact with a liquid over a certain surface differ in reactivity from solid phases hydrostatically compressed by the same liquid. The deformation absorbs energy, which is partly released as heat, but which mainly remains in the body as internal energy and influences the chemical activity. The chemical potential, which characterizes the energy increment on mass transfer, is now dependent on the state of stress and in general also on the orientation of the surface through which material is transferred. Associated processes are those of orientation recrystallization and creep caused by dissolution of stressed grain boundaries and so on. Numerous

---

\*Trans. from *Geokhimiya*, No. 12, pp. 1798-1812, 1982.

examples show that the equilibrium in that case is of local character\* and is substantially dependent on the state of stress in the solid phase at a given point on the interface.

Gibbs [2] developed the thermodynamics of nonhydrostatically stressed solid phases in equilibrium with the fluid; Gibbs assigned different values of the chemical potential to faces under different pressures and thus recognized the tensor nature of chemical potential and the local character of the equilibrium conditions. Kamb [4], McLellan [5], Ida [6], Green [7], Paterson [8], and Kumazawa [9] have made considerable contributions to geochemical applications of the theory of nonhydrostatic equilibria. Ostapenko [3] has surveyed current concepts and has examined many special aspects, and he has reviewed the arguments on local and absolute chemical potentials. Note that Gibbs used the nonlinear theory of elasticity, in contrast to most of those who came after him. There are relatively few experimental studies on the theory of nonhydrostatic equilibria; we may note the important one [10], which served to elucidate the role of the local chemical potential.

Here we will consider chemical equilibria in an open system involving nonhydrostatically stressed solid phases, where the fluid pressure is controlled by an external buffer. In describing such a system it is usually assumed that the solid phases are under a hydrostatic pressure differing from the pressure of the liquid or gas (theory of systems with unequal pressures on the phases) [1, 3, 11, 12]. It is found that for uniaxial deformation of the solids, the equilibrium in such a system can be described in terms of two pressures and a temperature. However, the chemical-equilibrium conditions, and in particular the analog of the Clausius-Clapeyron equation, differ from those used in the theory of systems with unequal pressures on the phases. An important point is that the chemical equilibria are examined within the framework of the nonlinear theory of elasticity. This theory is necessary when the system is at a high pressure and the strains cannot be considered as infinitely small.

For convenience, we will give the basic logic scheme of the nonlinear theory of elasticity. The Gibbs approach will be used to consider general aspects of phase equilibrium involving nonhydrostatically stressed phases. A complete analysis will be performed for the mechanical and chemical equilibria for simple uniaxial deformation, and phenomenological equations of state will be given for isotropic media, which can be used in calculations of particular equilibria. Geochemical applications will also be discussed.

The general theory will be illustrated by an example that forms an independent section and which is logically closed.

#### INFORMATION FROM THE THEORY OF ELASTICITY

The theory of elasticity involves the fundamental assumption that the strain is reversible. In the classical theory, the strain is taken as infinitely small (geometrically linear theory) and linear relations (Hooke's law) are used to relate the stresses to the strains. To describe the large stresses and strains existing within the Earth we have to use the nonlinear theory, although we must bear in mind that the assumption that the strains are reversible has only limited application [3, 13-15]. In fact, a real medium has complicated rheology, and we may get plastic strains, microscopic failure etc. Nevertheless, we consider a simple elastic model in order to carry out a reasonably complete analysis\*\*. For any particular substance we can always indicate characteristic

---

\*Here we do not consider the coherent transformations in solid phases, for which this is evidently not so [3].

\*\*The mechanical properties of an elastic body are defined by means of a deformation-energy function, which is dependent only on the state of strain and is not dependent on the history of the deformation. Then the stresses form a conservative system and are not dependent on the history of the deformation or on the rate at which the deformation was performed or altered. This rules out a static or dynamic hysteresis, stress relaxation, and creep phenomena.

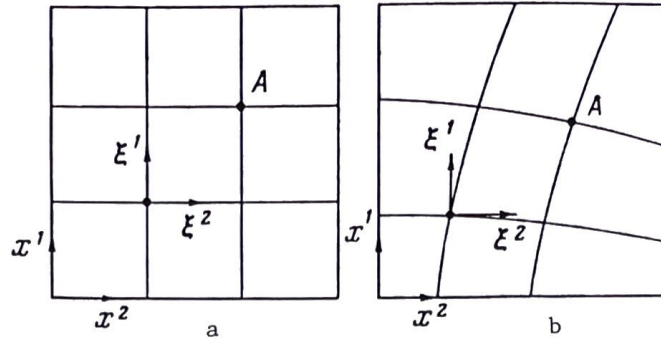


Fig. 1. Relation between Euler and Lagrange coordinates:

- a) material before deformation (reference state),  
 b) after deformation (actual state); the Lagrange coordinates of point A ( $\xi_1 = 1, \xi_2 = 1$ ) do not change, while the Euler coordinates of point A do change.

times and permissible degrees of deviation from the hydrostatic state for which such a description gives good agreement with experiment [3, 13]. For example, experiment shows that substances such as serpentine will withstand differential stresses up to some kilobars at 500-600° C.

Two coordinate systems are used in the theory of elasticity to describe deformations. The Lagrange coordinates  $\xi^\alpha$ ,  $\alpha = 1, 2, 3$ , are frozen into the medium and represent marks fixed once and for all for each infinitely small particle. The second coordinate system  $x_i$ ,  $i = 1, 2, 3$  (the Euler one) is rigidly fixed in space. For simplicity we assume that it is cartesian (Fig. 1).

The position of each point in the medium is known if the following functions are given:

$$x_i = x_i(\xi^1, \xi^2, \xi^3) = x_i(\xi),$$

which express the laws of motion for the points in the medium. The reference state is in general a deformed one:

$$x_{i0} = x_{i0}(\xi),$$

and therefore the resultant displacement from the reference state to the actual one takes the form

$$u_i = x_i(\xi) - x_{i0}(\xi).$$

If volume change is the measure of deformation for a liquid, shape change is also important for the solid. The deformation tensor is introduced by comparing infinitely small elements in the actual and reference states [13-15]:

$$\varepsilon_{\alpha\beta} = \frac{1}{2} (g_{\alpha\beta}(\xi) - g_{\alpha\beta}^0(\xi)),$$

where  $g_{\alpha\beta} = x_{i\alpha} x_{i\beta}$  is a metrical tensor in the actual configuration,  $x_{i\alpha} = \partial x_i / \partial \xi^\alpha$ ,  $g_{\alpha\beta}^0 = x_{i0\alpha} x_{i0\beta}$  is a metrical tensor in the reference configuration, and  $x_{i0\alpha} = \partial x_{i0} / \partial \xi^\alpha$  (as usual, summation is assumed with respect to the repeating subscripts). For definiteness, we assume that the Euler and Lagrange coordinate nets coincide in the reference state, i.e.,

$$g_{\alpha\beta} = \delta_{\alpha\beta} = \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix}.$$

The equation of continuity is equivalent to the geometrical definition of the density:

$$\frac{\rho_0}{\rho} = \det \left( \frac{\partial x_i}{\partial \xi^\alpha} \right),$$

where  $\rho_0$  is the density in the reference state and  $\rho$  is that in the actual one.

The analog of the hydrostatic pressure is the stress tensor  $P_{ij}$ . If  $F_i$  is the force acting on unit area with normal  $n_i$  in the actual configuration, then

$$F_i = P_{ij} n_j.$$

In the hydrostatic case, the tensor  $P_{ij}$  is spherical and the value of  $F_i$  is not dependent on the orientation of the area (Pascal's law).

It is assumed for the simple elastic medium that there is a specific internal energy  $u$  dependent on the components of the strain tensor  $\epsilon_{\alpha\beta}$  and the specific entropy  $s$  [2, 13-15]:

$$u = u(\epsilon_{\alpha\beta}, s).$$

Then

$$du = \frac{\partial u}{\partial \epsilon_{\alpha\beta}} d\epsilon_{\alpha\beta} + \frac{\partial u}{\partial s} ds, \quad (1)$$

and the generalization of the thermodynamic equations for pressure and temperature take the form

$$T = \frac{\partial u}{\partial s},$$

$$P_{ij} = \frac{1}{2} \rho x_{i\alpha} x_{j\beta} \left( \frac{\partial u}{\partial \epsilon_{\alpha\beta}} + \frac{\partial u}{\partial \epsilon_{\beta\alpha}} \right). \quad (2)$$

In the case of a liquid

$$u = u(\rho, s).$$

The standard formulas from tensor analysis give [13]

$$P_{ij} = -\rho x_{i\alpha} x_{j\beta} \frac{\partial u}{\partial \rho} \rho g^{\alpha\beta} = -\rho^2 \frac{\partial u}{\partial \rho} \delta_{ij} = \frac{\partial u}{\partial v} \delta_{ij} = -p \delta_{ij},$$

where  $v = 1/\rho$ ,  $p = -\partial u / \partial v$ ; the stress tensor is spherical and we arrive at the usual definition of the hydrostatic pressure in a liquid.

Thus basic definitions have been given for the state of strain, the strain tensor, and the stress tensor. No assumptions have been made about the smallness of the strains. The derivation of the equations in the theory of elasticity and the formulation of boundary-value problems can be found, for example, in [13-15].

#### CHEMICAL-EQUILIBRIUM CONDITIONS

In his classical study (p. 95 of [2]), Gibbs showed that the condition for phase equilibrium in a nonhydrostatically stressed solid in contact with a liquid amounts to continuity in the chemical potential of the solid material at

the interface. The solid phase is considered to consist of one component and the chemical potential at a given point on the surface is described by

$$\mu_s = f(\varepsilon_{\alpha\beta}, T) + p/\rho_s, \quad (3)$$

where  $f = u - Ts$  is the specific free energy of the solid phase,  $p$  is liquid pressure, and  $\rho_s$  is the density of the solid. Gibbs proposed a universal variational procedure for the static case for inferring the conditions of thermal, mechanical, and chemical equilibrium. In the latter case, we are concerned with equilibrium with respect to the passage of material from one phase to another, or in modern terms with variation of the phase boundary with respect to the Lagrange coordinates. Note that Gibbs in essence introduced a chemical-potential tensor [17, 18]:

$$\mu_{ik} = -\frac{1}{\rho} \frac{\partial(\rho f)}{\partial x_{i\alpha}} x_{k\alpha} = f\delta_{ik} - \frac{1}{\rho} P_{ik},$$

so the conditions for phase equilibrium at the interface are put as

$$\mu_s = \mu_{ik} n_i n_k = \mu_l,$$

where  $\mu_l$  is the chemical potential of the one-component liquid phase and  $n_i$  is the vector for unit normal to the interface. In the example considered by Gibbs, the equilibrium was that of a cube in contact with three liquids with pressures  $p_1, p_2$ , and  $p_3$ , and because the stress tensor is diagonal

$$P_{ij} = \begin{vmatrix} p_1 & 0 & 0 \\ 0 & p_2 & 0 \\ 0 & 0 & p_3 \end{vmatrix}$$

the chemical-potential one was also diagonal, with the expression  $\mu_{ik} n_i n_k$  dependent on the orientation of the normal (face choice). Gibbs' method has recently been applied to examining the equilibrium between two nonhydrostatically stressed solid phases, and this has shown that here the question of the equilibrium conditions is substantially more complicated [18].

The chemical potential for the material of the solid phase dissolved in the liquid, which in general consists of many components, can be put as

$$\mu_{s,l} = \mu_{s,l}(p, T, c_1, \dots, c_r),$$

where  $p$  and  $T$  are the pressure and temperature in the liquid and  $c_a, a=1, \dots, r$  are the mass concentrations of the components. Then the chemical-equilibrium conditions amount to

$$\mu_s = \mu_{s,l}. \quad (4)$$

The conditions for mechanical equilibrium at the interfaces\*

$$P_{ij} n_i = -p n_j$$

are the boundary conditions for the static problem in the theory of elasticity within the solid phase.

If the solid phase is in contact on some surface with a one-component liquid of the same composition, equilibrium is possible only if the chemical potential is the same in all points on the surface, and in particular if the strain is homogeneous. If the liquid has many components, we get an inhomogeneous concentration distribution in general along the interface, since the

---

\*Gibbs used a Piol-Kirchoff tensor  $\hat{P}_{.j}^\alpha$ , which is related to the Cauchy tensor  $P_{ij}$  by  $P_{ij} = (\rho/\rho_0) x_{i\alpha} \hat{P}_{.j}^\alpha$  so his conditions have a different form (p. 258 of [2]).

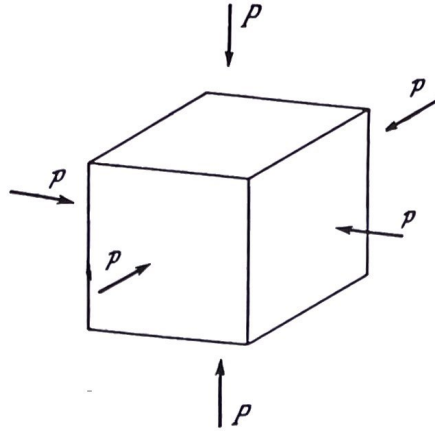


Fig. 2. Simple homogeneous state of stress characterized by two pressures  $P$  and  $p$ .

equilibrium concentration is dependent on the state of stress at a given point. Such a system is not an equilibrium one and dissolution continues until the chemical potential of the solid phase along the interface becomes equalized. Inhomogeneity in the state of stress results in chemical-potential gradients along the surface, which in turn gives rise to diffusion currents. Therefore, there is transfer of material from zones of high chemical potential to zones with lower ones, and in particular dissolution at the contacts between grains. Macroscopically this is seen as creep, which is limited by the dissolution rate.

Let us now write the expression for the differential of the solid-phase chemical potential. From (1) and (3) we have

$$d\mu_s = -s_s dT + v_s dp + \frac{1}{\rho_s} (P_{ij} + p\delta_{ij}) \xi_i^\alpha dx_{j\alpha},$$

where  $\xi_i^\alpha = \partial \xi^\alpha / \partial x_i$  is a matrix inverse to matrix  $x_{i\alpha}$ . In the hydrostatic case ( $P_{ij} = -p\delta_{ij}$ ), the latter term is absent and we arrive at a standard expression [1]. For the liquid phase

$$d\mu_{s,l} = -\bar{s}_{s,l} dT + \bar{v}_{s,l} dp + \frac{\partial \mu_{s,l}}{\partial c_a} dc_a,$$

where  $\bar{s}_{s,l}$ ,  $\bar{v}_{s,l}$  are the specific partial entropy and volume of the solid phase dissolved in the liquid. At equilibrium

$$d\mu_s = d\mu_{s,l}$$

or

$$0 = -(\bar{s}_{s,l} - s_s) dT + (\bar{v}_{s,l} - v_s) dp + \frac{\partial \mu_{s,l}}{\partial c_a} dc_a - v_s (P_{ij} + p\delta_{ij}) \xi_i^\alpha dx_{j\alpha}. \quad (5)$$

The latter relation, strictly speaking, is not an equation for displaced equilibrium, because the differentials in (5) are not independent. In fact, the quantities  $x_{i\alpha}$  that describe the deformation are dependent on the load supplied. To determine the independent factors in the chemical equilibrium we have to solve the thermoelastic problem relating to the mechanical and thermal equilibria of the solid phase and liquid subject to the additional condition (4) at the interface. The latter serves to define the position of the surface itself, which may move (on account of melting, dissolution, etc.). As an example we can quote the derivation of the form of a magmatic chamber if one assumes that

the corresponding boundary is a phase one. The shape of such a chamber is dependent on the state of stress in the surrounding rocks [19].

### CHEMICAL EQUILIBRIUM WITH UNIAXIAL DEFORMATION

The above general theory can be illustrated on the simple example, which is also of independent significance for applications. Let us consider uniaxial deformation of a crystal in the form of a rectangular parallelepiped (excess pressure along one of the axes). The crystal is compressed by a pressure  $P$  provided by a press along a pair of parallel faces. On the other four faces, the crystal is in contact with the liquid at a hydrostatic pressure  $p$  (Fig. 2). We assume that material can pass from one phase to the other through the side faces.

The crystal is specified by its dimensions  $a_{10}, a_{20}, a_{30}$  in the reference undeformed state, where it has the volume  $v_0 = a_{10}a_{20}a_{30}$  and the mass  $M = \rho_0 v_0 = 1$ ; we assume that the deformation is homogeneous and that the crystal has some symmetry not less than orthorhombic, with the coordinate axes coinciding with the crystallographic ones and the  $x_1$  axis forming the distinctive one (if there is such). Let the pressure  $P$  act on the faces perpendicular to the  $x_1$  axis. Then the deformation may be described by

$$\begin{aligned}x_1 &= x_1(x_{10}, x_{20}, x_{30}) = k_1 x_{10}, \\x_2 &= x_2(x_{10}, x_{20}, x_{30}) = k_2 x_{20}, \\x_3 &= x_3(x_{10}, x_{20}, x_{30}) = k_3 x_{30}, \\0 &\leq x_{i0} \leq a_{i0}, i=1, 2, 3,\end{aligned}$$

so the displacements take the form

$$u_i = x_i - x_{i0} = (k_i - 1)x_{i0}.$$

The coefficients  $k_i$  are dependent on  $P, p$  and temperature  $T$ . Only for an orthorhombic material do we have  $k_2 \neq k_3$ .

Crystal dimensions are different in the actual state:

$$a_1 = k_1 a_{10}, a_2 = k_2 a_{20}, a_3 = k_3 a_{30},$$

and the volume is  $v = a_1 a_2 a_3 = k_1 k_2 k_3 v_0$ ; the density in the actual state is given by

$$\rho = \frac{M}{v} = \frac{\rho_0 v_0}{v} = \frac{\rho_0}{k_1 k_2 k_3}. \quad (6)$$

Note that the density is determined by the product  $k_1 k_2 k_3$ , whereas the quantities  $k_i$  are not determined by the density.

The deformation measure is the tensor  $\epsilon_{\alpha\beta}$ , which in this case is diagonal:

$$\epsilon_{\alpha\beta} = \begin{vmatrix} \epsilon_{11} & 0 & 0 \\ 0 & \epsilon_{22} & 0 \\ 0 & 0 & \epsilon_{33} \end{vmatrix},$$

where

$$\begin{aligned}\epsilon_{11} &= \frac{1}{2} \frac{x_1^2 - x_{10}^2}{x_{10}^2} = \frac{1}{2} (k_1^2 - 1), \\ \epsilon_{22} &= \frac{1}{2} \frac{x_2^2 - x_{20}^2}{x_{20}^2} = \frac{1}{2} (k_2^2 - 1), \\ \epsilon_{33} &= \frac{1}{2} \frac{x_3^2 - x_{30}^2}{x_{30}^2} = \frac{1}{2} (k_3^2 - 1).\end{aligned}$$

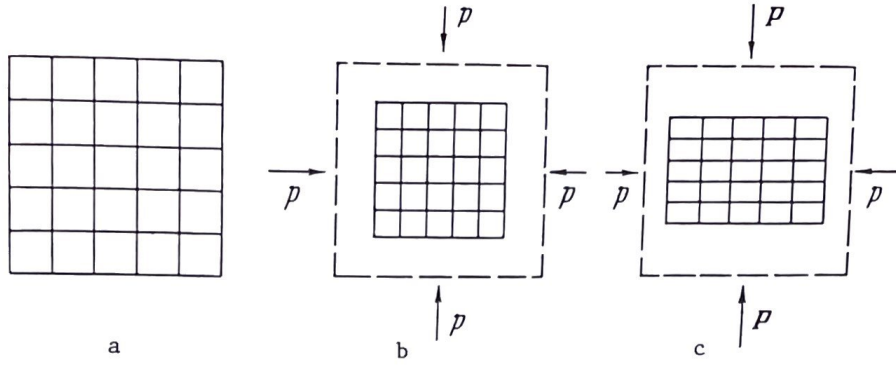


Fig. 3. Different forms of deformation for the cube:

- a) reference state, unstressed, b) state of hydrostatic compression,  
c) nonhydrostatic compression.

To determine the stress tensor we consider the specific Helmholtz free energy:

$$f(\varepsilon_{\alpha\beta}, T) = f(k_1, k_2, k_3, T),$$

$$df = \frac{\partial f}{\partial k_1} dk_1 + \frac{\partial f}{\partial k_2} dk_2 + \frac{\partial f}{\partial k_3} dk_3 + \frac{\partial f}{\partial T} dT. \quad (7)$$

From general formula (2) we get

$$P_{ij} = \begin{vmatrix} \frac{\rho_0}{k_2 k_3} \frac{\partial f}{\partial k_1} & 0 & 0 \\ 0 & \frac{\rho_0}{k_1 k_3} \frac{\partial f}{\partial k_2} & 0 \\ 0 & 0 & \frac{\rho_0}{k_1 k_2} \frac{\partial f}{\partial k_3} \end{vmatrix}.$$

We introduce the symbols

$$p_1 = -\frac{\rho_0}{k_2 k_3} \frac{\partial f}{\partial k_1}, \quad p_2 = -\frac{\rho_0}{k_1 k_3} \frac{\partial f}{\partial k_2}, \quad p_3 = -\frac{\rho_0}{k_1 k_2} \frac{\partial f}{\partial k_3}.$$

The meaning of these formulas is as follows. If we use (7) we can show that the force acting on a face perpendicular to the  $x_1$  axis with area  $a_2 a_3 = a_{20} a_{30} k_2 k_3$  is  $\partial f / \partial a_1 = 1/a_{10} (\partial f / \partial k_1)$ ; then the stress on that face (the pressure) is

$$p_{11} = \frac{1}{a_{20} a_{30} k_2 k_3} \cdot \frac{1}{a_{10}} \frac{\partial f}{\partial k_1} = \frac{1}{v_0 k_2 k_3} \frac{\partial f}{\partial k_1} = \frac{\rho_0}{k_2 k_3} \frac{\partial f}{\partial k_1}.$$

Because compressive stresses are negative, traditionally one uses nonnegative quantities instead of them, which are called pressures, for example  $p_1 = -p_{11}$ .

The expression for the stress tensor can be explained if we rewrite (7) on the basis of the definitions of  $p_1, p_2, p_3$ :

$$df = -\left[ p_1 \frac{k_2 k_3}{\rho_0} dk_1 + p_2 \frac{k_1 k_3}{\rho_0} dk_2 + p_3 \frac{k_1 k_2}{\rho_0} dk_3 \right] - s dT. \quad (8)$$

For fixed  $k_2$  and  $k_3$ , for example we have

$$df = -p_1 \frac{k_2 k_3}{\rho_0} dk_1 - s dT = -p_1 dv_1 - s dT,$$



where we have used (6). In the case of hydrostatic deformation of an isotropic material (Fig. 3)

$$P = p, k_1 = k_2 = k_3 = k.$$

If the free energy is given\* as a function of  $v$ ,

$$f(v, T) = f(k_1, k_2, k_3, T) = f(v_0 k^3, T),$$

we can use a standard thermodynamic formula to get

$$p = -\frac{\partial f}{\partial v} = -\frac{\partial f}{\partial k} \frac{\partial k}{\partial v} = -\frac{1}{3v_0 k^2} \frac{\partial f}{\partial k} = -\frac{\rho_0}{3k^2} \frac{\partial f}{\partial k}. \quad (9)$$

It is readily seen that (8) gives (9) if we put

$$p_1 = p_2 = p_3 = p; \quad k_1 = k_2 = k_3 = k.$$

To find the relationship between the strains and the applied loads, we have to solve a static problem in the theory of elasticity concerning the equilibrium of a parallelepiped. As the strain is homogeneous, it is sufficient to satisfy the boundary conditions, which amount to continuity of the normal stresses at the surfaces:

$$\begin{aligned} P &= p_1(k_1, k_2, k_3, T), \\ p &= p_2(k_1, k_2, k_3, T), \\ p &= p_3(k_1, k_2, k_3, T). \end{aligned} \quad (10)$$

Equations (10) inexplicitly define  $k_i = k_i(p, P, T)$ ,  $i = 1, 2, 3$ , which act as equations of state.

Let us write out the conditions for chemical equilibrium at the side surface of the crystal:

$$\mu_{s,i} = \mu_s = f(k_1, k_2, k_3, T) + p/\rho_s,$$

where  $\mu_s$  is the chemical potential of the solid phase, which is not dependent on the point at the surface because the strain is homogeneous. Expressing the  $k_i$  as a function of  $P, p$ , and  $T$ , we get

$$\begin{aligned} d\mu_s &= -\left[ s_s + \frac{\partial k_1}{\partial T} \frac{k_2 k_3}{\rho_0} (p - P) \right] dT + \\ &+ \left[ \frac{k_1 k_2 k_3}{\rho_0} + \frac{\partial k_1}{\partial p} \frac{k_2 k_3}{\rho_0} (p - P) \right] dp + \frac{\partial k_1}{\partial P} \frac{k_2 k_3}{\rho_0} (p - P) dP. \end{aligned} \quad (11)$$

If we consider the phase transition in a one-component system, then  $p$  and  $P$  are independent equilibrium factors, which is usually characterized by the term "unequal pressures on the phases." In that case

$$\mu_s(p, P, T) = \mu_{s,i}(p, T),$$

and the equilibrium temperature  $T$  is determined as a function of  $p$  and  $P$ . If the liquid is a solution of the solid phase, the equilibrium concentration  $c$  can be found from the condition for chemical equilibrium:

$$\mu_s(p, P, T) = \mu_{s,i}(p, T, c).$$

Here the independent equilibrium factors are  $p, P$ , and  $T$ . Gibbs showed [2] that this equilibrium is metastable with respect to the equilibrium between the liquid and the solid phase under hydrostatic pressure  $p$ , which results in the formation of nuclei of the solid phase in the liquid, which then grow.

---

\*Here the different functions are denoted by the single letter  $f$ .

The equation for the displaced equilibrium takes the form

$$\left[ \bar{s}_{s,l} - s_s + \frac{\partial k_1}{\partial T} \frac{k_2 k_3}{\rho_0} (p - P) \right] dT + \left[ \frac{k_1 k_2 k_3}{\rho_0} - \bar{v}_{s,l} + \frac{k_2 k_3}{\rho_0} \frac{\partial k_1}{\partial p} (p - P) \right] dp + \frac{k_2 k_3}{\rho_0} (p - P) \frac{\partial k_1}{\partial P} dP - \frac{\partial \mu_{s,l}}{\partial c} dc = 0. \quad (12)$$

Formula (12) shows that only three of the four quantities  $p$ ,  $P$ ,  $T$ , and  $c$  are independent in the equilibrium conditions.

If we fix  $P$  and  $c$ , we obtain an analog of the Clausius-Clapeyron equation:

$$\left. \frac{dp}{dT} \right|_{P,c} = \frac{\bar{s}_{s,l} - s_s + \frac{\partial k_1}{\partial T} \frac{k_2 k_3}{\rho_0} (p - P)}{\bar{v}_{s,l} - v_s - \frac{k_2 k_3}{\rho_0} \frac{\partial k_1}{\partial p} (p - P)}. \quad (13)$$

Clearly, in the hydrostatic case (13) amounts to the usual relation. For fixed values of the liquid pressure  $p$  and concentration  $c$  we get

$$\left. \frac{dT}{dP} \right|_{p,c} = \frac{\frac{k_2 k_3}{\rho_0} \frac{\partial k_1}{\partial P} (p - P)}{\bar{s}_{s,l} - s_s + \frac{k_2 k_3}{\rho_0} \frac{\partial k_1}{\partial T} (p - P)}. \quad (14)$$

Finally, for fixed  $T$  and  $c$

$$\left. \frac{dp}{dP} \right|_{T,c} = \frac{\frac{k_2 k_3}{\rho_0} \frac{\partial k_1}{\partial P} (p - P)}{\bar{v}_{s,l} - v_s - \frac{k_2 k_3}{\rho_0} \frac{\partial k_1}{\partial p} (p - P)}. \quad (15)$$

Equations (13)-(15) are exact within the framework of the elastic model and appear not to have been given before. They can be used to construct three-dimensional phase diagrams ( $c \equiv 1$ ) in  $p$ ,  $P$ , and  $T$  coordinates. The  $k_i = k_i(p, P, T)$  relations needed to construct the equilibrium diagrams are found from experiment. The function  $s_s$  is defined by

$$s_s = - \frac{\partial}{\partial T} f(k_1, k_2, k_3, T)$$

and can be derived by calorimetry. Note that the heat of the transformation

$$Q = T \Delta s = T (\bar{s}_{s,l} - s_s)$$

is substantially dependent on the state of strain.

Let us now calculate the change in chemical potential of the solid phase when the excess pressure  $P - p$  is applied along the  $x_1$  axis. Fixing  $p$  and  $T$  in (11), we get

$$d\mu_s = \frac{\partial k_1}{\partial P} \frac{k_2 k_3}{\rho_0} (p - P) dP.$$

Integration gives

$$\mu_s(p, P, T) = \mu_s(p, T) + \int_p^P \frac{\partial k_1}{\partial P} \frac{k_2 k_3}{\rho_0} (p - P) dP.$$

Here  $\mu_s(p, T)$  is the chemical potential of the solid phase under the hydrostatic pressure  $p$ , which can be calculated in the usual way [1, 11, 12]. Let us calculate the change in the equilibrium concentration in the solution when the differential stress  $P-p$  is applied. If we restrict ourselves to the ideal-solution approximation, we get

$$\Delta\mu = RT \ln \frac{c(p, P, T)}{c(p, T)}$$

or

$$c(p, P, T) = c(p, T) \exp \left[ \frac{1}{RT} \int_p^P \frac{k_2 k_3}{\rho_0} \frac{\partial k_1}{\partial P} (p - P) dP \right].$$

This scheme allows us to consider the chemical reactions between nonhydrostatically stressed solid phases involving the absorption or release of fluid.

We write the reaction equation

$$\sum_{s=1}^k A_s \nu_s = A_f,$$

where  $A_s$  is a symbol for the solid components,  $A_f$  is the fluid symbol, and  $\nu_s$  are the stoichiometric coefficients. Let the solid phases be in the identical state of strain that was described above. The reaction occurs through the fluid, and the chemical potentials of the solid components in the liquid are controlled by the equilibrium with the solid phase. Then the equilibrium condition takes the form

$$\sum_{s=1}^k \mu_s \nu_s = \mu_f,$$

where  $\mu_s$  are the chemical potentials of the solid phases, which are dependent on  $P$ ,  $p$ , and  $T$ , while  $\mu_f$  is the chemical potential of the fluid, which is dependent on  $p$  and  $T$ . This equation enables us to construct the equilibrium surface in  $p$ ,  $P$ , and  $T$  coordinates.

#### EQUATIONS OF STATE IN THE ISOTROPIC CASE

A knowledge of the thermodynamic potential as a function of its arguments gives complete thermodynamic information on the system [2]. In that case, the chemical and thermal equations of state can be derived. A fairly general form for these can be obtained from model concepts on the structure of matter (see for example, the potential method [20]). There is also a phenomenological method based on representing the free-energy function as a Taylor expansion with respect to some reference state. If the expansion is with respect to the strains, the coefficients (elastic moduli) are dependent on temperature and are determined by experiment. Examples of this type of expansion are Hooke's law [13], the Birch-Murnaghan formula [20-22], etc.

Let us consider a model for an isotropic material as used in effective description of polycrystalline materials. The reference state is the unstressed one at  $T = T_0$ . Then we can write out an expression for the specific free energy that contains cubic terms based on the strains (a Murnaghan body [15, 22]),

$$\rho_0 f = -\pi I_1 + \frac{1}{2}(\lambda + 2\mu) I_1^2 - 2\mu I_2 + \frac{l+2m}{3} I_1^3 - 2m I_1 I_2 + n I_3 + \rho_0 f_0, \quad (16)$$

where

$$I_1 = \varepsilon_1 + \varepsilon_2 + \varepsilon_3, \quad I_2 = \varepsilon_1 \varepsilon_2 + \varepsilon_1 \varepsilon_3 + \varepsilon_2 \varepsilon_3, \quad I_3 = \varepsilon_1 \varepsilon_2 \varepsilon_3$$

are invariants of the deformation tensor and

$$\varepsilon_1 = \varepsilon_{11} = \frac{1}{2}(k_1^2 - 1), \quad \varepsilon_2 = \varepsilon_{22} = \frac{1}{2}(k_2^2 - 1), \quad \varepsilon_3 = \varepsilon_{33} = \frac{1}{2}(k_3^2 - 1)$$

are the nonzero components of this. This choice of coefficients (first-order and second-order moduli) is traditional and is related to convenience in writing the dependence of the stresses on the strains. The coefficient  $\pi$ ,  $\pi(T_0) = 0$ , defines the thermal expansion at constant pressure, while  $\lambda$  and  $\mu$  are the isothermal Lamé moduli, and  $l$ ,  $m$ , and  $n$  are the isothermal second-order elastic moduli, which may be determined by experiments in nonlinear acoustics [15], and  $f_0$  is a nonmechanical term related to the energy in the undeformed state.

For a hydrostatically loaded isotropic body, we get the second-order equation of state in the Lagrange representation [21]:

$$p = -\frac{\partial f}{\partial v} = \frac{3}{2} K_0 (y^{1/3} - y^{-1/3}) \left[ 1 - \frac{3}{4} K'_0 (y^{1/3} - 1) \right] + \pi y^{1/3},$$

where

$$y = \rho/\rho_0, \quad K_0 = \lambda + \frac{2}{3} \mu, \quad K'_0 = -\frac{2}{3} \frac{9l + n}{3\lambda + 2\mu},$$

$$\varepsilon_1 = \varepsilon_2 = \varepsilon_3 = \frac{1}{2} (y^{1/3} - 1).$$

The following additional simplified assumptions are made in the physically linear theory of elasticity:

$$l = m = n = 0. \quad (17)$$

If we assume that there is a temperature change accompanying the strain, we get

$$\pi = \left( \lambda + \frac{2}{3} \mu \right) \alpha (T - T_0),$$

$$\alpha = \alpha(T_0), \quad \lambda = \lambda(T_0), \quad \mu = \mu(T_0), \quad (18)$$

where  $\alpha$  is the thermal-expansion coefficient. Let us substitute (17) and (18) into (16) and then use (10) on the basis that  $k_2 = k_3 = k$  for an isotropic material, to get that

$$P = -\frac{k_1}{k^2} \left[ \frac{\lambda + 2\mu}{2} k_1^2 + \lambda k^2 - \frac{3\lambda + 2\mu}{2} \left( 1 + \frac{2}{3} \alpha (T - T_0) \right) \right]$$

$$p = -\frac{1}{k_1} \left[ \frac{\lambda}{2} k_1^3 + (\lambda + \mu) k^2 - \frac{3\lambda + 2\mu}{2} \left( 1 + \frac{2}{3} \alpha (T - T_0) \right) \right]. \quad (19)$$

Therefore, we have derived mechanical equations of state within this approximation. To construct the phase diagrams, it is necessary to express the deformations  $k_1$  and  $k$  in (19) in terms of the stresses  $p$  and  $P$  and the temperature in the form

$$k = k(p, P, T), \quad k_1 = k_1(p, P, T). \quad (20)$$

Let us consider the case of small strains, i.e., the approximation usually employed in the classical theory of elasticity; let

$$k = 1 + \varepsilon, \quad k_1 = 1 + \varepsilon_1,$$

where  $\varepsilon$  and  $\varepsilon_1$  are small quantities. We neglect terms quadratic in the strains to get

$$P = -[\lambda\varepsilon_1 + 2(\lambda + \mu)\varepsilon] + \left(\lambda + \frac{2}{3}\mu\right)\alpha(T - T_0),$$

$$p = -[(\lambda + 2\mu)\varepsilon_1 + 2\lambda\varepsilon] + \left(\lambda + \frac{2}{3}\mu\right)\alpha(T - T_0).$$

These linear relationships are readily inverted:

$$\varepsilon_1 = \frac{1}{E}[2\sigma p - P] + \frac{\alpha}{3}(T - T_0),$$

$$\varepsilon = \frac{1}{E}[\sigma(p + P) - p] + \frac{\alpha}{3}(T - T_0),$$

where we have introduced by symbols

$$E = \frac{\mu(3\lambda + 2\mu)}{\lambda + \mu} \text{ — Young's modulus,}$$

$$\sigma = \frac{\lambda}{2(\lambda + \mu)} \text{ — Poisson's ratio.}$$

Similar formulas can be derived for a material with any crystallographic symmetry. The number of elastic moduli increases as the symmetry is reduced [14].

#### DISCUSSION

We are going to perform a qualitative analysis of (13)-(15). In the system where the independent parameters are pressure and temperature, we can construct the phase-equilibrium curves in the plane of  $p$  and  $T$  by means of the Clausius-Clapeyron equation:

$$\frac{dp}{dT} = \frac{\Delta s}{\Delta v}, \quad (21)$$

where  $\Delta s$  is the entropy change as a result of the transformation at given  $p$  and  $T$ ,  $\Delta v$  is the corresponding volume change, and  $dp/dT$  is the slope of the equilibrium curve at the point with coordinates  $p$  and  $T$ . The appearance of an additional equilibrium factor that is independent of the intensive parameter  $P$  increases the dimensions of the phase diagram by one, so the equilibrium curves are replaced by equilibrium surfaces. We now need a minimum of two equations of the type of (21) to construct the phase surface, e.g., (13) and (14).

Let us consider the physical significance of the expressions on the right in (13) and (14). It is readily seen that under hydrostatic conditions ( $p=P$ ) we get the usual Clausius-Clapeyron equation from (13), whereas (14) does not occur. There is an additional term in the numerator in (13), which is proportional to  $dk_i/dT$ , which is related to the thermal expansion and which is usually small for a real rock. Let us recall that the entropy of the solid phase is dependent on the state of strain, so that

$$T[\bar{s}_{,j}(p, T) - s_s(p, P, T)] = \Delta Q(p, P, T)$$

differs from its hydrostatic analog

$$T[\bar{s}_{,j}(p, T) - s_s(p, T)] = \Delta Q(p, T).$$

The denominator on the right in (13) is supplemented by an expression proportional to  $dk_i/dp$ , which is related to the longitudinal strains arising on applying the transverse load (pressure  $p$ ). This curve arises because a solid phase can withstand a shearing stress.

Particular interest attaches to (14), which related the equilibrium temperature and the equilibrium excess pressure on the solid phase. The main

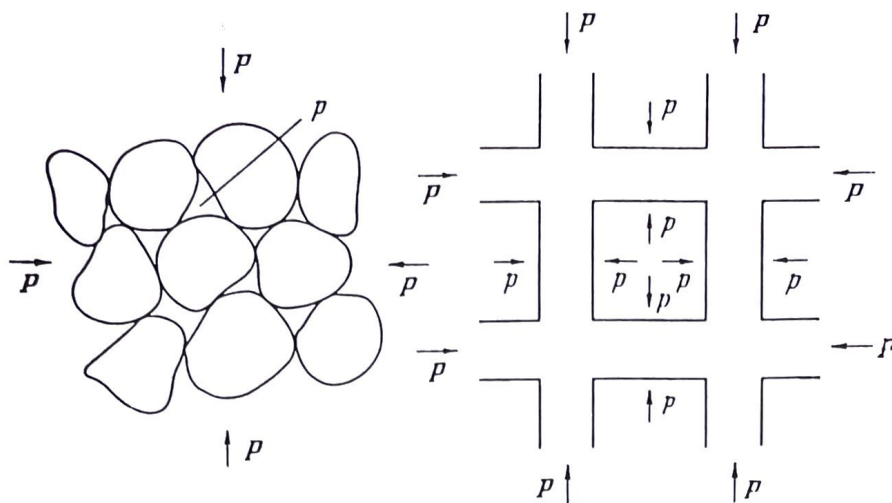


Fig. 4. Model for the structure of a porous medium with unequal pressures on the phases (three-dimensional framework).

effect, namely shift in the equilibrium temperature, is determined by  $dk_i/dP$ , i.e., the dependence of the longitudinal compression on the longitudinal stress.

In the theory of systems with unequal pressures on the phases, the numerator in the analogous expression contains the specific volume of the solid phase, which produces a systematic increase in the magnitude of the effect produced by the excess pressure on the solid phases. In that theory it is assumed that the solid phases involved in the reaction are under a high hydrostatic pressure  $P$ , which produces a considerable increase in the chemical potential. Let us note, however, that we are considering an ideal experiment, analyzing an extremely special homogeneous state of deformation. More complicated states may occur in real systems, and the theory of systems with unequal pressures on the phases evidently provides upper bounds to the corresponding effects. On the other hand, calculations within the framework of the linear theory of elasticity give lower bounds. Ostapenko has previously pointed this out [3, 23] and has emphasized the need to consider dehydration, melting, and dissolution taking into account the different pressures at the grain boundaries, and he carried through the corresponding analysis within the approximation of the linear theory of elasticity, which applies for small values of  $P - p$ .

#### CONCLUSIONS

There are numerous lines of evidence that nonhydrostatic conditions occur within the Earth [3]. This means that we need to reconsider the chemical and phase equilibria in such systems.

Reactions involving a fluid capable of free migration require us to consider them on the basis that there are different pressures in the liquid and on the solid phases. The approach in the theory of systems with unequal pressures on the phases [1, 3] involves the assumption that the phases are in a state of hydrostatic stress. The condition for mechanical equilibrium, which amounts to equality of the normal stresses at the phase interfaces, is no longer obeyed. A specific feature of solid phases, namely that they can withstand hydrostatic loads, thus is usually ignored.

Here we have performed a general analysis for heterogeneous equilibria in a nonhydrostatically stressed system involving a fluid within the framework of the nonlinear theory of elasticity. It has been found that excess pressure on the solid phases displaces the equilibrium and alters the heat of the chemical transformation.

The formulas that have been obtained can be used to examine metamorphic reactions when the pressure on the solid phases and the fluid pressure are independent equilibrium factors. The presence of an additional intensive parameter substantially complicates the phase diagrams by increasing the number of dimensions.

The following are possible areas of application of these results: 1) analysis of reactions involving the release or absorption of a volatile component under nonhydrostatic conditions, 2) research on partial melting when the system is open for the melt and the pressure in it differs from the pressure of the solid phases, and 3) analysis of mineral recrystallization processes when the nonhydrostatic state of strain produces metastability.

The simple states of strain considered here can be used as components in more complicated systems. For example, an average description can be given of a rigid framework immersed in a liquid and subject to lithostatic pressure by considering units in a state of uniaxial compression (Fig. 4).

In order to calculate equilibria in nonhydrostatic conditions, we need experimental information on the equations of state, which does not amount to  $p$ - $v$  data, and calorimetric results. The need for such experiments was long ago discussed in the literature [3]. At high pressures, for example, the corresponding data can be obtained from x-ray analysis of the lattice deformations in single crystals in given stress fields [24].

The lack of reliable experimental information is at present the main obstacle to calculations of particular equilibria.

We are indebted to N.I. Khitarov and V.P. Myasnikov for a valuable discussion.

#### REFERENCES

1. Akopyan, A.A., 1963. *Khimicheskaya termodinamika* [Chemical Thermodynamics], Vysshaya Shkola, Moscow, 523 pp.
2. Gibbs, J.W., 1950. *Thermodynamic Papers*, translated from English and edited by V.K. Semenchenko [Russian translation], Gostekhteorizdat, Moscow and Leningrad, 415 pp.
3. Ostapenko, G.T., 1977. *Termodinamika negidrostaticheskikh sistem i yeye primeneniye v teorii metamorfizma* [Thermodynamics of Nonhydrostatic Systems and Its Application to the Theory of Metamorphism], Naukova Dumka, Kiev, 240 pp.
4. Kamb, W.B., 1961. The Thermodynamic Theory of Nonhydrostatically Stressed Solids, *J. Geophys. Res.*, v. 66, 259.
5. McLellan, A.G., 1966. A Thermodynamical Theory of Systems under Nonhydrostatic Stress, *J. Geophys. Res.*, v. 71, 4341.
6. Ida, Y., 1969. Thermodynamic Theory of Nonhydrostatically Stressed Solid Involving Finite Strain, *J. Geophys. Res.*, v. 74, 3208.
7. Green, H., 1980. On the Thermodynamics of Nonhydrostatically Stressed Solids, *Phil. Mag. A*, v. 41, No. 5, 637.
8. Paterson, M.S., 1973. Nonhydrostatic Thermodynamics and Its Geologic Applications, *Rev. Geophys. and Space Phys.*, v. 11, No. 2, 355.
9. Kumazawa, M., 1961. A Note on the Thermodynamic Theory of Nonhydrostatically Stressed Solids, *J. Geophys. Res.*, v. 66, No. 11, 3823.
10. Ostapenko, G.T., A.N. Kovalevskiy, and N.I. Khitarov, 1972. Eksperimental'naya proverka teorii "absolyutnogo" khimicheskogo potentsiala negidrostaticheskoi napryazhennogo tverdogo tela [An Experimental Test of the Theory of Absolute Chemical Potential for a Nonhydrostatically Stressed Solid], *Dokl. AN SSSR*, v. 203, No. 2, 376.
11. Kuskov, O.L. and N.I. Khitarov, 1978. *Termodinamicheskaya kharakteristika prirody metallizatsii okislov pod davleniyem* [Thermodynamic Characterization of the Nature of Oxide Metallization under Pressure], *Pis'ma v ZhETF*, v. 27, 288.
12. Kuskov, O.L., and N.I. Khitarov, 1980. The Possible Nature of Reported Insulator-to-Metal Transitions in Oxides under High Pressure, High Temp.-High Pressure, v. 12, 61.

- 1/2 50g
13. Sedov, L.I., 1976. Mekhanika sploshnoy sredy. T. 2 [Mechanics of Continuous Media, Vol. 2], Nauka, Moscow, 574 pp.
  14. Green, A. and J. Adkins, 1965. Large Elastic Deformations and the Nonlinear Mechanics of Continuous Media, translated from English by Yu.V. Nemirovskiy and edited by Yu.N. Rabotnov [Russian translation], Mir, Moscow, 455 pp.
  15. Lur'ye, A.I., 1980. Nelineynaya teoriya uprugosti [The Nonlinear Theory of Elasticity], Nauka, Moscow, 509 pp.
  16. Raleigh, C.B. and M.C. Paterson, 1965. Experimental Deformation of Serpentine and Its Tectonic Implications, J. Geophys. Res., v. 70, No. 15, 3965.
  17. Bowen, R.M., 1976. Theory of Mixtures. In: Continuum Physics, edited by A.C. Eringen, Academic Press, Vol. 3.
  18. Grinfel'd, M.A., 1981. O dvukh tipakh geterogennykh fazovykh ravnovesiy [Two Types of Heterogeneous Phase Equilibrium], Dokl. AN SSSR, v. 258, No. 3, 567.
  19. Yoder, H., 1979. Basalt Magma Formation [Russian translation], Mir, Moscow, 237 pp.
  20. Zharkov, V.N. and V.A. Kalinin, 1968. Uravneniya sostoyaniya tverdykh tel pri vysokikh davleniyakh i temperaturakh [Equations of State for Solids at High Temperatures and Pressures], Nauka, Moscow, 312 pp.
  21. Thomsen, L., 1970. On the Fourth-Anharmonic Equation of State of Solids, J. Phys. Chem. Solids, v. 31, 2003.
  22. Murnaghan, F.D., 1951. Finite Deformation of an Elastic Solid, John Wiley and Sons, 140 pp.
  23. Ostapenko, G.T., 1979. Termodinamika protsessov metamorfizma pri negidrosticheski napryazhennom sostoyanii mineralov [Thermodynamics of the Processes of Metamorphism with Nonhydrostatically Stressed Minerals: D. Sc. Thesis], IGFM AN SSSR, Kiev, 56 pp.
  24. Kinsland, G. and W. Basset, 1977. Strength of MgO and NaCl Polycrystals to Confining Pressures of 250 kbar at 25° C, J. Appl. Phys., v. 48, 978.

Received for publication July 23, 1981