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THERMODYNAMICS OF SOLIDS UNDER NON-HYDROSTATIC STRESS WITH GEOLOGIC APPLICATIONS

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ABSTRACT. Using the methods of Gibbs, the general thermodynamics of elastic solids is developed. A phase under a non-hydrostatic stress defined by three principal pressures is unstable relative to the same phase under an equal hydrostatic pressure. The equation for the surface of equilibrium between two polymorphs in a one-component system in a general stress field is shown to contain terms involving the differences in the principal pressures acting on the solid. These terms will be small relative to the change in entropy and volume for first order transitions, such as andalusite to kyanite, and for stress differences of a few thousand bars.

It is shown that the anisotropic elastic properties of minerals *may* be important in the formation of an oriented fabric provided that the mechanism of deformation is one of solution and redeposition. If the mineral deforms by some mechanism of mechanical flow (twin gliding, etc.) then the orientation of the mineral results from the detailed mechanism of the mechanical deformation. In general, the driving potential in plastic flow is the difference in chemical potential between that part of the crystal at high pressure and that part at low pressure.

INTRODUCTION

The physical appearance of rocks from areas of regional metamorphism indicates that such rocks have in many cases undergone deformation beyond the elastic limit, and this deformation has taken the form of a plastic flow of the rock. A necessary condition for plastic flow to take place is that the rock be under a non-hydrostatic stress. The question then arises as to what is the influence of the non-hydrostatic pressure on the recrystallization of the rock; in particular, what will be the effect of non-hydrostatic pressure on the equilibrium mineral assemblage and how will the non-hydrostatic pressure influence the orientation of the crystallizing minerals. In discussing the role of non-hydrostatic stress in metamorphism, two aspects of the problem should be kept clearly separate. Non-hydrostatic stress may be expected to influence the equilibrium assemblage and also the rate at which equilibrium is attained. In the following we will investigate the time-independent effects of non-hydrostatic stress, omitting the much more difficult problem of the influence of stress on the rate of reaction.

The possible effect of a non-hydrostatic stress on the stability of various minerals has given rise to much controversy. Harker (1939) clearly states the geologic evidence for the effect of non-hydrostatic stress on mineral assemblages. Harker asserts that certain minerals are commonly found in rocks that have structures indicating non-hydrostatic conditions of crystallization, and are not found in rocks not showing such structures. Harker labels these minerals "stress minerals", while minerals not found in rocks showing structures attributed to non-hydrostatic stress are termed "anti-stress" minerals. Kyanite, staurolite and almandine are examples of "stress minerals", while andalusite, leucite and nepheline are considered to be "anti-stress minerals". In recent years various specific examples have been cited as exceptions to the association of "stress minerals" with flow structure (Miyashiro, 1949).

The geologic evidence on the existence of "stress minerals" is somewhat uncertain, and current theoretical treatments leave much to be desired. Bridgman (1936) states that there is no thermodynamic reason why transitions should not occur under non-hydrostatic stress which would never occur under any combination of temperature and hydrostatic stress. Verhoogen (1951) in a treatment of the chemical potential of a stressed solid, states that the effect of shear on chemical equilibrium appears to be small. However, there are inconsistencies in Verhoogen's treatment. Indeed, various attempts to interpret or extend Gibbs' (1906) analysis of the thermodynamics of elastic bodies are not completely correct. Verhoogen points out such inconsistencies in Goranson (1930) and Rice (1936).

The present paper deals with the thermodynamics of elastic bodies and in doing so, follows Gibbs' treatment closely. Gibbs gives a masterful treatment of elasticity, a treatment that has been uniformly neglected by workers in elastic theory. An example of this neglect is that Gibbs is not mentioned once in Love's (1945) classic treatise on elasticity. On the basis of the present analysis of the thermodynamics of elastic bodies, the effect of non-hydrostatic stress on mineral equilibrium is considered and an attempt is made to state the problem of the orientation of anisotropic minerals in a stress field.

THERMODYNAMICS OF ELASTIC BODIES

In treating the thermodynamics of elastic bodies we will consider a special case that illustrates the main features of the thermodynamics of solids under a non-hydrostatic stress. By considering this special case we find the mathematics is simplified and the physics of the problem is emphasized. The generalization of the results will be indicated but not treated in detail.

Consider one mole of a solid in the form of a rectangular parallelepiped. The edge lengths of the parallelepiped in the state of initial strain are X_1^0, X_2^0, X_3^0. Due to forces f_1, f_2, f_3 acting perpendicular to the pairs of faces 1, 2 and 3, the parellelepiped is deformed to another parallelepiped with edges X_1, X_2, X_3, as is illustrated in figure 1. The deformation in each direction is assumed to be uniform, so that the position of a fixed point (x_1, x_2, x_3) in the strained solid is related to a point (x_1^0, x_2^0, x_3^0) in the stage of initial strain by the relations

$$x_i = \frac{x_i^0 X_i}{X_i^0} \qquad (i = 1, 2, 3)$$

We are thus assuming that the solid is undergoing a pure homogeneous strain with lines parallel to one of the three principal directions in the solid remaining unchanged in the strained state.

The first and second laws of thermodynamics can be combined in the form

$$dU = TdS + dW$$

where U is the internal energy per mole, S is the entropy per mole, and dW is the work done on the system. The system we are considering is the solid in the form of a parallelepiped. The work done on the system by the external forces f_1, f_2, f_3 will be the sum of the products of the various forces and the distance over which they act.

$$dW = f_1dX_1 + f_2dX_2 + f_3dX_3$$

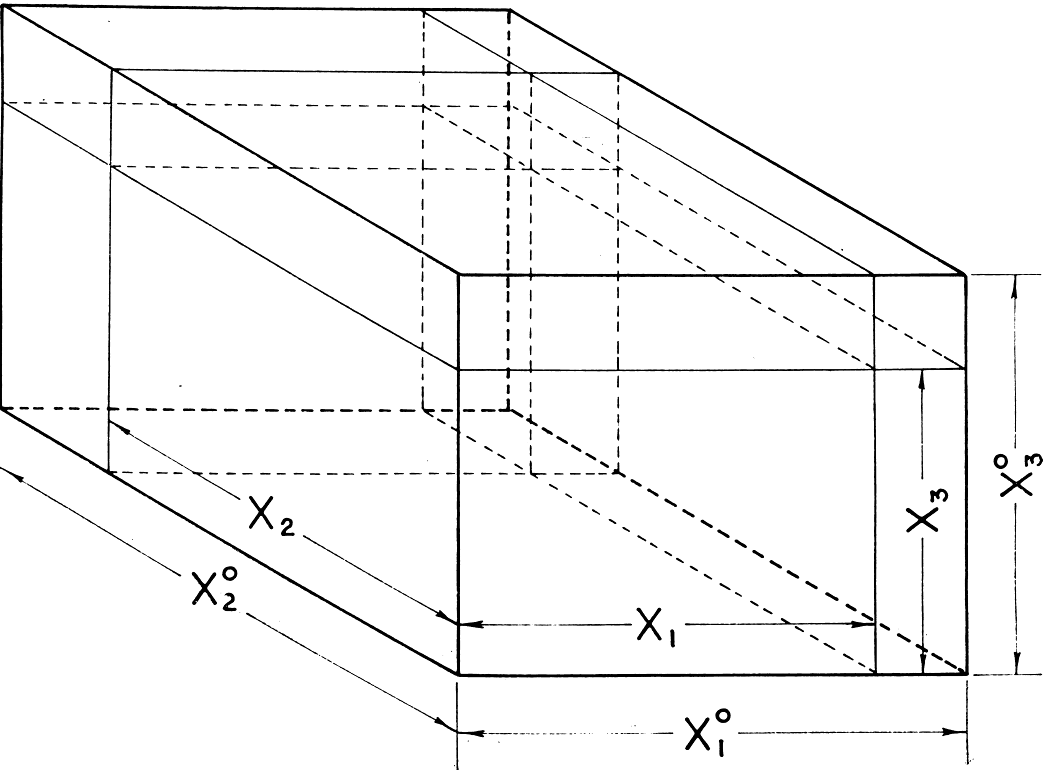

Fig. 1. Pure homogenous deformation of a parallelepiped having edge lengths X_1^0, X_2^0 and X_3^0 in state of initial strain.

By changing variables in the expression for internal energy from entropy to temperature we obtain the expression for the Helmholtz free energy of the strained solid.

$$dF = \sum_{i=1}^{3} f_i dX_i - SdT$$

This expression reduces to the more familiar form

$$dF = -SdT - PdV$$

where V is the molar volume, when the solid is under a uniform hydrostatic pressure P. In this case the forces acting on any face will be equal to the negative product of the pressure and the area of the face,

$$f_1 = -PX_2X_3 \qquad f_2 = -PX_1X_3 \qquad f_3 = -PX_1X_2$$

$$V = X_1X_2X_3$$

$$dV = X_2X_3dX_1 + X_1X_3dX_2 + X_1X_2dX_3$$

$$\sum_{i=1}^{3} f_i dX_i = -PdV$$

where X_1, X_2 and X_3 are the edge lengths at any stage of the deformation.

We now consider the condition for equilibrium of a strained solid. The condition for thermal equilibrium requires that the temperature be uniform throughout the solid. The condition of mechanical equilibrium requires that the surfaces bounding the solid be stationary; that is, that the forces acting on each of the six faces be exactly balanced by the internal forces of the solid. In general the forces acting on the solid can be specified by indicating the three principal pressures acting on the pairs of opposing faces of the solid.

We can denote these three principal pressures by P_1, P_2 and P_3 where

$$P_1 = -f_1/X_2X_3 \qquad P_2 = -f_2/X_1X_3 \qquad P_3 = -f_3/X_1X_2$$

The condition for equilibrium with respect to diffusion may not be so obvious, and to demonstrate these conditions we follow Gibbs and imagine the solid to be bounded by a fluid, where the fluid acting on the faces perpendicular to the edge X_1, is at a pressure P_1, the fluid acting on the faces perpendicular to edge X_2 is at a pressure P_2, and the fluid acting on the faces perpendicular to X_3 is at a pressure P_3. Since the fluids are at different pressures, this requires that the fluids acting on the various faces be separated by rigid impermeable membranes. Now we need the conditions for equilibrium of the solid with respect to solution of the solid in the fluid with which it is in contact. For simplicity we assume that the solid can be treated as a one-component system. The Helmholtz free energy of the solid is simply

$$dF = \sum_{i=1}^{3} \mu_i dn_i$$

Now consider the system composed of the solid under a non-hydrostatic stress system and the fluid in contact with the solid across the faces perpendicular to edge X_1. The fluid is at a pressure P_1. The Helmholtz free energy of the system solid plus fluid is given by

$$dF = dF^s + dF^f$$

where dF^f for the fluid at constant volume and temperature is given by

$$dF^f = \sum_{i=1}^{n} \bar{\mu}_1{}' d\bar{n}_1{}'$$

where $\bar{\mu}_1{}^j$ is the chemical potential of the ith component of the fluid at pressure P_1

$$dF = \mu_1{}^s dn_1{}^s + \Sigma\bar{\mu}' d\bar{n}' \qquad dn_2 = dn_3 = 0$$

The system fluid plus solid is at equilibrium when the Helmholtz free energy is at a minimum. The subsidiary condition on this minimum is that the total mass of each component be a constant. The system of fluid plus solid is a closed system since the membranes between the fluids are impermeable. Since the solid is a one-component system, the conditions for a closed system can be written as

$$dn_1{}^s + d\bar{n} = 0$$

where $dn_1{}^s$ is the number of moles of the component of the solid going into solution across faces perpendicular to X_1. Using the method of Lagrange multipliers, the condition for the Helmholtz free energy to be a minimum is then that

$$\mu_1{}^s = \bar{\mu} = \mu$$

The condition for equilibrium with respect to solution of the solid in the fluid acting on the face perpendicular to X_1, is that the chemical potential of the component of the solid in the fluid be equal to the chemical potential of the component along the surface of the solid.

Similarly, the condition for equilibrium across surfaces in contact with fluid is that the chemical potential of the component be equal in the two phases in contact. In general the three pairs of faces will be at different pressures, so the chemical potentials of the component of the solid will be different in the three fluids. This means that the chemical potential of the component of the solid will in general have three different values corresponding to the three pairs of faces under the three principal pressures. This important result was obtained by Gibbs (1906, p. 196) and emphasized by him in his subsequent discussion. Verhoogen (1951) quotes this result but proceeds to consider the chemical potential as uniform throughout the solid.

Perhaps the best experimental evidence that Gibbs is correct in his deduction that the chemical potential varies from face to face of a stressed solid, can be found in the behavior of stressed ice. Pressure tends to decrease the melting point of ice, since the volume of the water at low pressures is less than the volume of ice. If two cubes of ice at 0° C. are pressed together, the ice will melt along the surface of contact between the cubes. If the chemical potential of the ice were uniform over the entire surface, the cubes should melt uniformly over their surface and not just at the surface where the pressure is greatest.

In deriving the conditions for diffusion equilibrium we assumed the solid to be in equilibrium with a fluid. The chemical potential of the component of the solid, of course, does not depend on the presence of the fluid. The chemical potential is still defined regardless of whether a fluid or another solid is acting upon the system and producing the non-hydrostatic pressure.

We now examine how we might express a quantity analogous to the Gibbs free energy of the solid. If we subtract

$$d(f_1X_1 + f_2X_2 + f_3X_3)$$

from both sides of

$$dF = -SdT + \sum_{i=1}^{3} f_i dX_i$$

we obtain

$$dG = -SdT - \sum_{i=1}^{3} X_i df_i$$

where G is given by

$$G = F - \sum_{i=1}^{3} f_i X_i$$

and F is the Helmholtz free energy per mole of the solid. The function G defined in this way reduces to the familiar form of the Gibbs free energy for a hydrostatic pressure, provided we set

$$dP = \frac{dP_1 + dP_2 + dP_3}{3}$$

and

$$df_1 = -X_2X_3dP_1$$
$$df_2 = -X_1X_3dP_2$$
$$df_3 = -X_1X_2dP_3$$

as we then have

$$dG = -SdT + VdP$$

We thus have to introduce a factor of 1/3 in our expression for G in order to have it reduced to the ordinary Gibbs free energy. The factor of 1/3 enters since we are defining an average Gibbs free energy for the solid as a whole, the chemical potential of the solid having three principal values. The average Gibbs free energy for the solid with three principal pressures can be written as

$$dG = -SdT - 1/3 \sum_{i=1}^{3} X_i df_i$$

In the case of a solid under a general non-hydrostatic stress, the average Gibbs free energy can be written as

$$dG = -SdT - V_o \sum_i \sum_j \left(\frac{\delta ij}{3} + \varepsilon_{ij} d\sigma_{ij} \right)$$

where V_o is the initial volume of the solid, ε_{ij} the strain tensor, σ_{ij} the stress tensor, and δ_{ij}, Kronecker delta. It should be emphasized that this is the average Gibbs free energy for the solid. In considering phase equilibrium we will have to examine how the chemical potential varies over the surface of a solid.

GEOLOGIC PROBLEMS

We now consider how the above formulation of thermodynamics of elastic solids can be used to solve specific geologic problems. We first examine the stability of a solid under a non-hydrostatic stress with reference to a solid under hydrostatic stress. This problem was originally treated by Gibbs and as it forms the basis for our discussion of various other problems, we will treat it in detail. Consider a solid in the form of a rectangular parallelepiped under a hydrostatic pressure P_x. The chemical potential, μ_x, of the component of the solid will then be given by

$$\mu_x{}^* = PV^* + U^* - TS^*$$

where V^*, U^* and S^* are the volume, internal energy and entropy per mole of the solid. Now, keeping the pressure constant on the faces perpendicular to the edge X_1, and keeping the temperature constant, change the pressures acting on the faces perpendicular to X_2 and X_3 to P_2 and P_3, where in general $P_2 \neq P_3$, $P_3 \neq P_1$. This situation is illustrated diagrammatically in figure 2. Solid A^0 with edge lengths $X_1{}^0$, $X_2{}^0$ and $X_3{}^0$ represents the solid in the initial state of strain at a hydrostatic pressure P_1. Solid A represents the solid with the pressures P_2 and P_3 acting on the faces normal to X_2 and X_3, where in general P_2 and P_3 are not equal to P_1. In changing the pressures we will do work on the solid and will in general alter the internal energy, volume and entropy of the solid. The chemical potential of the component of the solid along the faces acted on by the constant pressure P_1 will be given by

$$\mu_1 = P_1V + U - TS$$

where in general V, U and S are not the same as for the solid under a hydrostatic pressure. The chemical potential along the face at pressure P_1 in the non-hydrostatically stressed solid differs from that of the hydrostatically stressed solid by

$$\mu_1 - \mu_1^* = P_1(V - V^*) + (U - U^*) - T(S - S^*)$$

The last two terms represent the work done on the solid in straining it, since by the first and second law we have that

$$W = \Delta U - T\Delta S$$

The term $P_1(V - V^*)$ represents the work done by the solid in displacing the fluid. The work done on the solid will always be positive and by the second law will always be greater than or equal to the work done by the solid on the fluid. The work done on the fluid by the solid will equal the work done on the solid only in the case of a hydrostatic pressure. Since for non-hydrostatic stress, the work W done on the solid is greater than $P_1\Delta V$, the work done by the solid on the fluid, the chemical potential of the 1 face of the solid under a non-hydrostatic stress is greater than the chemical potential of the solid under a hydrostatic pressure P_1. As Gibbs emphasizes, if the face of the strained solid is in contact with a fluid in which is immersed a piece of the solid, material will tend to dissolve from the face of the strained solid and deposit on the solid under a hydrostatic pressure. Figure 2 shows diagrammatically the direction in which material would move for the given stress distribution, provided both solids A and A^0 were in contact with a fluid.

In general, if a solid is in a state of strain fixed by three principal pressures P_1, P_2 and P_3 acting on three pairs of faces, then the chemical potential of the component of the solid along these faces will be greater than the chemical potential for the component in a solid under an equal hydrostatic pressure. These considerations thus answer the general question as to whether there exist *stable* phases under non-hydrostatic stress that would not be stable under hydrostatic stress. The non-hydrostatically stressed phase will *always* be unstable relative to a phase under a hydrostatic pressure equal to the least of the principal pressures acting on the non-hydrostatically stressed solid. It is thus theoretically impossible for a phase to be stable only under conditions of non-hydrostatic stress. This does not rule out the theoretical possibility mentioned by Bridgman (1936) of transitions under shearing stress which would never occur under any combination of temperature and hydrostatic pressure. In order to examine the probability of such transitions actually taking place, we need to consider the effect of shearing stress on the position of equilibrium surface. Polymorphic transitions in stressed solids are considered in the following sections.

In order to illustrate the numerical magnitude of the effects of non-hydrostatic stress, we consider a cube of quartzite originally at one bar hydrostatic pressure, then subjected to compression of 1000 bars normal to the X_3 edge, the faces parallel to the X_3 edge being kept at atmospheric pressure.

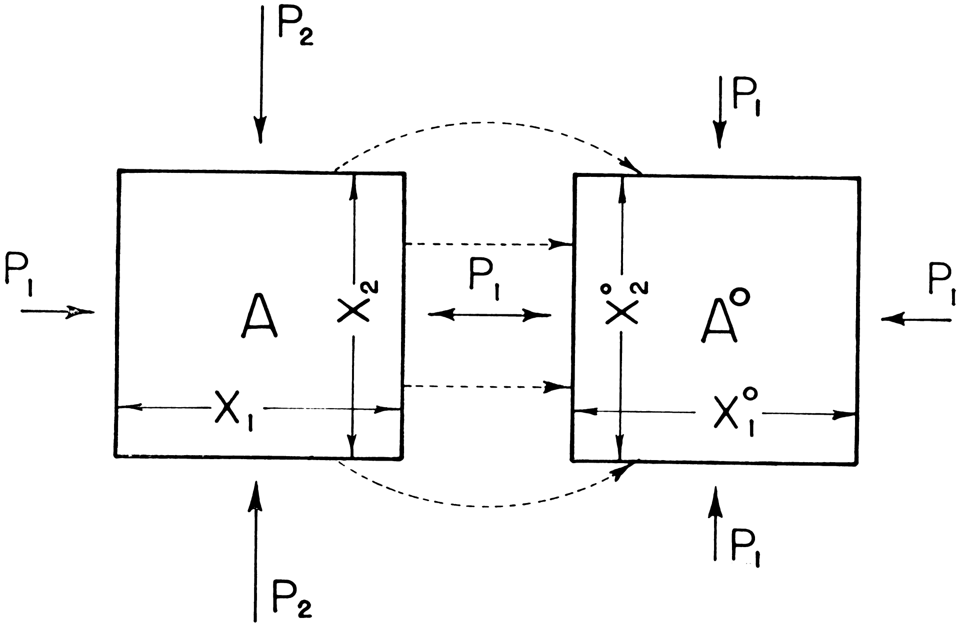

Fig. 2. Solid A is under a non-hydrostatic stress with $P_2 \neq P_1$. Solid A^0 under hydrostatic pressure P_1.

In order to calculate the difference in chemical potential of SiO_2 at one bar in the stressed and unstressed state, we have to assume a mechanical equation of state for the solid, and in addition we need to know the elastic constants of the material. We assume that the solid obeys Hooke's law, that the strain is a linear function of the stress. The work done on the solid in raising the pressure to 1000 bars on the face perpendicular to X_3 will be given by

$$\int dW = X_1^0 X_2^0 X_3^0 \int_0^{1000} \frac{P_3}{E} dP_3$$

since

$$dX_3 = X_3^0 \frac{dP_3}{E}$$

at a constant temperature, where E is Young's modulus for the material and is equal to about 7 x 10^5 bars for quartzite (Birch, Schairer and Spicer, 1942). The work done on the solid is then given by $W = 1/1.4\ V_0$ bar cc/mole $= 0.29$ cal./mole, where V_0 is the volume per mole in the unstrained state. The chemical potential of SiO_2 along the faces at one bar in the sample subjected to a unidirectional compression of 1000 bars is 0.3 cal/mole greater than the chemical potential of SiO_2 in the sample at a hydrostatic pressure of one bar. The variation of the chemical potential along the stressed face is given to a first order approximation by

$$\left(\frac{\partial \mu_1}{\partial P_1}\right) = V$$

The chemical potential of SiO_2 along the faces subjected to a pressure of 1000 bars is 540 cal/mole greater than the chemical potential of the faces at one bar. If both the stressed and free face were in contact with fluid through which SiO_2 could diffuse, there would be a driving potential of about 540 cal/mole tending to move material from the stressed face to the free face.

POLYMORPHIC TRANSITIONS IN STRESSED SOLIDS

Consider two polymorphs A and B in equilibrium with each other and with a fluid at a hydrostatic pressure P_1 and temperature T. On polymorph A alter the pressure on faces perpendicular to the edges X_2 and X_3 to P_2 and P_3 where $P_2 \neq P_3$, P_3, $\neq P_1$. This situation is the same as that depicted in figure 2. considering the solid A^0 of figure 2 to be polymorph B. From the arguments of the preceding section we see that the chemical potential along the face of A at a pressure P_1 will be greater than the chemical potential of B under a hydrostatic pressure P_1. There will be a tendency for A to dissolve in the fluid and precipitate on B. This conclusion is independent of the volume or elastic properties of A and B.

We can modify the preceding problem to study the effect of the same non-hydrostatic stress system on the transition temperature of two polymorphs. Imagine two polymorphs in equilibrium with each other at a hydrostatic pressure P_1 and temperature T. Now alter the pressures acting on both polymorphs such that $P_2 \neq P_1$, $P_3 \neq P_1$, so that both polymorphs are in identical stress fields as shown in figure 3. The problem is then to determine which poly-

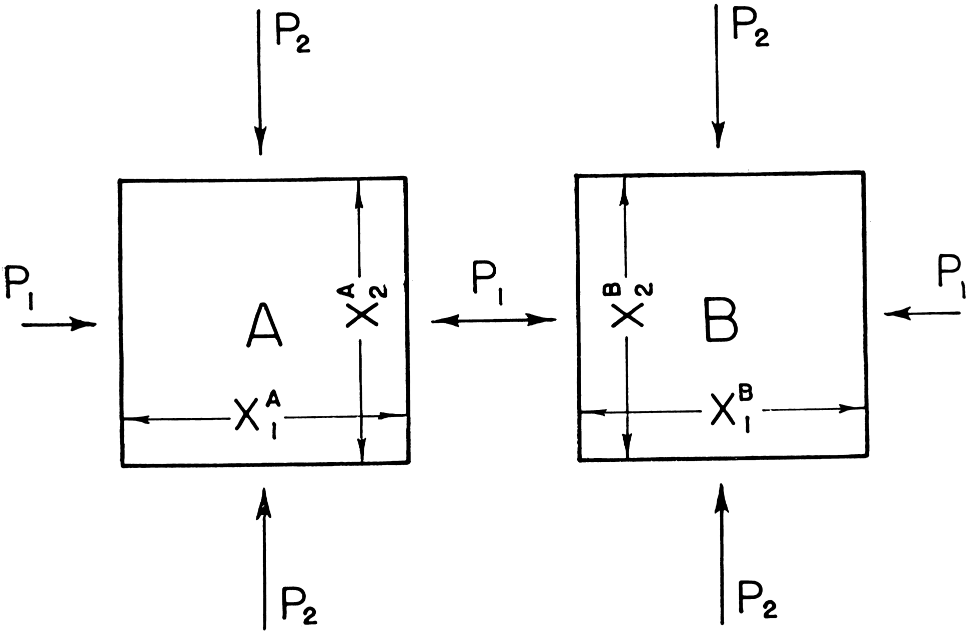

Fig. 3. Polymorphs A and B under identical conditions of non-hydrostatic stress.

morph has the lower chemical potential along the faces which are at a pressure P_1. At the original condition of equilibrium we have

$$\mu_1^{*A} = \mu_1^{*B}$$

where μ_1^{*A} is the chemical potential of the component in A at a hydrostatic pressure P_1, and similarly for μ_1^{*B}. The chemical potential along the faces at a pressure P_1 will then be given in the strained state by

$$\mu_1^{A} = P_1(V^A - V^{*A}) + W^A + \mu_1^{*A}$$

$$\mu_1^{B} = P_1(V^B - V^{*B}) + W^B + \mu_1^{*B}$$

In general the chemical potential will be lower in the phase on which is done the least work. Since for perfect elastic behavior the work is inversely proportional to the elastic constants, the elastically "harder" phase will be the more stable.

As an example, consider calcite and aragonite. These two phases of $CaCO_3$ are in equilibrium at 2500 bars hydrostatic pressure and 298.16° K. (MacDonald, 1956). Suppose that both minerals are subjected to a compression of 5000 bars on the faces perpendicular to the c-axis. The pressure on the faces parallel to the c-axis is maintained at 2500 bars. The problem is then to determine in which of the two phases $CaCO_3$ has a lower chemical potential along the surfaces subjected to 2500 bars. In order to evaluate the work done and the volume change involved in going from a hydrostatic pressure of 2500 bars to a state of non-hydrostatic stress, we need the elastic constants of calcite and aragonite. The values listed by Birch, Schairer and Spicer (1942) show that aragonite is "stiffer" along the c-axis than calcite and consequently less work will be done on aragonite and thus less strain energy is stored in aragonite. Using numerical values for the elastic constant, it turns out that the chemical potential of $CaCO_3$ in calcite is 3.7 cal/mole greater than the chemical potential in aragonite along the surfaces kept at 2500 bars.

We now obtain the expression for the variation of temperature of transition of two polymorphs with change of non-hydrostatic pressure. We assume two polymorphs in the form of rectangular parallelepipeds with pressures P_1, P_2 and P_3 acting in the three principal directions. We assume that the chemical potentials of the common component in the two phases are equal along the surfaces acted on by the pressure P_1. We next alter the pressure P_1, keeping P_2 and P_3 constant, and determine the change in temperature required to maintain the equality of chemical potential along surfaces at pressure P_1. From the definition of chemical potential we have for phases A and B

$$\mu_1^{A} = P_1V^A + U^A - TS^A$$

$$\mu_1^{B} = P_1V^B + U^B - TS^B$$

Using the following relations:

$$d\mu = PdV + VdP + dU - TdS - SdT$$

$$dU = TdS + \sum_{i=1}^{3} f_i dX_i$$

$$dV = X_2X_3dX_1 + X_1X_3dX_2 + X_1X_2dX_3$$

we obtain that the variation of chemical potential with P_1 and T is given by

$$d\mu = (P_1 - P_2)X_1X_3dX_2 + (P_1 - P_3)\ X_1X_2dX_3 + VdP_2 - SdT$$

The condition for equilibrium between phases A and B is then that

$$d\mu_1^A = d\mu_1^B$$

which leads to

$$\left(\frac{\partial T}{\partial P_1}\right)_{X_2^A,\, X_2^B,\, X_3^A,\, X_3^B,\, P_2,\, P_3} = \frac{V^A - V^B}{S^A - S^B} = \frac{\Delta V}{\Delta S}$$

That is, if both polymorphs are constrained so that the edges X_2 and X_3 remain constant during the change of pressure P_1, we obtain a formula that is analogous to the more familiar relation of change of melting point with hydrostatic pressure. In general, however, the ΔV and ΔS in the equation will be almost but not equal to the change of volume and entropy in the case of hydrostatic pressure.

The constraints on the X_2 and X_3 can be removed by assuming isotropic solids having a linear dependence of the edge lengths on temperature and pressure such that

$$dX = \left(\frac{\partial X}{\partial P_1}\right) dP_1 + \left(\frac{\partial X}{\partial T}\right) dT$$

$$dX = \frac{\sigma X^0}{E}\, dP_1 + X^0 \alpha\, dT$$

where α is the linear thermal expansion defined by

$$\alpha = \frac{1}{X^0}\left(\frac{\partial X}{\partial T}\right)_P$$

σ is Poisson's ratio, and E is Young's modulus. Substituting these relations for dX_2 and dX_3 in our expression for the variation of chemical potential, we obtain

$$\left(\frac{\partial T}{\partial P_1}\right)_{P_2 P_3} = \frac{V^{OA}\left[(P_1-P_2)\frac{\sigma^A}{E^A} + (P_1-P_3)\frac{\sigma^A}{E^A}\right] - V^{OB}\left[(P_1-P_2)\frac{\sigma^B}{E^B} + (P_1-P_3)\frac{\sigma^B}{E^B}\right] + \Delta V}{\Delta S - [V^{OA}(P_1-P_2)\alpha^A - V^{OB}(P_1-P_3)\alpha^B]}$$

This equation gives the variation of the equilibrium temperature of two nonhydrostatically stressed phases with variation of the pressure P_1, keeping P_2 and P_3 constant. The important feature of this equation is that the ΔV term is the dominant term in the numerator and ΔS the dominant term in the denominator. The terms in the numerator involving the stress differences $P_1 - P_2$ and $P_1 - P_3$ are small in comparison with ΔV for stress differences on the order of 10^3 bars, since these terms depend on the elastic constant σ/E, which for most materials is on the order of 10^{-5} bars. Similarly, the terms involving the thermal expansion in the denominator will be small, since α is on the order of 10^{-5} deg^{-1}. Thus to a good approximation the variation of transition temperature with pressure P_1 along the surface acted on by pressure P_1 will be given by

$$\left(\frac{\partial T}{\partial P_1}\right)_{P_2 P_3} = \frac{\Delta V}{\Delta S}$$

where ΔV and ΔS will be approximately equal to the differences of volume and entropy between the two phases under a hydrostatic pressure.

A non-hydrostatic stress should have a very large effect on the equilibrium curve in a second order transition. In a second order transition the difference in entropy and volume between the two phases approaches zero and thus the terms involving the elastic constants will be important. If the transition from low to high quartz is a true second order transition, then this is an example of a transition that would be influenced greatly by non-hydrostatic stress.

Changing the pressure on the surface of two polymorphs in equilibrium across this surface has to a first order approximation the same effect on a non-hydrostatically stressed solid as on solids under a hydrostatic pressure. We now show that the effect of changing the pressure on the surfaces not in equilibrium is much less. Consider two polymorphs in equilibrium at a hydrostatic pressure P_1. Change the pressure P_3 such that $P_3 \neq P_1$ on both polymorphs. How will the temperature have to be altered to maintain equilibrium along the surfaces at a pressure P_1? Using our general expression for the variation of chemical potential, and assuming that the polymorphs can be treated as isotropic solids obeying Hooke's law, we have that

$$\left(\frac{\partial T}{\partial P_3}\right)_{P_1} = \frac{V^{0A}\,(P_1-P_2)\,\frac{\sigma^A}{E^A} - V^{0B}(P_1-P_3)\,\frac{\sigma^B}{E^B}}{S^A - S^B - [V^{0A}(P_1-P_2)\,\alpha^A - V^{0B}(P_1-P_3)\,\alpha^B]}$$

Since the numerator involves only terms multiplied by an elastic constant, we should expect the change of equilibrium temperature along the surfaces at P_1 with a change of P_3 to be small for $P_1 - P_3$ on the order of a few thousand bars. As a numerical example of this effect we consider again calcite and aragonite in equilibrium at 2500 bars and room temperature. We increase the pressure on the surface perpendicular to the c-axis of both crystals to 5000 bars, maintaining the pressure of 2500 bars on the surfaces parallel to the c-axis. To maintain equilibrium along the surfaces at 2500 bars, the temperature would have to be lowered by about 3 degrees; while in order to maintain equilibrium across the surfaces at 5000 bars, the temperature would have to be increased about 150°. The effect of the non-hydrostatic pressure is therefore far greater on the surfaces subjected to a change in pressure than on the surfaces kept at a constant pressure.

As an illustration of the application of thermodynamics to the concept of stress minerals, we examine the equilibrium between andalusite and kyanite. Since andalusite is less dense than kyanite, andalusite should be stable at a lower pressure than kyanite. If equilibrium could be maintained at some temperature, an increase of pressure acting on the andalusite should result in the conversion of andalusite to kyanite, provided temperature—pressure conditions were such that there were no other phases more stable than either kyanite or andalusite. If the stress mineral concept were valid, the transition of andalusite, an anti-stress mineral, to kyanite, a stress mineral, should take place at a lower pressure if andalusite were under a non-hydrostatic stress than if andalusite were under a hydrostatic pressure.

Let us assume that for a given temperature T, the equilibrium hydrostatic pressure between andalusite and kyanite is P_i. Consider a cube of andalusite in simple uniaxial compression as illustrated diagrammatically in figure 3, with a pressure P_2 acting on the faces normal to X_2, and $P_1 = P_3$ acting on the other faces. The pressure on the free faces, P_1, is less than the equilibrium pressure P_i. If equilibrium is maintained as the pressure P_2 is raised, kyanite will begin to form along the stressed face at some pressure P_j. The theory we have developed shows that

$$P_j \cong P_i$$

for $P_1 - P_2 \cong 10^3$ bars. This result follows from the expression for the variation of chemical potential with pressure P_2 in a stressed solid at constant temperature.

$$\left(\frac{\partial \mu}{\partial P_2}\right)_T = 2(P_1 - P_2)\, V^0 \frac{\sigma}{E} + V$$

and since for $P_1 - P_2 \cong 10^3 - 10^4$ bars, we have that

$$\left(\frac{\partial \mu}{\partial P_2}\right)_T \cong V$$

The variation of chemical potential in the stressed solid is to a good approximation equal to the variation of chemical potential in a body under hydrostatic stress. Similarly we have shown that the slope of the curve relating the equilibrium temperature T to the equilibrium pressure P_j in the stressed solid will be very nearly the same as the slope of the equilibrium curve in the hydrostatic case for transitions in which the change of entropy and volume are large compared with the terms involving the stress differences and elastic constants. Transitions such as andalusite to kyanite involving large volume and entropy changes should not be affected by shearing stress. The difference in volume and entropy between andalusite and sillimanite is much smaller and stress might have an effect on the slope of the equilibrium curve. A transition between two phases as alike as α and β quartz would be affected by shearing stress. We can summarize the effect of stress on a polymorphic transition A→B by the following condition. The slope of the transition curve between polymorphs A and B will be unaffected by a maximum stress difference $P_1 - P_2$ acting on the system, provided the following inequalities hold:

$$\Delta V >> (P_1 - P_2) \left[V^{0A} \frac{\sigma^A}{E^A} - V^{0B} \frac{\sigma^B}{E^B} \right]$$

$$\Delta S >> (P_1 - P_2)\ [V^{0A} \alpha^A - V^{0B} \alpha^B]$$

These inequalities follow directly from our expression for the slope of an equilibrium curve in a general stress field.

ORIENTATION OF MINERALS IN A NON-HYDROSTATIC STRESS FIELD

The problem of the orientation of minerals in a given stress field can be divided into two parts: determination of the most stable orientation of a mineral in a given stress field and the process by which the mineral attains this orientation. The first problem is a problem of thermodynamics, the second a problem of the kinetics and mechanics of such processes as plastic flow and solution and recrystallization. We will consider only the thermodynamic problem.

If a crystal is loaded in simple compression, the stressed faces have a higher chemical potential than the unstressed faces. If a fluid is in contact with both faces, there will be a tendency for material to move through the fluid from the stressed face to the free face, the crystal thus growing in a direction perpendicular to the axis of compression. The crystal in so growing would tend to increase the area under the load, thus reducing the pressure acting on the stressed face. The orientation of a given grain would not change in such a process. Only the shape of the original grain would be altered. If the mineral were anistropic there would be at least one orientation in which the elastic work done on the crystal would be a minimum, and thus the strain energy stored within the grain would be minimized. The grains having an orientation with a minimum strain energy might be expected to grow at the expense of grains in which the strain energy was greater. For a given stress field, and provided the elastic constants of the material are known, the orientation in which the strain energy is minimized can be easily calculated. For calcite the strain energy is a minimum when the c-axis of a grain of calcite is parallel to the axis of minimum stress. Quartz has a minimum strain energy when the c-axis of the grain is parallel to the axis of maximum stress. Thus if solution and redeposition were the major mechanism of recrystallization in a marble, the c-axis of the calcite should be parallel to the axis of minimum stress. In a quartzite the c-axis of the quartz should represent the axis of maximum stress, provided solution and redeposition were the mechanism of recrystallization. It should be emphasized that the difference in strain energies between various orientations is small, on the order of calories per mole for stress differences of thousands of bars. If the grains deform by a mechanism other than that of solution and redeposition, then the influence of strain energy on the orientation of the grains might be expected to be negligible.

If a crystal is put in simple compression in the absence of a fluid, there is still the potential difference between the stressed and unstressed faces. Removing the fluid removes a mechanism of solution and redeposition by which the potential difference can be ironed out. Other mechanisms by which a difference in chemical potential can be reduced include a mechanical flow of the crystal. These mechanisms are probably characterized by an "activation energy" which must be exceeded before flow can take place. We should expect that this activation energy would be determined by the maximum stress difference times the volume of the crystal, since this quantity gives the potential difference between the stressed and unstressed faces. We should also expect that the activation energy would be greater for mechanical flow in a dry system than for deformation in the presence of a fluid. The rate of strain $\frac{d\varepsilon}{dt}$ should be given by an expression of the form

$$\frac{d\varepsilon}{dt} = A\varepsilon - \frac{V(P_3 - P_1)}{RT}$$

where $P_3 - P_1$ is the maximum stress difference and A is a constant.

The importance of the mechanism of deformation in producing an oriented fabric is illustrated by the detailed studies of Griggs, Turner, Borg and Sosoka (1951, 1953) on the Yule marble. Cylinders of marble were subjected to uniaxial compression at various conditions of temperature and pressure. The resulting fabric showed a strong orientation of the c-axis of calcite parallel to the axis of compression. If solution and redeposition had been the mechanism of recrystallization, the c-axis should be oriented perpendicular to the axis of compression, since such an orientation would minimize the strain energy stored in the crystals. In the experiments the crystals deformed by a mechanical flow in which "twin gliding" was the most important mechanism.

The actual mechanism of twin gliding results in an oriented fabric with the c-axis parallel to the axis of compression. In terms of the thermodynamic theory this fabric is explained by the fact that the potential difference tending to flatten the crystals perpendicular to the axis of compression is much greater than the potential difference between crystals having differing orientation. Since the twin glide mechanism of flow results in both the crystal flattening out and in the orientation of the c-axis parallel to the axis of compresssion, the increase of area perpendicular to the axis of compression reduces the chemical potential much more than the orientation of the c-axis parallel to the axis of compression increases the chemical potential. The potential difference tending to flatten the grains for stress differences of a thousand bars is on the order of hundreds of calories per mole, while the potential difference tending to orient the c-axis perpendicular to the axis of compression is only on the order of a calorie per mole. The biggest reduction in chemical potential results from flattening of the crystal, even though the mechanism of flattening results in an orientation of maximum strain energy in the crystals.

CONCLUSIONS

In the detailed application of theory it must be remembered that any single mineral grain in a rock undergoing metamorphism is seldom if ever under a homogeneous strain. The non-homogeneity of strain means that the chemical potential will in general vary over the grain in a much more complicated way than in the case of a rectangular parallelepiped subjected to three principal pressures. This complication, however, will not alter the major conclusions of this paper. A portion of the non-homogeneously stressed mineral is unstable relative to the same mineral under equal hydrostatic stress. The difference of chemical potentials between hydrostatically and non-hydrostatically stressed minerals will be on the order of a few calories per mole for a maximum stress difference on the order of 10^4 bars, since this difference depends on the elastic constants of the material. The slope of equilibrium curves in a general stress field will be, to a good approximation, equal to the slope of the curve in the hydrostatic case for transitions satisfying the conditions

$$\Delta V >> (P_1 - P_2)\left[V^{0A}\frac{\sigma^A}{E^A} - V^{0B}\frac{\sigma^B}{E^B}\right]$$

$$\Delta S >> (P_1 - P_2)\,[V^{0A}\alpha^A - V^{0B}\alpha^B]$$

where ΔV and ΔS are the changes in volume and entropy for the transition; $(P_1 - P_2)$ is the maximum stress difference acting on the system; V^{0A} and

V^{0B} are the volumes of polymorphs A and B; σ, E and α are the Poisson's ratio, Young's modulus, and thermal expansion.

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