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# Nonhydrostatic Thermodynamics and Its Geologic Applications

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The general principles of equilibrium thermodynamics are briefly stated in a form conveniently applicable to nonhydrostatic problems, i.e., with emphasis on the aspects, absent from hydrostatic applications, that have sometimes caused confusion. The importance of taking into account fully and clearly the constraints involved in a particular problem and of treating the work term very, carefully in considering an energy variation are particularly emphasized. For illustration the following problems of geologic interest are treated: (1) equilibrium between a stressed solid and its solution, including the 'pressure solution' problem; (2) recrystallization under stress and the resulting crystallographic preferred orientation in aggregates; (3) coherent phase transitions under stress; and (4) diffusion in a stressed solid.

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### A. INTRODUCTION

This paper aims to review, critically but in a fairly elementary way, the application of thermodynamics to systems in which nonhydrostatic stresses in the solid phases are of importance. In both geologic field studies and experimental work the question of the influence of stress on the development of particular assemblages, features, or fabrics has often been raised and has led to a substantial literature on what is often referred to, for brevity, as 'nonhydrostatic thermodynamics.' The topic is, of course, of much wider interest and has often entered into metallurgical discussions, but the present review has been assembled with the geologic applications in mind. Geologic applications that have been suggested include (1) 'pressure solution' phenomena, (2) recrystallization under stress, (3) phase transitions, (4) diffusion in a stressed solid, and (5) other, more specialized applications.

1. Pressure solution phenomena, which are most familiar in sedimentary or low-grade metamorphic rocks, include the indentation of one particle into another, the formation of stylolites, the truncation of fossils, and the formation of 'pressure shadows.' Some of these occurrences were already well known by the time of Sorby [1863, 1879], and it would be inappropriate to attempt a comprehensive listing of publications here. Many papers are referred to by Trurnit [1968]; other recent papers include those by Plessmann [1966], Dunnington [1967], Glover [1968, 1969], and Durney [1972]. Similar notions have from time to time been carried over into discussions of the deformation of rocks, when overall change of shape is attributed to local solution and redeposition under the influence of stress [e.g., Ramsay 1967, pp. 195, 226, 249]; the detailed physics of the deformation process is usually not very clearly stated, however, and the definition of the relative roles of cataclastic, crystal-plastic, and diffusion-type (including solution-redeposition) deformation mechanisms remains one of the major problems in rock deformation. There have also been suggestions that the development of small-scale structural features such as some types of crenulation cleavage and slaty cleavage has involved differential solubility under stress [e.g., Plessmann, 1964, 1966].

2. Recrystallization under stress may include 'syntectonic' recrystallization, although the deformational aspects are often not discussed since the emphasis is placed on the development of preferred crystallographic orientation of mineral grains. The preferred orientation problem has been the main stimulus for many of the papers on nonhydrostatic thermodynamics, and references to this aspect will be given later. Standard books such as those by *Sander* [1970] and *Turner and Weiss* [1963] set the problems of preferred orientation in their geologic context.

3. Phase transitions are known in some cases to be influenced by shear stress, especially in the case of displacive or martensitic transitions. Such situations have been studied more in metallurgy than in mineralogy, although *Harker*'s [1932] notion of 'stress' and 'antistress' minerals has received a great deal of attention, often not very critical from the point of view of thermodynamic theory. The recent experimental demonstration of the role of nonhydrostatic stress on

the  $\alpha$ - $\beta$  transition in quartz by Coe and Paterson [1969] constitutes a clearer example in mineralogy.

4. Diffusion in a stressed solid has entered into geologic discussions less than the above three topics, but it could conceivably be of importance in determining solute distribution around heterogeneities such as inclusions since such effects are known in metallurgy.

5. Among other, more specialized applications, two recent papers deal with possible implications for earthquakes: one paper is in connection with melting [*Ida*, 1970], and the other is in connection with phase transitions [*Hanyga*, 1970; cf. *Kumazawa*, 1963].

A point to be emphasized is that it is not always clear whether particular problems involve only questions of thermodynamic equilibrium or whether kinetic considerations of various sorts are of greater importance. That is, from the point of view of theory the problems are often not well posed. However, to be able to appeal to a well-founded body of theory in either area may, conversely, help to define the problems. Therefore, in the context of problems such as those listed above, it is worthwhile to aim at as clear an understanding as possible of the fundamental principles of nonhydrostatic thermodynamics.

There has been a good deal of controversy in the literature on some quite basic aspects of the application of thermodynamics in nonhydrostatic situations; see, for example, the paper by Kamb [1961a] and the extensive discussion of it in the same volume [Hoffer, 1961; Kumazawa, 1961; MacDonald, 1961; Kamb, 1961b]. It would therefore seem that this is a difficult subject, and, because of the attendant confusion and obscurities, great care is needed in applying it to particular problems. One of the sources of difficulty is the carrying over of concepts that are special to hydrostatic situations without a realization of these restrictions. It is therefore important to begin at the most general and elementary level and then to introduce the necessary restrictions explicitly. The present review attempts to follow this procedure, perhaps at the risk of appearing trite in places. The aim is to present a consistent and usefully intuitive outlook on the basic theory and on how this theory is developed in various applications.

### **B. FUNDAMENTAL PRINCIPLES**

This section attempts to present the main steps in developing a thermodynamic theory that is applicable to situations involving nonhydrostatic stress and to highlight the main assumptions and restrictions involved. No pretense is made to give a rigorous and complete development, and some of the more subtle aspects tend to be glossed over; the aim is rather to chart a course to help the nonspecialist appreciate the applicability or validity of particular thermodynamic results in particular situations. The point of view to be given is derived largely from the books by *Denbigh* [1966] and *Pippard* [1957] for general principles and from the articles by Gibbs, Kamb, McLellan, Ida, Li, and others cited later for nonhydrostatic aspects. This section attempts as far as possible to present a synthesis of what would be commonly agreed on. Because of its intuitive value, this inductive approach rather than a more elegant axiomatic approach [cf. *Callen*, 1960] has been followed.

Thermodynamics is concerned with the relationships in physical systems between the various contributions to energy (including heat and work) and with the state of these systems in terms of parameters such as temperature, pressure (or stress), and chemical composition. Here we shall only consider equilibrium situations, comprising, properly speaking, the field of thermostatics. However, the results are also commonly used as a starting point for speculating about the directions and rates of change in systems that are not in equilibrium. The proper development of theory in the latter case is difficult and is subject also to considerable controversy, although some progress has been made in dealing with steady state transport processes (diffusion of heat or matter) in what is known as 'irreversible thermodynamics' [e.g., *Prigogine*, 1961; *de Groot and Mazur*, 1962; *Coleman*, 1964; *Truesdell*, 1969]; this field is not touched on here.

We shall take as defined the main concepts and terms such as system, environment, isolated, closed and open systems, reversible and irreversible changes, extensive and intensive variables, phase, and component [e.g., *Denbigh*, 1966, chapter 1]. Heat, work, and temperature are also taken as defined concepts, although in more rigorous developments the notion of temperature is usually derived from more general concepts [e.g., *Truesdell and Toupin*, 1960, p. 621]. Work done on a system by its environment is taken as positive.

The first law of thermodynamics, a statement about the conservation of energy, defines the internal energy of a system as an energy content that characterizes the internal state of the system. This law leads to the fundamental relation

$$U_B - U_A = \Delta Q + \Delta W \tag{1}$$

for any change in a closed system from a state A to a state B, where  $U_A$  and  $U_B$  are the internal energies in the two states,  $\Delta Q$  is the amount of heat added to the system, and  $\Delta W$  is the amount of work done on the system during the change. Sometimes potential energy and kinetic energy are listed separately on the left-hand side of (1) [e.g., Andrews, 1972], but here we take them as being included in the internal energy. If (1) is written in the form

$$dU = dQ + dW \tag{2}$$

it has to be remembered that, in general, only dU is a total differential in the sense that it is independent of path (depending only on initial and final states) whereas dQ and dW may depend on the path taken in a particular change; this latter property is often indicated by the use of different symbols, such as  $\delta Q$  and  $\delta W$ or dQ and  $dW_{\bullet}$ .

In the case of an open system, we suppose that the reversible addition of material, under the notional conditions that no heat or work is exchanged with the environment, increases the internal energy in proportion to the amount (mass) added. So, for any reversible change in an open system,

$$dU = dQ + dW + \mu_{,}dN, \qquad (3)$$

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where  $N_i$  is a measure of the mass (usually the number of moles) of a particular component *i*,  $\mu_i$  is a parameter known as the chemical potential of the component, and summation over all values of *i* is implied. The restriction to reversible addition of material is made to permit the last term in (3) to be written in this product form. It is also implicit in (3) that the system is homogeneous, but this implication is not restrictive because we can always take a small part of a nonuniform system as the system for the purpose of defining the chemical potential, just as is done in defining temperature or stress. The chemical potential can thus be defined as

$$\mu_{i} \equiv \partial U / \partial N_{i} \tag{4}$$

under the constraints that dQ + dW and  $dN_i$   $(j \neq i)$  are 0. Defining the chemical potential at this point is somewhat unorthodox and clumsy, but the form (4) seems intuitively useful pending the introduction of the notion of entropy and a suitable generalization of the volume coordinate. Note that a slightly different type of definition is used in irreversible thermodynamics [*Truesdell* and *Toupin*, 1960, p. 636].

The second law of thermodynamics evolves out of the distinction between irreversible processes (also called 'natural' or 'spontaneous') and reversible processes and so is a sort of qualification of the first law. It introduces another function of state, the entropy, which enables one to establish a criterion for whether or not a particular change or process is possible. The second law can be paraphrased in two statements:

1. For a reversible change, dS = dQ/T; this relation gives a measure of entropy S. For any other change, dS > dQ/T.

2. Under adiabatic conditions, S is unchanged in a reversible change and increases in an irreversible one. Thus for a reversible change we can rewrite (2) and (3) to give the fundamental or Gibbs equations, as follows. For a closed system,

$$dU = TdS + dW \tag{5}$$

For an open system,

$$dU = TdS + dW + \mu_{,}dN, \tag{6}$$

(For an irreversible change the equality is replaced by <.)

The second law also allows useful criteria of equilibrium to be set up. A system is said to be at equilibrium under a given set of constraints when there is no possibility that the system will change spontaneously to any other state. For an isolated system, it follows from the second law that the equilibrium state is that for which S is a maximum. Criteria of equilibrium under other conditions follow from this definition. Thus it is a useful corollary of the above criterion that U is a minimum for the equilibrium state under the constraints that no entropy or matter is exchanged with the environment and no work is done by the environment on the system [cf. Gibbs, 1906; McLellan, 1968; Hanyga, 1971]. When such a criterion is applied in practice, it is sufficient that only the effect

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of small reversible changes in the system be examined, since these will produce the greatest change in U [cf. *Pippard*, 1957, p. 101].

In addition to discussing the equilibrium of the whole system in terms of its extensive parameters, we can consider equilibrium between parts of the system in terms of intensive parameters for specific interchanges. For example, equilibrium between two parts of a system in respect to interchange of heat or matter requires that the temperature or chemical potential, respectively, be the same in both parts. Specifying the equilibrium conditions in terms of the intensive parameters involved in all possible processes in the system is equivalent to specifying the equilibrium in terms of the extensive parameters for the whole system.

We have by now introduced all the essential concepts of equilibrium thermodynamics. However, three additional aspects should be commented on before we consider applications.

The form of the work term dW in (5) and (6) has deliberately been 1. left unspecified so far. In hydrostatic thermodynamics it is normally dW =-PdV, where P is the pressure and V the volume, provided the rate of change is slow in comparison with the rate of equilibration of pressure so that the change can be regarded as reversible. But, in more general situations, great care is needed in arriving at the appropriate and correct form of the work term since error or confusion has often arisen at this point. In particular, the work term may take different forms depending on the particular process involved, even if the state of stress is the same (e.g., contrast the cases of crystallization of material onto the surface of a stressed solid and diffusion of solute in the same stressed solid, discussed below). For a reversible change the work term can usually be expressed as a sum of terms of the form  $Y_i dX_i$ , where  $Y_i$  is generalized force and  $dX_4$  is generalized displacement [*Pippard*, 1957, p. 27]; however, the specification of  $Y_i$  and  $dX_i$  then depends on the particular application and has to be done with care.

2. In hydrostatic thermodynamics it has been found very useful to introduce certain auxiliary functions, or thermodynamic potentials. These are additional extensive quantities with the dimensions of energy that are used, in particular, in discussing equilibrium under given sets of constraints. However, these functions do not introduce any new concepts since they are derived entirely from quantities already defined above. The auxiliary functions are Helmholtz free energy  $F \equiv$ U - TS (useful where temperature and volume are treated as the independent variables), enthalpy  $H \equiv U + PV$  (useful where pressure and entropy are the independent variables), and Gibbs function  $G \equiv U + PV - TS$  (useful where temperature and pressure are the independent variables). The Gibbs function, in particular, assumes prominence in hydrostatic chemical thermodynamics since temperature and pressure are commonly the quantities that are controlled in experimental work. In this case the appropriate criterion of equilibrium is that the Gibbs function be a minimum for a system held at constant temperature and pressure. Another important property of the Gibbs function is that, in any reversible change at constant temperature and pressure, dG is identical with  $\mu_i dN_i$ . Thus the chemical potential of the *i*th component can be regarded as a partial molar Gibbs function, as expressed by the identity  $\mu_{,} \equiv (\partial G/\partial N_{,})_{T,P,N_{i}}$ , where  $j \neq i$ ; this identity is derived from  $\mu_{i} \equiv (\partial U/\partial N_{,})_{S,V,N_{i}}$ , where  $j \neq i$ . The Gibbs function, and enthalpy, can be generalized for nonhydrostatic situations by writing a suitable work potential in place of -PV, but the form of this potential will depend on the particular processes concerned, as was the case with the work term dW discussed above; the forms such as  $v_0\sigma_{,i}\epsilon_{ij}$  given by *Thurston* [1964] (see also *Barron and Munn* [1970]) are only valid under certain restrictions, such as the absence of exchange of material between phases. Therefore, to avoid difficulties or pitfalls associated with attempts to formulate such generalizations, it would seem better to leave this aspect open. On the other hand, there are no such problems in using the Helmholtz free energy in nonhydrostatic situations (as was done by *Gurney* [1947]), because its form is unchanged, although suitable coordinates must be chosen in place of the volume when the Helmholtz free energy is used in differential form [*Gurney*, 1947; *Thurston*, 1964].

3. Another aspect of hydrostatic thermodynamics has been the setting out of a number of relationships between the various parameters and functions, such as  $T = (\partial U/\partial S)_{V,N_i} = (\partial H/\partial S)_{P,N}$ , and so on, the Maxwell relations  $(\partial T/\partial V)_{S,N_i}$  $= -(\partial P/\partial S)_{V,N_i}$  and so on, and the Gibbs-Duhem equation  $-SdT + VdP - N_i d\mu_i = 0$  [e.g., *Denbigh*, 1966, pp. 89–94]. These relationships also introduce no new concepts, but they are useful in mathematical manipulations. Again we postpone any attempt to develop analogous relationships in the more general nonhydrostatic situations.

#### C. SPECIFIC APPLICATION

So far we have only mentioned the fundamental thermodynamic principles that apply generally to systems in equilibrium and have introduced the essential quantities involved. Further progress is difficult at this level of generality, and for the discussion of practical problems it is necessary to introduce restrictions. The universality of thermodynamic arguments is illusory since no practical problem can be attacked until the appropriate restrictions are specified. These restrictions or constraints primarily concern the types of macroscopic processes or changes that are possible or need to be considered in the particular situation (although not necessarily the specific atomic or other mechanisms). Thus, to make practically meaningful the statement that a system is at equilibrium, it is necessary to specify the types of practical processes by which the system could conceivably depart from equilibrium. Then, strictly speaking, we should speak of the system as being at equilibrium in respect of these processes. (A similar emphasis on the importance of specifying particular restrictions is implicit in the distinction between 'absolute equilibrium' and 'local equilibrium' by Ida [1969] as well as in various earlier writings from Gibbs onward; equilibrium with respect to a particular process has been called a 'partial equilibrium' by Hanyga [1971].)

Lack of clarity at this point (i.e., in specifying precisely and adequately the practical problem or class of problems being dealt with) has often been the root of the apparent discrepancies that have arisen in the various treatments of nonhydrostatic problems. The first step therefore in applying thermodynamic arguments to nonhydrostatic problems is to describe clearly the model situation that is being assumed to represent or idealize the practical situation. When models, such as those discussed below, are specified, the following concepts are often useful: (1) heterogeneity and homogeneity, (2) mobility and immobility, (3) coherence, and (4) constitutive relations.

1. The concepts of heterogeneity and homogeneity (i.e., nonuniformity and uniformity) are applied in many ways and generally do not need additional explanation [cf. *Paterson and Weiss*, 1961]. However, it may be worth elaborating on one use in connection with chemical change, namely, that a heterogeneous change or process is one that occurs at a specific site or sites (especially at interphase boundaries) and not everywhere whereas a homogeneous change is one that occurs throughout the body or system concerned. This concept is not to be confused with the concept of heterogeneous equilibrium often referred to in connection with multiphase systems, i.e., the equilibrium between different phases; such an equilibrium may be an equilibrium with respect to heterogeneous processes (e.g., pressure solution) or with respect to homogeneous processes (e.g., diffusion of a solute in the phases).

2. Mobility is the property, usually ascribed to components, of being able to move from one place to another in the system [cf. Li et al., 1966; McLellan, 1970]. It is implied that the rates of movement can be significant on the time or distance scale considered. The mobility or immobility of components leads to important constraints when model situations are specified. The concept of immobility may sometimes be usefully extended to cover the permanence of a framework or configuration of positions (such as a crystal lattice), but this use tends to overlap the concept of coherence, to be discussed next. In other cases, one may wish to distinguish different ranges of mobility, e.g., local or widespread or within certain phases or boundaries.

3. In the present context, coherence refers to a correlation or relationship between the internal configurations of two phases across their common boundary or to the correlated nature of the transformation or process whereby one phase changes into the other. The same concept exists in metallurgy in relation to small precipitate particles within which the lattice is a continuation of, or shares a sublattice with, the lattice in the host. The concept is somewhat analogous to the correlation in phase to which the term refers in optics. McLellan [1970] describes a coherent transformation or process as one in which 'the atoms, ions or molecules of the solid which form the immobile base structure and which are neighbours before the process occurs remain neighbours throughout the process,' but the concept is really a macroscopic one that need not be stated in terms of the position of atoms. The essential notion lies in there being a continuity of internal structural framework or 'natural' coordinate systems to which the configuration of material points in both phases is related and that makes it possible to define a reversible transformation strain. The concept can therefore only normally apply to solid phases. The  $\alpha$ - $\beta$  inversion in quartz is an example of a coherent transformation, whereas melting is an incoherent one.

4. The constitutive relations introduce the distinguishing properties of particular materials or classes of materials in the form of relations between extensive and intensive variables, such as between forces and displacements or motions. Mechanical, thermal, or chemical quantities may be involved. Two of the best known constitutive relations are the equation of state for perfect gases and Hooke's law for elastic materials.

At this point, one might attempt to set out a classification of model situations based on common restrictions or constraints. For example, McLellan in 1968 and 1970, respectively, refers to two classes of situations; in the first, all components are said to be mobile, whereas, in the second, some components are immobile. In the second class are included coherent phase transformations, equilibrium with respect to diffusion through a solid phase under stress, and equilibrium of a stressed solid in contact with its solution. It is not easy to see what real nonhydrostatic situations are included in the first class because of the difficulty of imagining changes in a system involving the mobility of all components on a given time scale that do not relax the shear stresses. However, in this review, it seems presumptuous to attempt a comprehensive classification of situations in view of the relatively few applications of nonhydrostatic thermodynamics that have so far been made. We shall therefore only consider some specific situations that illustrate the application of the general principles and that have received attention because of their possible practical importance. The specific situations considered are equilibrium between a stressed solid and its solution, recrystallization under stress with application to preferred orientation in aggregates, coherent phase transitions under stress, and diffusion in a stressed solid.

### D. EQUILIBRIUM BETWEEN A STRESSED SOLID AND ITS SOLUTION

### 1. Theory

This classic problem was first treated in 1875 by Gibbs [1906], whose results have been rederived or expounded by Kamb [1959, 1961a] and by several more recent writers [Li et al., 1966; Ida, 1969; McLellan, 1970; Hanyga, 1971] (see also MacDonald [1957] and comments on his treatment by Kamb [1959, 1961a, b]). It concerns the equilibrum between a solid phase under stress and a fluid consisting of a solution of the component forming the solid phase, the fluid being under pressure and in contact with the solid. Material from the surface of the solid can go into solution or precipitation can occur on the surface from the solution, but no diffusion within the solid is considered. Usually the state of stress in the solid is assumed to be such that its component normal to the surface in contact with the fluid is equal to the pressure in the fluid; i.e., the surface of contact is loaded by the pressure in the fluid. However, the separate roles of the pressure in the fluid and the stress in the solid are made clearer and a slight generalization is achieved by considering a system in which the loading of the solid is effected by a permeable loading frame entirely contained within the system (cf. Kamb's [1959, p. 158] 'inert constraining solid')

so that the components of stress in the solid can be specified independently of the pressure in the fluid. We now treat this situation as a closed system within rigid containing walls (Figure 1) and follow a procedure similar to that of McLellan [1970].

Consider a small reversible change consisting of the following steps:

1. A small piece of the solid, containing m moles, is detached from the surface of the solid at a site A, where the component of stress normal to the surface is  $\sigma_n$ , and is removed from the system. This step changes the internal energy of the system by  $-u_sm$ , where  $u_s$  is the molar internal energy of the stressed solid.

2. The loading frame is adjusted to regain contact with the surface of the solid by means of displacements normal to the surface. The change in potential energy of the loading frame, which will be included in the internal energy of the system, is  $-(\sigma_n - p)v_sm$ , where p is the pressure in the fluid and  $v_s$  is the molar volume of the solid in its stressed state.<sup>1</sup> (There may be conceptual difficulties with this adjustment procedure in cases where the surface being loaded is not normal to a principal stress axis in the solid. Further study is needed of the logical admissibility of an equilibrium model in which there is a component of uniform shear loading on the surface of a solid that can dissolve in a surrounding fluid.)

3. A quantity, m moles, of the component of the solid, in the same state in which it occurs in the solution, is introduced into the system and is dispersed in the solution in the vicinity of the site A. This step changes the internal energy of the system by  $u_Lm$ , where  $u_L$  is the partial molar internal energy of the component of the solid in the solution. The total amount of mass in the system has thus been conserved.

4. Since a different volume will be occupied by the *m* moles in the solution than by the *m* moles in the solid, the changes so far will have involved a net volume change of  $(v_L - v_s)m$ ; to accommodate this change, the boundary of the system would have had to have been moved  $(v_L)$  is the partial molar volume of the solute in the solution). Now move the boundary of the system back to its original position; in so doing, work is performed on the system of amount  $p(v_L - v_s)m$ . This step establishes the condition that the total work done on the system is 0 by virtue that the boundaries are eventually unmoved.

5. Finally, add to the system a quantity of heat equal to  $-T(s_L - s_S)m$  to compensate for the changes  $-s_Sm$  and  $s_Lm$  in entropy incurred in taking m moles of solid from the system and adding m moles of solute in steps 1 and 3 above ( $s_S$  and  $s_L$  are, respectively, the molar entropy of the solid in its stressed

<sup>&</sup>lt;sup>1</sup> Note that here, as elsewhere in the paper, compressive stress is reckoned as being positive; this convention has often been found to be useful in the geologic context [cf. Jaeger and Cook, 1969] and replaces the convention commonly used in physics and engineering, and therefore in most writings on thermodynamics, of reckoning tensile stress as being positive. Compressive strain will also be reckoned as being positive; i.e.,  $\epsilon = -\Delta l/l$ , where  $\epsilon$  is an infinitesimal normal strain component and l is an elementary length. The latter convention is rather unorthodox but has the advantage that strain energy is still a positive quantity. It should be noted that in this convention the volumetric strain  $\epsilon_{ii} = -\Delta v/v$ , where v is the volume.



Fig. 1. Schematic representation of closed system containing a solid under stress  $\sigma_{ij}$  and a fluid under pressure p, in which the solid can dissolve. The hatching represents a notional permeable loading frame.

state and the partial molar entropy of the component of the solid in the solution). This addition of heat establishes the condition that the entropy of the system has been unchanged.

The total change in internal energy in the above reversible change achieved by this path is then by the first law

$$\Delta U = -u_s m - (\sigma_n - p) v_s m + u_L m + p (v_L - v_s) m - T(s_L - s_s) m.$$

The same calculation with all signs reversed could be carried through for the reverse change, and the same result must hold for any other possible reversible path. Since we have satisfied the constraints  $\Delta S = \Delta W = 0$  under which the criterion of equilibrium for a closed system is  $\Delta U = 0$  (see above) and since *m* can be given any arbitrary value, we have thus established the equilibrium condition that

$$-u_{s} - (\sigma_{n} - p)v_{s} + u_{L} + p(v_{L} - v_{s}) - T(s_{L} - s_{s}) = 0$$

i.e.,

$$u_L - Ts_L + pv_L = u_S - Ts_S + \sigma_n v_S \tag{7}$$

Infinitesimal changes in the pressure of the fluid and in the stress in the solid occurring during the above change have been neglected; this neglect is justified since the changes always involve amounts of work that are small in comparison with the energy changes taken into account.

It is well known from hydrostatic thermodynamics that the quantity on the left of (7) is equal to the chemical potential  $\mu_L$  of the component of the solid in the solution. Therefore the condition of equilibrium between the stressed solid and its solution in the vicinity of the site A at which the stress component normal to the surface of the solid is  $\sigma_n$  is given by

$$\mu_L = u_S - Ts_S + \sigma_n v_S \tag{8}$$

This important result, due to Gibbs [1906], then enables us, given the appropriate data for the solid, to determine its solubility at the given site by using the normal relationship between chemical potential and solubility and, in particular, to calculate the influence of the state of stress in the solid on its solubility (see section 3 below).

### 2. Comments

The following comments refer to several important aspects of this result and its derivation:

1. Relations 7 and 8 refer only to a local equilibrium in the vicinity of the site concerned. The local equilibrium value of  $\mu_L$  in the fluid may be different in the vicinity of other sites on the surface of the solid where any of the quantities on the right-hand side of (7) and (8) is different; for example, even if the stress  $\sigma_{ij}$  is the same everywhere in the solid,  $\sigma_n$  can vary with the orientation of the surface and so lead to a variation in  $\mu_L$ . Hence the solubility can be different at different faces. If the fluid phase is continuous, no overall equilibrium is therefore possible on a time scale on which significant diffusion occurs on the scale of dimensions of the whole body. Moreover, the solid as a whole is unstable relative to an identical solid under no stress in the same system if diffusion can occur between the solids at a significant rate. It is therefore important that the constraints implied for the scale of diffusion in the model be borne in mind in applying relations 7 and 8.

2. The molar quantities  $u_s$ ,  $s_s$ , and  $v_s$  all refer to the solid in its stressed state and so are functions of  $\sigma_{ij}$ . In particular, the molar internal energy includes the elastic strain energy in the solid, with the consequence that the molar internal energy is sensitive to the orientation of the solid if the solid is elastically anisotropic, as in the case of crystals; in crystals, even for a given  $\sigma_{ij}$  and  $\sigma_n$  the solubility may vary with the orientation of the structure of the solid. Similarly, if  $\sigma_n$  is fixed but other components of the stress  $\sigma_{ij}$  are changed, the solubility may be changed. On the other hand, if  $\sigma_n$  is held fixed by suitable adjustment to the loading frame and the pressure p in the fluid is changed, the chemical potential of the solute in the fluid  $\mu_L$  will not be changed; in other words, the solubility, expressed as a mole fraction, will be independent of the pressure in the fluid if the state of stress is unchanged in the solid (provided that the same degree of ideality holds in relating chemical potential to solubility, i.e., that the activity coefficient of the solute is not changed).

3. This problem illustrates clearly the importance of expressing correctly the work term in the fundamental energy balance (1). An essential aspect of the present problem is the heterogeneous nature of the changes permitted under the constraints on diffusion, whereby only attachment or removal of material at the surface of the solid, not insertion of material within the solid, is allowed. The work term  $\sigma_n v_s$  then derives from the displacement of the interface and not from any change in specific volume of the stressed solid. Therefore it would be irrelevant, for example, to construct a potential containing a work term of

the type  $v_0\sigma_{ij}\epsilon_{ij}$ , where  $\epsilon_{ij}$  is the infinitesimal elastic strain in the solid and  $v_0$ a reference volume (the elastic strain energy of the solid is already counted in the internal energy, as is noted in comment 2). However, if desired, a general expression for the work in terms of tensorial quantities can be set up for a situation such as this one by the use of 'generalized volume coefficients'  $V_{ij}$  [Kumazawa, 1961, 1963; Ito, 1966; McLellan, 1970] (cf. also the 'surface partial molal volume' of Li et al. [1966]).

4. In spite of the dictum of Kamb [1961a] that 'it is not possible usefully to associate a chemical potential or Gibbs free energy with a non-hydrostatically stressed solid' in situations such as the above, many attempts have been made to set up potential functions of general applicability in nonhydrostatic situations analogous to the Gibbs function in hydrostatic thermodynamics. Kamb [1961a] discusses the unsatisfactory nature of such attempts by Goranson [1930], Verhoogen [1951], MacDonald [1960], and Kumazawa [1961]; Ida [1969] similarly comments on the attempts by Kumazawa [1963] and Ito [1966]. However, insofar as it is worth pursuing the Gibbs function type of approach, it is possible to construct functions that serve as potentials for determining equilibrium locally under particular constraints, but these potentials may not be applicable at all sites in the system [e.g., Li et al., 1966]. A similar purpose is served by generalizations of such functions that apply ostensibly to the whole system, e.g., the 'Gibbs functions' of McLellan [1970] and Hanyga [1971]. However, these functions are not fully analogous to the Gibbs function in hydrostatic thermodynamics because they must depend on particular constraints introduced in particular situations, e.g., the constraint on the range or scale over which diffusion is effective in the situation considered above. A similar point is recognized by McLellan [1970] in his comment that his 'Gibbs function' is 'not truly extensive.' Therefore, in view of the confusion that may arise when particular constraints are overlooked, it is probably better to deal with each situation from first principles and not to attempt to go beyond deriving chemical potentials relating to local equilibriums.

#### 3. Application to Pressure Solution

The influence of stress on solubility, which is presumably fundamental to pressure solution phenomena in geology (see the introduction), can be treated by introducing from the theory of solutions the usual relation for the chemical potential of the solute in the solution:

$$\mu \equiv \mu^*(p, T) + RT \ln \gamma c \tag{9}$$

whereby the activity coefficient  $\gamma$  is defined, c being the concentration (mole fraction) of solute, R the gas constant (per mole), and T the absolute temperature;  $\mu^*$  is a function of the pressure p and temperature T only and so is independent of the concentration c. Applying this relation to the system discussed above, we can therefore write the following by using (8):

$$\mu^*(p, T) + RT \ln \gamma_{\delta} c_{\delta} = u_{\delta} - Ts_{\delta} + \sigma_n v_{\delta}$$
(10)

where  $u_{\delta}$ ,  $s_{\delta}$ , and  $v_{\delta}$  are now written in place of  $u_s$ ,  $s_s$ , and  $v_s$  to designate the molar

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quantities for the solid when it is under the stress  $\boldsymbol{\sigma}$  (whose components are  $\sigma_{ij}$ ) and where  $\gamma_{\boldsymbol{\sigma}}$  and  $c_{\boldsymbol{\sigma}}$  are the activity coefficient and concentration of the component of the solid in the solution at equilibrium in the vicinity of the site where  $\sigma_n$  is the component of stress in the solid normal to the surface, the fluid being at pressure p. Alternatively, if the state of stress in the solid were a hydrostatic pressure equal to the pressure p in the solution (i.e.,  $\sigma_{ij} = p\delta_{ij}$  and therefore also  $\sigma_n = p$ ), then

$$\mu^{*}(p, T) + RT \ln \gamma_{p} c_{p} = u_{p} - Ts_{p} + pv_{p}$$
(11)

where  $u_p$ ,  $s_p$ , and  $v_p$  are the molar quantities for the solid when it is under hydrostatic pressure p and where  $\gamma_p$  and  $c_p$  are the activity coefficient and concentration of the component of the solid in the fluid at equilibrium at the same pressure p. From (10) and (11) we then obtain

$$RT \ln \frac{\gamma_{s}c_{s}}{\gamma_{p}c_{p}} = (u_{s} - Ts_{s}) - (u_{p} - Ts_{p}) + \sigma_{n}v_{s} - pv_{p} \qquad (12a)$$

Or, writing  $f_d \equiv u_d - Ts_d$  and  $f_p \equiv u_p - Ts_p$  for the corresponding molar Helmholtz free energies of the solid, we obtain

$$RT \ln \frac{\gamma_{\delta}c_s}{\gamma_{p}c_{p}} = (f_{\delta} - f_{p}) + \sigma_{n}(v_{\delta} - v_{p}) + (\sigma_{n} - p)v_{p}$$
(12b)

The first term on the right-hand side of (12b) is equal to the difference between the elastic strain energy of the solid at stress  $\boldsymbol{\sigma}$  and at hydrostatic pressure p. Under the assumption of linear elasticity, used throughout this paper, the elastic strain energy is  $\frac{1}{2}v_0\sigma_i,\epsilon_{ij}$ . Therefore, the third term is normally large in comparison with the other two, unless  $\sigma_n \approx p$ . Consequently, at a face subjected to compressive (or tensile) loading additional to the pressure in the fluid, the solubility is significantly increased (or decreased) relative to that of the solid under hydrostatic pressure only; the effect is determined mainly by  $\sigma_n - p$  through the third term and is only slightly modified by the other stress components in the solid through the first two terms. On the other hand, at a 'free' face subjected only to the pressure in the fluid, because the third term is now 0, the solubility is always increased by additional stress in the solid, but the effect is relatively small.

These predictions from thermodynamic theory are contained in Gibbs [1906] and are set out clearly by Williamson [1917]. Bridgman [1916] gives some very general formulas, the basis of which is not clear, and he does not apply them to this problem; the papers of Riecke [1895, 1912] are mainly concerned with melting under stress and only refer briefly to the equilibrium between a stressed body and a solution. The influence of stress on solubility had already been discussed qualitatively by Sorby [1863, 1879], but he did not distinguish clearly between the 'loaded' face and 'free' face aspects; Thompson [1862] had demonstrated an effect experimentally for compression applied to rock salt in the presence of its solution in water. The naming of the effect after Thompson and Sorby, sometimes done, is therefore more appropriate than the more frequent attribution enshrined in 'Riecke's principle' in geologic writing. Similar predictions have been made by several later authors, including Goranson

[1940a, b] and Gurney [1947]; Gurney also considered the converse problem of the absorption of the fluid in the solid, which is applied to the swelling of wood.

The situation is usually illustrated, for clarity, with the simple case of uniaxial stress  $\sigma$  in the solid and zero pressure in the fluid, taken to be a liquid; relation 12 then reduces to the following forms (neglecting second-order quantities in the first two expressions). For the loaded faces (those normal to the applied stress),

$$\gamma_{\sigma}c_{\sigma} = \gamma_0 c_0 \exp v_0 \sigma / RT \tag{13a}$$

or

$$\partial/\partial\sigma \ (\ln \gamma_{\sigma}c_{\sigma}) = v_0/RT$$
 (13b)

For the free faces (those parallel to the applied stress),

$$\gamma_{\sigma}c_{\sigma} = \gamma_0 c_0 \exp v_0 \sigma^2 / 2ERT \qquad (14a)$$

or

$$\partial/\partial\sigma \ (\ln \gamma_{\sigma}c_{\sigma}) = v_0\sigma/ERT$$
 (14b)

The quantity E is Young's modulus of the solid.

For the slightly more general case of a uniform uniaxial stress  $\sigma - p$  superimposed on a hydrostatic pressure p, (12), now including all terms, gives the following for the loaded faces:

$$\gamma_{\sigma}c_{\sigma} = \gamma_{p}c_{p} \exp \frac{v_{0}}{RT} \left[ (\sigma - p) + \frac{1}{2} \frac{p^{2}}{K} + \frac{1}{2}\sigma_{ij}\epsilon_{ij} - \sigma\epsilon_{ij} \right]$$
(15a)

where K is the bulk modulus of the solid,

$$\sigma_{i,i} \equiv \begin{bmatrix} \sigma & 0 & 0 \\ 0 & p & 0 \\ 0 & 0 & p \end{bmatrix}$$

and  $\epsilon_{ij}$  is the linear elastic strain resulting from this stress  $\sigma_{ij}$ . Unless p is very large, the first term under the exponential in (15a) predominates and thus leads to an approximate expression similar to (13a) but with  $\sigma - p$  substituted for  $\sigma$ . For the free faces,

$$\gamma_{\sigma}c_{\sigma} = \gamma_{p}c_{p} \exp \frac{v_{0}}{RT} \left( \frac{1}{2} \frac{p^{2}}{K} + \frac{1}{2}\sigma_{i}, \epsilon_{i}, -p\epsilon_{i} \right)$$
(15b)

In the particular case of isotropic elasticity the full expressions 15a and 15b, respectively, become the following. At the loaded faces,

$$\gamma_{\sigma}c_{\sigma} = \gamma_{p}c_{p} \exp \frac{v_{0}}{RT} \left[ (\sigma - p) \left( 1 - \frac{\sigma + 2p}{3K} \right) + \frac{1}{2} \frac{(\sigma - p)^{2}}{E} \right]$$
(15c)

At the free faces,

$$\gamma_{\sigma}c_{\sigma} = \gamma_{p}c_{p} \exp \frac{v_{0}}{2ERT} (\sigma - p)^{2}$$
(15d)

In the general case the influence of the elastic anisotropy enters through the terms  $\frac{1}{2}\sigma_{ij}\epsilon_{ij} - \sigma\epsilon_{ii}$  in (15a) and  $\frac{1}{2}\sigma_{ij}\epsilon_{ij} - p\epsilon_{ij}$  in (15b). Not only is there an orientation dependence of the solubilities at both the loaded and free faces of the stressed solid relative to the solubility of the solid under hydrostatic pressure alone, but the relative solubility at loaded and free faces of the stressed solid itself can depend on the crystallographic orientation in the solid.

Goranson [1940a, b] has discussed the application of relations 13 and 14 to creep. Weyl [1959] has made calculations for some models involving pressure solution phenomena that assume a relation  $c = c_0 + b\sigma$ , where  $c_0$  and b are constants; this relation is consistent with (13a) if the stress is small, but it is only applicable to the loaded face. The formula quoted by Durney [1972] is inconsistent with the above theory, but, if his dubious  $\nu_2 dp$  term were eliminated, his formula would correspond to (13b) and would then be in exactly the same form as that given by Williamson [1917, case 2, (B), p. 280].

### E. RECRYSTALLIZATION UNDER STRESS AND PREFERRED ORIENTATION IN AGGREGATES

### 1. General

The need to define carefully the constraints effective in particular situations is well illustrated in the application of thermodynamics to recrystallization in aggregates under nonhydrostatic stress, since differences in the processes that are permitted lead to differences in predicted preferred orientations. The general problem is to determine which crystal orientation is stable relative to all others when an aggregate of crystals of all orientations is placed under stress, the principal factor to be taken into account being the elastic strain energy of the crystals. However, when an energy balance is set up, the work term must be expressed very carefully with regard to the particular constraints. In all of the papers reviewed under the present heading the following two general assumptions have been stated or are implicit.

1. The internal state of the crystals, except in regard to elastic strain, is the same before and after recrystallization. This assumption eliminates from consideration all situations such as annealing recrystallization (where crystal defects and stored energy introduced by prior plastic deformation are eliminated or changed during recrystallization) or recrystallization accompanied by chemical change.

2. All crystals in the aggregate are assumed to be under the same homogeneous stress as the aggregate as a whole. It is therefore implicit that any local changes in stress resulting from local recrystallization are ephemeral, the state of uniform stress being restored eventually by processes that are effective on this local scale but negligible on such larger scales as would lead to relaxation of the overall state of stress in the aggregate. In practice, there are serious reservations about this assumption (see comment 1 below).

Of the many papers concerned with this thermodynamic problem, the most important are those of *Kamb* [1959, 1961a], whose development, based on the same Gibbsian approach as outlined above, will be summarized here. *Kamb*  [1959] treats two specific recrystallization models, here designated as 1 and 2, for which the following characteristics are assumed in addition to the two general properties given above:

1. It is assumed that the substance whose orientation is in question does not form most of the polycrystalline aggregate or that intercrystalline fluid is present.

2. It is assumed that the substance in question forms all or most of the polycrystalline aggregate and that no intercrystalline fluid is present.

In both models it is clearly recognized that the recrystallization is a heterogeneous process, but there are important differences in the role of diffusion and in the state of stress at the grain boundary.

### 2. Kamb Model 1

In this model [Kamb, 1959, sections 3-5] the growth or disappearance of a given crystal occurs, in effect, by the interchange of material with some sort of matrix of which the component of the crystal forms only a part and within which that component can diffuse. Thus diffusion is allowed from all faces of the crystal into other parts of the system, but no diffusion through the crystal itself is taken into account. It is implicit that the crystals of interest are not generally in direct contact with one another. Examples suggested by Kamb that such a model might represent are biotite crystals in a gneiss or calcite crystals in marble containing intercrystalline water.

The conditions of local equilibrium follow from the same argument as that given above for a stressed solid in contact with its solution since the matrix acts as the loading frame (it is assumed that no work is involved in slippage between matrix and crystal). Thus, from (8), for equilibrium between crystal and matrix at any particular site on the boundary of the crystal the chemical potential of the component of the crystal in the matrix  $\mu_{CM}$  must be given by

$$\mu_{\rm CM} = u - Ts + \sigma_n v \tag{16}$$

where, as before, u, s, and v refer to the crystal in its stressed state (the S subscripts are now dropped) and  $\sigma_n$  is the normal stress across the boundary at this site. We introduce, for convenience, the molar Helmholtz free energy  $f \equiv u - Ts$ so that  $u - Ts + \sigma_n v$  can be written as  $f + \sigma_n v$ . Let  $f_0$  and  $v_0$  be the values of f and v in the unstressed state, and write  $f = f_0 + \Delta f$  and  $v = v_0 + \Delta v$ . Then the equilibrium condition is

$$\mu_{\rm CM} = f + \sigma_n v = f_0 + \sigma_n v_0 + (\Delta f + \sigma_n \Delta v) \tag{17}$$

The term  $f_0$  is independent of orientation and stress and does not enter further considerations. Local equilibrium conditions therefore tend to be determined predominantly by the relatively large  $\sigma_n v_0$  term, whereas the term  $\Delta f + \sigma_n \Delta v$ has a second-order effect (taking the elastic strains to be infinitesimal). Thus  $f + \sigma_n v$  will generally be greatest at the crystal faces approximately normal to the greatest compressive stress; then, for local equilibrium,  $\mu_{\rm CM}$  will be maximal in the matrix nearby. Correspondingly,  $\mu_{\rm CM}$  will generally be minimal for equilibrium in the vicinity of faces approximately normal to the least principal stress (compression positive). However, the actual values of these maxima and minima will depend on the crystal orientation through the second-order term  $\Delta f + \sigma_n \Delta v$ .

Such a system cannot be at equilibrium as a whole when diffusion can occur at significant rates in the matrix since the diffusion of material from parts of the matrix where  $\mu_{CM}$  is higher to where it is lower will upset the local equilibrium conditions discussed in the previous paragraph and will thus lead to dissolution at some crystal boundaries and growth at others. The consequences of this diffusive transfer of material for preferred orientation depend on the second-order term  $\Delta f + \sigma_n \Delta v$ . Kamb [1959] asserts that for a given crystal to grow the matrix must be at least saturated with the component of the crystal at the faces normal to all three principal stresses (and hence at all faces) and that the tendency to grow or not is therefore determined by conditions at the face at which the solubility is the greatest, namely, the face normal to the maximum compressive stress. This view leads Kamb to the conclusion that 'the preferred orientation for a given mineral is that for which the chemical potential required for equilibrium across a surface perpendicular to the axis of greatest compressive stress is a minimum.' This criterion is equivalent to minimizing  $\Delta f + \sigma_1 \Delta v$ , where  $\sigma_1$  is the maximum compressive stress. If  $\sigma_{ij}$  and  $\epsilon_{ij}$  are the complete set of stress and infinitesimal elastic strain components (see the footnote for sign convention), Kamb's criterion for model 1 is therefore that the preferred orientation is the one for which  $\frac{1}{2}\sigma_{ij}\epsilon_{ij} - \sigma_1\epsilon_{ii}$  is a minimum.

Further examination of model 1 suggests that some qualifications of Kamb's conclusion are needed, depending on the relative proportion of crystals and matrix. It is convenient to distinguish only the two extreme cases in which this proportion is low (model 1a) and in which it is high (model 1b).

a. Model 1a. In this model the spacing of the crystals is large in comparison with their dimensions, so the shortest diffusion path via the matrix is to other faces of the same crystal. This situation would seem to be the one to which Kamb's criterion would be most likely to apply, and the preferred orientation would then be the one for which  $\frac{1}{2}\sigma_{ij}\epsilon_{ij} - \sigma_1\epsilon_{ii}$  is a minimum. However, it should be noted that, because of the  $\sigma_n v_0$  term in (17), the most pronounced trend will be for crystals of all orientations to dissolve at those parts of their boundaries that are approximately normal to the greatest compressive stress and to grow at parts of the boundaries normal to the least principal stress (compression positive). The flattening of grain shape to which this trend would lead is mentioned by Kamb [1959, p. 160] and elaborated on by Hartmann and den Tex [1964], but the implications for overall strain have not been much discussed (see introduction). To meet the second general assumption above, the matrix must undergo adjustments to maintain the stress in the grains during this transfer of material; these adjustments will lead to an overall shortening parallel to the maximum compressive stress direction, which might be described as a pressure solution mechanism of deformation. It is analogous to Coble creep or change of shape by diffusion along grain boundaries [Coble, 1963] and has been discussed in detail by Green [1970] for the case where the crystals in question occupy most of the body.

b. Model 1b. In this model the dimensions of the crystals are large in comparison with their spacing. The case of marble with intercrystalline water may be a relevant example. Interchange of material between the proximate faces of adjacent crystals via the solution will now tend to be the dominant process. Since these faces are essentially parallel to each other and since the  $\sigma_n v_0$  term in (17) will therefore be the same for each, the relative solubility will be determined by the  $\Delta f + \sigma_n \Delta v$  term, and a given crystal will grow at the expense of its neighbor at any point on its boundary where the value of  $\Delta f + \sigma_n \Delta v$  is less for the given crystal than for the neighbor at that point. The preferred orientation will be the one for which the net relative growth in volume (i.e., the mean relative growth over the whole crystal boundary) is greatest. For crystals that are roughly equidimensional, this preferred orientation will be the one for which  $\frac{1}{2}\sigma_{ij}\epsilon_{ij} - \bar{\sigma}\epsilon_{ii}$  is a minimum, where  $\bar{\sigma}$  is the mean stress. If the crystals are appreciably flattened normal to  $\sigma_1$ , however, the parts of the crystal boundary nearly normal to  $\sigma_1$  will predominate in the averaging, and the preferred orientation will then be nearer to that for which  $\frac{1}{2}\sigma_{ij}\epsilon_{ij} - \sigma_{i}\epsilon_{ij}$  is a minimum. (Note that it is implicit in this discussion that the intrinsic growth rates in the absence of stress are isotropic; anisotropic growth rates may accentuate or nullify the above predicted trends.)

It would appear, therefore, that the preferred orientation actually predicted on Kamb model 1 will depend on further assumptions made about details of the recrystallization process, especially as affected by the relative proportions of crystal and matrix and by the crystal shapes, as well as by anisotropic intrinsic growth rates. It should be emphasized that this qualification does not reflect on the fundamental local equilibrium condition (17) but involves questions of a kinetic character arising because the polycrystalline system can never be at equilibrium as a whole.

### 3. Kamb Model 2

This model [Kamb, 1959, section 6] assumes a monomineralic material without fluid at the grain boundaries and at a temperature sufficiently low that diffusion along the grain boundaries is negligible. The only process allowed therefore is the slight readjustment in position of atoms whereby they change from being at the lattice sites belonging to one crystal to those belonging to the other; this process is familiar in the grain growth of single-phase metals; the maximum movement required of any given atom is less than the dimensions of a unit cell.

The condition of local equilibrium at a boundary between two crystals can be derived by an argument along similar lines to that used for the case of equilibrium between a stressed crystal and its solution. Let the superscripts I and II identify the molar quantities u, s, and v for the two crystals of different orientation, and let m moles of crystal I be transferred to crystal II by a local rearrangement of the positions of the atoms. Let  $\sigma_n$  be the normal stress component perpendicular to the boundary (compression positive). The following three quantities are involved in the total internal energy change under the constraint  $\Delta S = \Delta W = 0$ . 1. The internal energy is changed by an amount  $(-u^{I} + u^{II})m$ , owing to the transfer of material.

2. An amount of work  $-\sigma_n(v^{I} - v^{II})m$  must then be done. This requirement is most easily seen if we choose the boundary of our closed system to coincide with the original position of the grain boundary between the two crystals, the system then being initially within crystal I. After the change, the outer surface of the new portion must be moved back to the original boundary position to establish the condition that no net work is done on the system. It should be noted that it is implicit that the length of the recrystallizing portion parallel to the boundary remains unchanged and that no slip occurs parallel to the boundary.

3. The third quantity involved in the total energy change is an addition of heat  $-T(s^{II} - s^{I})m$ . This quantity is required to establish the condition that no entropy is added to the system. Then, as before, invoking the equilibrium criterion that  $\Delta U = 0$  when no work is done on and no entropy is added to the system during the change and allowing m to have any arbitrary value, we have for equilibrium

$$\Delta U = (-u^{I} + u^{II}) - \sigma_{n}(v^{I} - v^{II}) - T(s^{II} - s^{I}) = 0$$

or

$$u^{\mathrm{I}} - Ts^{\mathrm{I}} + \sigma_{n}v^{\mathrm{I}} = u^{\mathrm{II}} - Ts^{\mathrm{II}} + \sigma_{n}v^{\mathrm{II}}$$
(18)

Designating u - Ts by f, the molar Helmholtz free energy, we can write the local equilibrium condition as

$$f^{\mathrm{I}} + \sigma_n v^{\mathrm{I}} = f^{\mathrm{II}} + \sigma_n v^{\mathrm{II}} \tag{19}$$

Kamb [1959] arrives at this result by a slightly different but equivalent argument in which he explicitly considers work done by the shear components of stress parallel to the boundary. Under the definition (4), the quantity  $f + \sigma_n v$  can be said to be the chemical potential of the component of the crystal appropriate to equilibrium with respect to this process of recrystallization, although this quantity is not necessarily a valid chemical potential for other processes, e.g., diffusion through a crystal.

Since the quantity  $f + \sigma_n v$  will, in general, be unequal for two contiguous crystals of different orientation in an aggregate under homogeneous stress, the aggregate will not be at equilibrium. As in model 1, there will therefore be a tendency for recrystallization to occur whereby a preferred orientation will be approached, this time by migration of the grain boundary through local rearrangement of atoms. Following an argument similar to that used in applying (17) to model 1b, the difference in  $f + \sigma_n v$  between a given crystal and its neighbor across a given point on their mutual boundary is given by the difference in the value of  $\Delta f + \sigma_n \Delta v$  between the crystals, where  $\Delta f$  is the molar elastic strain energy and  $\Delta v$  is the molar volume increment due to the applied stress. To predict the preferred orientation that will be favored, some kinetic assumptions are again needed. *Kamb* [1959] makes the assumption that to a first approximation the rate of migration of the crystal boundary at any point on it will be proportional to the difference between the chemical potential  $\mu = f + \sigma_n v$  for the crystal in question and the average of  $\mu$  for all crystals present; he then applies this assumption under the restriction that all grains are initially equant in dimensions so that these grains can be assumed to be spherical for purposes of calculation. Under Kamb's assumption the rate of migration of the crystal boundary at the given point is therefore proportional to  $(\langle f \rangle + \sigma_n \langle v \rangle) - (f + \sigma_n v)$ , where  $\langle f \rangle$  and  $\langle v \rangle$  are averages taken over all orientations. The resultant growth rate in volume of the given crystal is then found by averaging over all orientations of its grain boundary; thus a growth rate is given that is proportional to  $(\langle f \rangle + \bar{\sigma} \langle v \rangle) - (f + \bar{\sigma} v)$ , where  $\bar{\sigma}$  is the mean stress. The maximum growth rate therefore occurs for the orientation for which  $\Delta f + \bar{\sigma} \Delta v$  is a minimum, so this orientation will tend to predominate. That is, in the approximation of infinitesimal strain the preferred orientation will be the one for which  $\frac{1}{2}\sigma_{ij}\epsilon_{ij} - \bar{\sigma}\epsilon_{ij}$  is a minimum.

The preferred orientation predicted for model 2 is therefore different from that for model 1*a* but, not surprisingly, is the same as that for model 1*b*. As examples of both, the specific predictions for quartz, calcite, olivine, and micas are given in Table 1 for the particular case of axisymmetric stress where the unique axis is that of the maximum compressive stress  $\sigma_1$ .

### 4. Comments

1. The assumption has been made throughout that the stress is homogeneous. This assumption is rather artificial and, strictly, is untenable because of implied discontinuities in strain across grain boundaries and, in the case where a fluid phase is assumed to exist, because shear stress cannot be transmitted across the solid-fluid boundaries. The question remains of whether this assumption is a satisfactory approximation for representing real behavior. *Kumazawa* 

Mineral	Kamb Model 1a	Kamb Model 2 (also 1b)
α quartz [Kamb, 1959]	small circle girdle of $c$ axes at about 60° to $\sigma_1$	small circle girdle of $c$ axes at about 40° to $\sigma_1$
Calcite [Kamb, 1959]	c axis maximum parallel to $\sigma_1$	great circle girdle of $c$ axes normal to $\sigma_1$
Olivine [Hartmann and den Tex, 1964; den Tex, 1969, 1970]	optical $\alpha$ -axis, [010], maximum parallel to $\sigma_1$	optical $\gamma$ axis, [100], maximum parallel to $\sigma_1$
Mica [Schwerdtner, 1964]	pole of (001) maximum parallel to $\sigma_1$	great circle girdle of (001) poles normal to $\sigma_1^*$

TABLE 1. Predicted Preferred Orientations for Particular Minerals in Rocks under Axisymmetric Compressive Stress

Predictions are also listed by Kamb [1959] for several metals and other minerals, by Schwerdtner [1964] for hornblende, and by Schwerdtner [1970] for anhydrite.

\* This result is not given by Schwerdtner but it follows from substituting the elastic compliances of Alexandrov and Ryzhova [1961] (as given by Clark [1966]) into formulas 39 and 40 of Kamb [1959]; however, the preference for the girdle over an (001) pole maximum parallel to  $\sigma_1$  is small. These results apply to biotite, muscovite, and phlogopite.

[1968a] suggests that the assumption is satisfactory for the aggregate as a whole. On the other hand, one would expect that, on a local scale, heterogeneity in the stress field would give rise to important deviations from the average situation and that, in particular, new grains might nucleate under local stress conditions that depart markedly from the average. Kamb [1959] points out that as new grains grow to significant size, they must eventually come under stresses similar to those in the aggregate as a whole and so then conform to the general behavior; however, there may be thermodynamic, kinetic, or deformational factors during the development to this stage, the influence of which will persist during subsequent changes. Fletcher [1968; also private communication, 1973] has attempted to take the local stress conditions around a growing crystal nucleus into account and he states that predicted stable orientations differ from those for homogeneous stress. M. A. Etheridge, M. S. Paterson, and B. E. Hobbs (unpublished manuscript, 1973) have also discussed the possible role of localized contact stresses on grains in the development of preferred orientation in synthetic phlogopite aggregates with a fluid phase present. Therefore there are serious reservations about the usefulness of the homogeneous stress hypothesis and, in the long run, both stress distribution and orientation are probably variables to be solved for when the thermodynamically (and/or kinetically) most favored situation is calculated.

2. The initial grain shape can influence the predicted preferred orientation (especially in models 1b and 2), and so special care is needed in discussing minerals, the grains of which are commonly inequant, e.g., micas. There is also a tendency to produce a change of shape (especially in model 1a); it should be noted that this effect is independent of any tendency for growth rates to depend intrinsically on the crystallographic orientation of the growing face, a factor not taken into account here (M. A. Etheridge, M. S. Paterson, and B. E. Hobbs (unpublished manuscript, 1973) have considered anisotropic growth rate effects). Also, no account has been taken of the possibility that new grains will be nucleated with preferred orientation.

The elastic strain energy within the crystals due to the applied stress 3. is the only orientation dependent factor in the internal energy taken into account. However, as has often been pointed out [Verhoogen, 1951; MacDonald, 1957, 1960; Kamb, 1959], the concomitant variations in  $f + \sigma_n v$  with orientation are very small, much less than 1 cal mole<sup>-1</sup> for quartz and calcite even under stresses of the order of 1 kb. Thus other variations in internal energy may also play an important role, e.g., grain boundary energy or stored energy from plastic deformation (associated with increased dislocation and other crystal defect content); these quantities can, in practice, be at least of magnitude comparable to the above [cf. Paterson, 1959; Gross, 1965]. Also, quite small changes in composition could be expected to produce similar variations (M. A. Etheridge and B. E. Hobbs, personal communication, 1972). Any such factors, as well as purely kinetic factors controlling the rate of migration of crystal boundaries, may therefore have to be taken into account in the determination of the preferred orientation arising in recrystallization in a real situation, although not all are related to the applied stress.

4. There have been many other papers concerned with this problem, but the papers prior to Kamb [1959] were generally not very satisfactory in their derivation of the conditions of equilibrium, although MacDonald [1959] did start out soundly on the basis of Gibbs [1906]; see Kamb [1959, 1961a] for a discussion of the earlier papers. In the more recent papers on the same topic, little significant theoretical progress seems to have been made beyond the point reached by Kamb [1959, 1961a]. Although Kumazawa [1961, 1963] has some interesting points of view and has appreciated the role of shape, there are defects in his general theory (especially in regard to criteria of equilibrium) and a doubtful preoccupation with potentials [Kamb, 1961a; McLellan, 1966; Ida, 1969]; his predictions for preferred orientation have only been given in an abstract [Kumazawa, 1968b]. The theory of Ito [1966], which introduces notions from irreversible thermodynamics and places emphasis on the role of the orientation of the interface between crystals, is also defective in its equilibrium criteria because of the treatment of the work term, although the theory has some resemblance to Kamb's (see also comment by McLellan [1966] and Ida [1969]).

De Vore [1966, 1969a, b] and Dreyer [1970] have largely followed Mac-Donald's [1960] theory, as did Brace [1960], in assuming that the elastic strain energy is a maximum for crystals in the preferred orientation. There are suggestions that this principle (or, under uniaxial stress, the equivalent principle of Sonder [1933, 1948] that the preferred orientation is the one with smallest Young's modulus parallel to the axis of greatest compressive stress) is obeyed in some real situations [e.g., Wenk et al., 1973]. However, such behavior must be for reasons independent of MacDonald's considerations, since his theory has already been shown by Kamb [1961a] to be invalid. Parlange [1968] has predicted preferred orientations of recrystallized nuclei by minimizing a quantity  $\frac{1}{2}\sigma_{ij}\epsilon_{ij} - \frac{1}{2}\sigma'\epsilon_{ii}$ , where  $\sigma'$  is one of the principal stresses, chosen according to a criterion of minimum work that is not easy to follow. Although cast in the form of nucleation theory, Parlange's treatment involves thermodynamic considerations that are defective in the treatment of the work term (note that the factor  $\frac{1}{2}$  in the second term is not present in either of Kamb's criteria).

Ida[1969] follows the Gibbs-Kamb philosophy in placing emphasis on the concept of local equilibrium at interfaces between phases, but he expresses the elastic strain energy in terms of finite strains. He considers preferred orientations of crystals in cases where small axially symmetric ('uniaxial') stresses or shearing stresses are superimposed on a body under an initial hydrostatic stress, and, insofar as he goes, his conclusions agree with those of Kamb [1959], provided the hydrostatic pressure has not significantly affected the relative values of the elastic constants. However, Ida does not take Kamb's step (in model 2) of assuming that the behavior of a given crystal is determined by the generalized equivalent of  $f + \sigma_n v$  for the crystal relative to its average value for the other crystals in the aggregate. Instead, he only goes as far as distinguishing 'simple' and 'complex' situations; in simple situations the local equilibrium conditions are independent of interface orientation and are therefore the same everywhere in the body, whereas in complex situations the local equilibrium conditions

depend on the interface orientation so that the relative stability of two adjacent crystals can be opposite in different parts of the same boundary [cf. *Ito*, 1966] (a somewhat analogous notion of a complex state is also contained in the 'compatible structure' of *Kumazawa* [1963]).

### F. COHERENT PHASE TRANSITIONS UNDER STRESS

### 1. Theory

Coherent phase transitions present a particularly interesting problem in nonhydrostatic thermodynamics because of the role of shape changes as well as volume changes in determining the stability fields of the phases. Shape change, usually expressed as the deviatoric part of a 'transformation strain,' can enter because the coherency between the two phases enables the configuration of material points (or lattices) in both phases to be uniquely related to a common coordinate system; then a reversible transformation strain can be meaningfully defined in relation to the system of phases as a whole (such a relationship would be lost if, for example, arbitrary amounts of slip were permitted on the boundary between the phases in violation of the concept of coherency). Twinning can be regarded as a simple type of coherent phase transition, the shape in this case being the only property to be changed. Polymorphic transitions of the displacive type (in the classification of Buerger [1948, 1951]) constitute a broader class of coherent transitions. These include martensitic-type transitions (such as  $\alpha$  to  $\gamma$  iron) where quite large macroscopic shear may be involved and 'low-high' type transitions (such as  $\alpha$  to  $\beta$  quartz) involving slight changes in atomic configuration accompanied by only small macroscopic shears.

The conditions of equilibrium can again be derived by arguments similar to those in the previous sections on the basis of the criterion that internal energy be a minimum under the constraints  $\Delta S = \Delta W = 0$ . When the interface is moved so that *m* moles of phase I are transformed to phase II under these constraints, the following three quantities contribute to the total energy change:

1. Internal energy  $(-u^{I} + u^{II})m$  is added.

2. Work  $-v_0\sigma_{ij}\Delta\epsilon_{ij}m$  is involved to satisfy  $\Delta W = 0$ . A notional process similar to that described under Kamb model 2 can be used to establish this term. The variable  $\Delta\epsilon_{ij}$  is a strain tensor representing the transformation strain; it is related to axes in the unstrained configuration, as is the stress  $\sigma_{ij}$ , but is applied to the strained configuration. So this expression for the work is only valid for infinitesimal strains (see comment 1 below). Also, the molar volume  $v_0$  enters here instead of v because the transformation strain is referred to the unstrained configuration.

3. Heat  $-T(s^{II} - s^{I})m$  is added to satisfy  $\Delta S = 0$ . Then, from  $\Delta U \leq 0$  (*m* having any arbitrary value), the equilibrium condition becomes

$$(-u^{\mathrm{I}}+u^{\mathrm{II}})-T(s^{\mathrm{II}}-s^{\mathrm{I}})-v_{0}\sigma_{ij}\Delta\epsilon_{ij}=0$$

or

$$\Delta f \equiv \Delta u - T \Delta s = v_0 \sigma_{ij} \Delta \epsilon_{ij} \tag{20}$$

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where  $\Delta f$  is the change in Helmholtz free energy and  $\Delta \epsilon_{ij}$  is the transformation strain (case of infinitesimal strain only). This result is equivalent to that derived by *McLellan* [1970, equations 29 and 30] and expressed in terms of 'volume coefficients.'

The influence of stress on the transition temperature can be obtained by differentiating (20) to give

$$\partial T/\partial \sigma_{kl} = -v_0 \Delta \epsilon_{kl}/\Delta s \qquad k, l = 1, 2, 3$$
 (21)

where  $\partial/\partial\sigma_{kl}$  means partial differentiation with respect to one particular stress component  $\sigma_{kl}$ , all other components of  $\sigma_{ij}$  being held constant during the differentiation (in this differentiation, it is assumed that  $\Delta u$ ,  $\Delta s$ , and  $\Delta \epsilon_{ij}$  for the transformation do not vary at a significant rate along the phase boundary in the  $\sigma_{kl}$ -T plane). Coe and Paterson [1969] give a rigorous and more formal derivation of (21) by using an appropriate thermodynamic potential. A similar derivation is given by Forsbergh [1956], but he does not prove that his Gibbs function has the assumed properties at equilibrium. Relation 21 is a generalization of the Clausius-Clapyron relation in hydrostatic situations:

$$dP/dT = \Delta S/\Delta V \tag{22}$$

Different expressions were obtained by MacDonald [1957], Kumazawa [1961, 1963], and Hanyga [1971].

In various forms, relation 21 has been applied to the martensitic transformation in an indium-thallium alloy [Burkart and Read, 1953], to a reversible transition in protein fibers [Flory, 1956], to the ferroelectric Curie point [Forsbergh, 1956], and to the  $\alpha$ - $\beta$  transition in quartz [Coe and Paterson, 1969]. As an illustration of the anisotropic nature of the stress dependence of a coherent phase change, the above study on quartz showed that the  $\alpha$ - $\beta$ transition temperature is raised by 10.6°C/kb for uniaxial compression perpendicular to the c axis and by 5.0°C/kb for compression parallel to the c axis. This example shows clearly that simply substituting mean stress for hydrostatic pressure to find the position of a phase equilibrium boundary [cf. Verhoogen, 1951; Andrews, 1971] is incorrect for coherent transitions.

### 2. Comments

1. Relations 20 and 21 are valid only in the approximation of infinitesimal strain and homogeneous stress, but the same principles apply generally. Coe [1970] has extended the theory to finite simple shear, and McLellan [1970] has sketched in broad terms how a general treatment in terms of finite strain can be developed. Fuller treatments in finite strain have been given by A. G. McLellan (personal communication, 1972) and P.-Y. F. Robin (personal communication, 1973). There is, of course, a large literature on the mathematical procedures for dealing with finite strain, but the following papers may be useful as background to the application to nonhydrostatic thermodynamic problems: Truesdell and Toupin [1960], Thurston [1964], and Barron and Munn [1970].

2. The treatment given above applies only to first-order transitions, i.e.,

those in which there is a discontinuity in entropy and dimensions at the transition. Second-order or  $\lambda$ -type transitions require a different treatment, such as that of *Garland* [1964], who generalized the hydrostatic theory of *Pippard* [1956, 1957] to nonhydrostatic situations; the method of *Buckingham and Fairbank* [1961] can also be used to derive the generalized Pippard relations [*Coe and Paterson*, 1969]. Many 'high-low' transitions are  $\lambda$  transitions. Whereas it is debatable whether quartz is such a case, its behavior is close to that of a  $\lambda$  transition and can be rationalized approximately, although not completely successfully, in terms of generalized Pippard relations [*Coe and Paterson*, 1969].

3. It should be emphasized that the absence of diffusion is an essential part of the model of a coherent phase transition. If diffusion is allowed, the conditions of equilibrium will be quite different [cf. McLellan, 1968; Hanyga, 1971].

4. Hanyga [1971, section 6] discusses three models of phase transitions and suggests that one of them (model 2) represents coherent phase transitions. In fact, the only property that he takes into account in this model is the change in specific volume, 'disregarding the additional troubles associated with the misfit of phases across the interfaces.' His equilibrium condition [Hanyga, 1971, equation 33] is therefore not applicable to coherent transitions as defined above.

5. The particular equilibrium condition (20) is independent of the orientation of the interface. However, this independence is not a general property of equilibrium in nonhydrostatic situations for either coherent or incoherent transitions [cf. *Ito*, 1966; *Ida*, 1969; P.-Y. F. Robin, personal communication, 1973].

6. The work of *Thomas and Wooster* [1951] has shown how the application of stress can influence twinning (specifically, the Dauphiné twinning in quartz) even when there is no macroscopic twinning shear involved in the unstressed state. This phenomenon arises essentially through the elastic anisotropy of the crystals whereby, under a given stress, small differences can occur in certain strain components between the twin individuals. The transformation strain  $\Delta \epsilon_{ij}$  above is therefore now simply the difference in the elastic strain of the twin individuals under the given stress due to their different orientations. If we designate the twin individuals as I and II, the condition  $\Delta U \leq 0$  for the change I  $\rightarrow$  II becomes from (20)

$$\Delta f - v_0 \sigma_{ij} \Delta \epsilon_{ij} \leq 0$$

i.e.,

$$\frac{1}{2}v_0\sigma_{ij}\epsilon_{ij}^{II} - \frac{1}{2}v_0\sigma_{ij}\epsilon_{ij}^{I} - v_0\sigma_{ij}(\epsilon_{ij}^{II} - \epsilon_{ij}^{I}) \leq 0$$

or

$$\frac{1}{2}v_0\sigma_{ij}\epsilon_{ij}^{II} \geq \frac{1}{2}v_0\sigma_{ij}\epsilon_{ij}^{I}$$

Thus the stable twin individual is the one with the greater elastic strain energy under the given homogeneous stress, as was postulated and experimentally demonstrated by *Thomas and Wooster* [1951]. The case of Dauphiné twins of quartz under a given stress is therefore one to which the stability criterion of maximum elastic strain energy validly applies. The discussion of *Ida* [1969] on this point is incorrect, as was pointed out by *Tullis* [1970], since Ida is essentially applying an equivalent of the Gibbs relation (8), in which the work term is inappropriate for coherent phase transitions. *Tullis and Tullis* [1973] give a detailed treatment of the thermodynamics of mechanical Dauphiné twinning, from which it should also be noted that under a given strain the twin individual with the minimum elastic strain energy is the stable one. The importance of the phenomenon for preferred orientation in quartz aggregates is discussed by *Tullis* [1970] and *Tullis and Tullis* [1973].

7. The treatment in this section does not apply to incoherent transitions. The simplest example of an incoherent transition is melting. The analysis in this case is formally similar to that of the equilibrium between a solid and its solution. In particular, the influence of a uniaxial stress on melting is given by equations that have the same form as (13) and (14) but in which melting temperature is substituted for  $\gamma c$  and latent heat of melting is substituted for RT [e.g., *Williamson*, 1917]. Presumably, similar relations are applicable for solid-solid incoherent transitions provided the assumption of homogeneous stress is valid (which may be doubtful, especially for nuclei of one phase embedded in another phase) and provided there is no work of shearing involved at the interface.

### G. DIFFUSION IN A STRESSED SOLID

### 1. Theory

Equilibrium with respect to diffusion through a solid under stress presents a situation that is somewhat different from the situations considered so far, which have essentially involved processes at interfaces, i.e., heterogeneous processes. Nevertheless, a Gibbs approach can be applied, as was done by Yang et al. [1959] in connection with equilibrium electrode potentials of stressed metals. We use such an approach here and follow to some extent the procedure of *McLellan* [1970], although it should be noted that his conclusions about equilibrium with respect to diffusion are based on a postulated Gibbs function, written down by analogy with functions derived for other situations. In two pioneering papers of central importance in this topic, *Li et al.* [1966, 1971] have followed a slightly different but equivalent argument based on the theorem (Moutier's theorem) that the net work done in a closed cycle under isothermal and reversible conditions is 0.

The main aim here is the thermostatic one of calculating the equilibrium concentrations of solute in a body under stress when the solute can be exchanged with a similar body under a different state of stress. The calculation of the equilibrium distribution of solute in a heterogeneously stressed body then follows; the concentration of solute will, of course, be uniform within a homogeneously stressed body. The interest so far has centered largely in metallurgical applications such as the distribution of solute in the neighborhood of a dislocation or in the local stress field induced around an inclusion by an applied stress, but similar applications may be of interest in geology. Consider a model system containing a solid that is under stress in one part and stress-free in another part, and suppose that there is a mobile component that can diffuse between the two parts. As in the problem discussed above of a stressed single-component solid in contact with its solution, imagine the state of stress in the stressed part to be achieved by some sort of loading frame contained entirely within the system, and take the part to be small enough that the stress can be regarded as uniform within it. Now consider the following changes that occur when a small amount, m moles, of the mobile component is transferred from the unstressed to the stressed part:

1. The internal energy is increased by  $m\Delta w$ , where  $\Delta w$  is a partial molar elastic strain energy that can be defined as follows: (a) relax the stress in the stressed part and thereby recover the elastic strain energy Mw, where w is the mean molar elastic strain energy of the stressed part and M is the total number of moles of all components in it; (b) transfer the m moles of mobile component into this part while it is stress free; and (c) restore the state of stress in it by adding the appropriate elastic strain energy (M + m)w' (note that both the unstressed dimensions and the elastic properties will have been changed by the addition of the m moles of mobile component, which will result in the mean molar elastic strain energy being changed from w to w'); the partial molar strain energy  $\Delta w$  for the mobile component is then defined by  $m\Delta w = (M + m)$ w' - Mw.

2. Adjust the loading frame, doing work  $m\Delta W$  on it, so as to accommodate the changed configuration of the parts and to restore the original position of the boundary of the system ( $\Delta W$  is the work done on the surroundings when 1 mole of the mobile component is transferred from an unstressed part to a stressed part of the solid). An additional amount of work  $-m\Delta W$  must then also be done on the system to establish the condition that no net work is done on the system.

3. So that  $\Delta S = 0$ , add an amount of heat  $-mT\Delta s$ , where  $\Delta s = s' - s$ ; s' and s are the partial molar entropies of the mobile component in the stressed and unstressed parts, respectively.

Therefore, applying the equilibrium condition  $\Delta U = 0$  under the constraint  $\Delta S = \Delta W = 0$ , we have  $\Delta U = m\Delta w - m\Delta W - mT\Delta s = 0$  for arbitrary *m*; i.e.,

$$\Delta w - T \Delta s = \Delta W \tag{23}$$

or

$$\Delta f = \Delta W \tag{24}$$

at equilibrium, where  $\Delta f$  is the change in Helmholtz free energy.

Li et al. [1966, expressions 6 and 7] have given formulas for  $\Delta w$  and  $\Delta W$  that can be written as follows:

$$\Delta w = \sum_{i} \sum_{j} \int_{0}^{\sigma_{i}} \left[ v_{m} s_{ij} + (1-c) v \frac{\partial s_{ij}}{\partial c} \right] \sigma_{i} d\sigma_{j}$$
(25)

$$\Delta W = v(1 - c) \sum_{i} \sigma_{i} \frac{\partial \epsilon_{i}}{\partial c}$$
(26)

where  $\sigma_i$ ,  $\epsilon_i$ , and  $s_{ij}$   $(i, j = 1, 2, \dots, 6)$  are the stress and strain components and elastic compliances, respectively, in contracted or matrix notation [Nye, 1957],  $v_m$  is the partial molar volume of the mobile component, v is the mean molar volume of the solid solution, and c is the concentration (mole fraction) of solute. Note that the notation  $\Delta w$  and  $\Delta W$  used here is equivalent to the  $\bar{w}_k$  and  $W_k$ used by Li et al. [1966]. The quantity  $T\Delta s$  contains terms that depend on the concentration. Therefore, to obtain explicit expressions for the relative concentrations of the mobile component in the stressed and unstressed parts in equilibrium, further development of the equilibrium condition (23) or (24) is needed. This development is conveniently done in terms of chemical potentials by using the definition given by (4).

A chemical potential can be satisfactorily ascribed to the mobile component under the present constraints, which are that the component can move freely within the system without relaxing stresses where they exist (cf. Li et al. [1966] for a rationalization of the use of chemical potentials in these circumstances). In analogy with the usual procedure for solutions [e.g., Denbigh, 1966, chapter 9] the chemical potential of the mobile component can be written in the form

$$\mu \equiv \mu^*(\sigma_{ij}, T) + RT \ln \gamma c \tag{27}$$

which defines an activity coefficient  $\gamma$  for the mobile component at the molar concentration c and at a point where the stress is  $\sigma_{ii}$  and the temperature is T; R is the gas constant, and  $\mu^*(\sigma_{ii}, T)$  is constant for changes of composition at constant stress and temperature. This form permits the roles of stress and concentration to be separated.

In the model above the chemical potential of the mobile component in the parts under zero stress and under stress  $\delta \equiv \sigma_{ij}$  can then be written, respectively, as

$$\mu_0 = \mu^*(0, T) + RT \ln \gamma_0 c_0 \tag{28}$$

$$\mu_{\delta} = \mu^*(\delta, T) + RT \ln \gamma_{\delta} c_{\delta}$$
<sup>(29)</sup>

where  $\gamma_0$  and  $\gamma_d$  and  $c_0$  and  $c_d$  are the activity coefficients and concentrations, respectively, of the mobile component in the unstressed and stressed parts. However, at equilibrium the chemical potential is everywhere the same; i.e., at equilibrium

$$\mu^*(0, T) + RT \ln \gamma_0 c_0 = \mu^*(\mathfrak{d}, T) + RT \ln \gamma_{\mathfrak{d}} c_{\mathfrak{d}}$$

or

$$RT \ln \frac{\gamma_{o}c_{a}}{\gamma_{0}c_{0}} = -[\mu^{*}(\sigma, T) - \mu^{*}(0, T)]$$
(30)

Since the temperature is also everywhere the same at equilibrium, the quantity on the right-hand side of (30) is associated only with the difference in stress in the two parts. Because of (4), this quantity is equal to the change in internal energy involved in transferring 1 mole of mobile component from the unstressed part to the stressed part under the constraints that no work is done on and no

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heat is added to the system, i.e., the constraints under which the chemical potential is defined in (4). These constraints are met for the sum of the terms 1 and 2 of the energy balance listed earlier in this section (namely,  $\Delta w - \Delta W$ ) so that

$$RT \ln \gamma_* c_* / \gamma_0 c_0 = -\Delta w + \Delta W \tag{31}$$

From (31) the relation given by Li et al. [1966, equation 26] for positional variation of composition in an inhomogeneously stressed system follows by substituting from (25) and (26) and by making the approximations that they mention.

It may be noted that, because of the equilibrium condition (23), (31) can also be written as

$$RT \ln \gamma_{d}c_{d}/\gamma_{0}c_{0} = -T\Delta s$$

or

$$\Delta s = -R \ln \gamma_{d} c_{d} / \gamma_{0} c_{0} \qquad (32)$$

This equation is simply a roundabout way of showing that  $\Delta s$  is the difference in partial molar entropy of mixing for the mobile component between the stressed and unstressed parts.

### 2. Comments

1. In the above model the concentration of the mobile component in a region at a particular stress has been derived relative to the concentration in a stress-free region of the same solid in diffusional equilibrium with the stressed region in respect of the mobile component. This reference state is purely a matter of convenience, as was the use by  $Li \ et \ al.$  [1966] of a reference fluid containing the component in solution and being in equilibrium with the stressed solid. Any other reference state such as the solid in a reference state of stress could have been used (compare the derivation of the positional variation of composition in an inhomogeneously stressed solid, mentioned above).

2. The theory of the above model only applies strictly to interstitial solid solutions or equivalent situations in which the mobile component of interest can move in a way that is quite independent of the movement of any other components. Li et al. [1971] point out that this restriction excludes substitutional solid solutions because substitutional atoms cannot move by themselves but can only move by exchange with vacancies. However, provided that the elastic strain can be defined with respect to a lattice or similar sort of natural coordinate system that can be identified at all stages (implying conservation of lattice sites), Li et al. show that the diffusional equilibrium of substitutional atoms can be treated by considering a reaction:

lattice atom  $\rightleftharpoons$  interstitial + vacancy

This reaction leads to an expression similar to (31) except that the equilibrium constants for the reaction in the stressed and unstressed states appear in place of the quantities  $\gamma c$ . Li et al. also point out that such an expression is very

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general and can be applied to any chemical reaction in a stressed solid. The terms  $\Delta w$  and  $\Delta W$  are now called the (molar) strain energy of reaction and the work of reaction, respectively.

3. Several applications of the theory have been considered by Li et al. [1966, 1971]. These applications include the distribution of nitrogen in ferrite containing inclusions with which a stress field is associated and the distribution of solute around dislocations; the latter topic has often been treated in the metallurgical literature [e.g., Cottrell, 1953, p. 56; Friedel, 1964, chapter 13; Hirth and Lothe, 1968, chapter 14], but the thermodynamic principles have not usually been very clearly set out. The form of  $\Delta W$  is much simplified if the lattice strains are purely dilatational; this form can often be expected in simple systems (e.g., in cubic crystal structures), but, in general, the strains associated with change in concentration of the mobile component can be anisotropic, as, for example, in the absorption of moisture in wood [cf. Gurney, 1947].

4. The present discussion refers only to equilibrium with respect to the distribution of a mobile component in a stressed solid, not to the transport problem that exists when the system is not at equilibrium. However, the chemical potentials that have been established above for local equilibrium can be carried over in the usual way as 'driving forces' into discussions of the rates of diffusion under the basic assumptions upon which irreversible thermodynamic treatments rest. Such considerations are involved, for example, in Nabarro-Herring creep (note that in the light of this section it is not immediately obvious that the use of the Kamb chemical potential by *Green* [1970] in his treatment of creep by lattice diffusion is strictly correct, although its use is fully applicable in his grain boundary diffusion model; however, in practice, the use of the Kamb chemical potential leads to substantially the same creep law as that obtained by other approaches).

### **H. CONCLUSION**

This review has examined the literature on nonhydrostatic thermodynamics with special regard to its application in geologic problems. Despite the subject's reputation for difficulty, controversy, and obscurity, there is a well-established basis of theory that has been successfully developed in several important areas. It is therefore possible, at least in principle, to predict the practical implications of assumed models of situations involving equilibrium with respect to processes occurring under nonhydrostatic conditions.

It must be emphasized, however, that it is always important to distinguish clearly between the valid prediction of the implications of an assumed model and the validity of the model itself in representing the essential characteristics of the practical situations to which it is supposed to be relevant. This review has been concerned with the former aspect. To what extent equilibrium thermodynamic arguments are relevant to given real situations is a bigger question. These arguments are probably always important in setting limits or points of reference, but often in practice it will be in kinetic factors that the explanation of many phenomena will be found. Acknowledgments. I am grateful to R. S. Coe, W. B. Kamb, A. G. McLellan, V. M. Oversby, P.-Y. F. Robin, and T. E. Tullis for very useful criticism of a first draft of this paper, which led to the elimination of a number of errors and obscurities; Terry Tullis, in particular, gave a very detailed criticism, which included some reservations with which I agree about the extent to which shear work at interfaces inclined to the principal stress axes can be neglected at the various points where attention is drawn to matter. The mention of these persons does not imply that they agree with all the statements made in the paper. I also thank R. C. Fletcher, P.-Y. F. Robin, T. E. Tullis, and H. R. Wenk for making available manuscripts of papers prior to publication.

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