

NON-HYDROSTATIC THERMODYNAMICS OF CHEMICAL AND PHASE CHANGES

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ABSTRACT

The problem of chemical or phase equilibrium under non-hydrostatic stresses is discussed. It is shown how to formulate a formal thermodynamic theory, the essential step being the correct definition of the mechanical coordinates so that they describe not only the change of shape but the work done in such processes as deformation, chemical action, crystallization or solution at a surface, or a phase change. A useful Gibbs function is defined to give the conditions of equilibrium for the above processes. The theory agrees with experiments on the α - β quartz transition and on the de-twinning of quartz.

1. INTRODUCTION

The problem of chemical or phase equilibrium under non-hydrostatic stresses is of considerable interest in the earth sciences as well as in solid state physics generally, and it has been the source of some considerable controversy¹⁻⁷. The discussion centres on the possibility of the treatment of such equilibrium by formal thermodynamic procedures. For instance Kamb² stated 'that it is not possible usefully to associate a chemical potential or Gibbs free energy with a nonhydrostatically stressed solid'. Verhoogen⁶, however, defined a Gibbs free energy by analogy with, and by extension of, the hydrostatic case and thus not rigorously deduced.

It will be shown how it is possible to formulate a formal thermodynamic theory and that the essential step is the correct definition of mechanical coordinates which must satisfy the requirement that they determine the work done on a system in a change which may be due to deformation, chemical action, crystallization or solution, or a phase change. Using the correct coordinates, a useful Gibbs function may be defined and used to give easily the conditions of equilibrium for such systems as a stressed solid in contact with a solution of the solid, quartz at the transition surface for the α - β transition and similar phase changes, coexisting crystal twins, stressed solids into which homogeneous diffusion of a chemical component may occur. The application of this theory justifies the empirical theory of Thomas and Wooster⁸ inferred from experimental work on de-twinning of quartz, and agrees with experimental work on the α - β quartz transition^{9, 10}.

2. DEVELOPMENT OF THE THEORY

When a phase changes its shape and bulk, this may be due to the material in it being deformed, or its structure being altered as in a phase change, or

to the material being added to either at the external surfaces by crystallization from solution, or by homogeneous diffusion.

Although it is not necessary to the argument at this stage it is desirable to distinguish these processes as to whether they are coherent or not. Coherent here is used in the sense that a process is coherent if the atoms or ions of the basic solid material which were neighbours remain neighbours during the change. Pure deformations, homogeneous diffusion, phase changes such as α - β quartz, twinning of the Dauphiné type in quartz are all coherent, whereas crystallization from solution is incoherent.

In this paper the treatment will be confined to the case of infinitesimal deformations but it may easily be extended to that of finite deformations⁶.

In the infinitesimal case, the virtual work done on the phase in a virtual change is given by

$$\delta W = T_{\alpha\beta} \int_{A_0} \frac{1}{2} \{ \delta u_\alpha n_\beta + \delta u_\beta n_\alpha \} dA_0 \quad (1)$$

where $T_{\alpha\beta}$, the stress tensor, is always taken as uniform throughout the phase. \mathbf{u} is the vector displacement of the surface element dA_0 occurring in the change, \mathbf{n} is the unit outward drawn normal at dA_0 , and A_0 is the surface area of the reference state of the phase. Here and throughout the paper the summation convention is used for Greek suffices.

We thus define

$$V_{\alpha\beta} = \frac{1}{3} V_0 \delta_{\alpha,\beta} + \int_{A_0} \frac{1}{2} \{ u_\alpha n_\beta + u_\beta n_\alpha \} dA_0 \quad (2)$$

and thus

$$\delta W = T_{\alpha\beta} \delta V_{\alpha\beta} \quad (3)$$

since the integration in 1 and 2 is over a fixed surface A_0 . The first term in 2 is added as a constant of integration so that

$$V_{\alpha\alpha} = V \quad (4)$$

and this leads to the correct formulae in the hydrostatic case.

It is important to realize that \mathbf{u} must be determined at every stage by the criterion that 1 and hence 3 must be satisfied. In the case of crystallization or solution at an external surface in contact with a solution, the pressure of the fluid is normal and if a mass δN is crystallized on a plane face it is easy to see that

$$\begin{aligned} \delta W &= -\delta N v P \\ &= \delta N v n_\alpha n_\beta T_{\alpha\beta} \end{aligned} \quad (5)$$

where \mathbf{n} is the unit normal to the face and v is the specific volume of the solid, and hence

$$\delta V_{\alpha\beta} = \delta N v n_\alpha n_\beta \quad (6)$$

In an example where a solid phase in the shape of a cube is in equilibrium with two different solutions under different pressures, one of which is in contact with a face normal to the y axis and the other in contact with a face normal to the x axis, a virtual change may be imagined where the shape of the cube becomes that of a rectangular prism by the uniform solution of mass δN of the solid from the face whose outward normal is in the y direction, and the uniform crystallization of the same mass on the face whose outward

normal is in the x direction. In this case it is easy to see that although the total mass is constant, and the temperature and stress remain the same, the $V_{\alpha\beta}$ change.

That is

$$\delta V_{yy} = -v \delta N, \quad \delta V_{xx} = v \delta N \quad (7)$$

all other coordinates being unchanged.

Thus in general

$$V_{\alpha\beta}(T, T_{\alpha\beta}, \lambda N_1, \lambda N_2 \dots) \neq \lambda V_{\alpha\beta}(T, T_{\alpha\beta}, N_1, N_2 \dots) \quad (8)$$

although for a definite process such as described by equation 6 $V_{\alpha\beta}$ has an extensive property. This property leads to no difficulty in practice.

For a pure infinitesimal deformation, it is easy to see that

$$\delta V_{\alpha\beta} = V_0 \delta e_{\alpha\beta} \quad (9)$$

where $e_{\alpha\beta}$ is the infinitesimal strain tensor.

For a coherent phase change, the structure alters in a definite fashion, for instance in the α - β quartz transition both forms have a unit cell which is a right-angled prism with a rhombus base of angles 60° and 120° , and when the transition occurs the prism axes retain the same direction, however the a and c lattice constants change in length. If we assume that these changes are infinitesimal in this case, it is easy to see that if mass δN of α -quartz changes to β -quartz at constant temperature and stress, then the change of dimensions and the work done are given by

$$\begin{aligned} \delta V_{zz} &= \delta N v (\Delta c / c) \\ \delta V_{xx} &= \delta V_{yy} = \delta N v (\Delta a / a) \end{aligned} \quad (10)$$

all other mechanical coordinates remaining constant. If these changes cannot be described by the infinitesimal deformation theory, the treatment is easily modified⁶.

For homogeneous diffusion of a chemical component d into a solid at constant temperature and stress, the change of shape and bulk will be given by

$$\delta V_{\alpha\beta} = (\partial V_{\alpha\beta} / \partial N_d)_{T, T_{\alpha\beta}} \delta N_d \quad (11)$$

As a final example, Dauphiné twinning of quartz may be considered. Here a twin may be produced by small rotations of the SiO_4 tetrahedra to give a structure which may be obtained by rotating the original form through 180° about the c axis⁸. Thus in a virtual change from one twin to another all

$$\delta V_{\alpha\beta} = 0 \quad (12)$$

since the shape of the unit cell as described above is invariant to the 180° rotation about the c axis.

Equations 6, 9, 10, 11 and 12 not only describe the change of shape and bulk of the phase, but also the work done in a virtual change at constant T and stress. A more detailed justification of this is given in ref. 6. In all these equations

$$\text{Lt}_{\delta N \rightarrow 0} (\delta V_{\alpha\beta} / \delta N)_{T, T_{\alpha\beta}} = v_{\alpha\beta} \quad (13)$$

where δN is an increment of mass describing the change, and $v_{\alpha\beta}$ depends on the actual process; in particular in 6 it depends on the direction in the stress field of the surface element at which crystallization or solution is being considered. It is easily seen that when this process is adequately defined, $v_{\alpha\beta}$ is a function of the intensive variables T , $T_{\alpha\beta}$ and the chemical concentrations.

Before concluding this section, the definition of $V_{\alpha\beta}$ may easily be extended so that 2 describes the coordinates of a multiphase system, and it can be an additive quantity in the sense that for the system

$$V_{\alpha\beta} = \sum_i V_{\alpha\beta}^{(i)} \quad (14)$$

where the summation is over the phases. This is so if no slip is allowed between solid phases. For a fluid/solid interface since any displacements \mathbf{u} are allowed which describe the change of shape of the external surfaces bounding the fluid, we may choose \mathbf{u} as continuous at the interface, and thus 14 is satisfied.

3. EQUILIBRIUM CONDITIONS VIA THE GIBBS FUNCTION

For a multiphase closed system

$$dU = (T dS + \sum_i T_{\alpha\beta}^{(i)} dV_{\alpha\beta}^{(i)}) \quad (15)$$

if T is the same for all phases. Hence if we define a Gibbs function

$$G = U - TS - \sum_i T_{\alpha\beta}^{(i)} V_{\alpha\beta}^{(i)} \quad (16)$$

where U and S are the internal energy and entropy of the whole system, then

$$dG = -S dT - \sum_i V_{\alpha\beta}^{(i)} dT_{\alpha\beta}^{(i)} \quad (17)$$

$$= 0$$

for

$$dT = dT_{\alpha\beta}^{(i)} = 0 \text{ all } i.$$

The equilibrium conditions may easily be obtained by the usual arguments. First for the case of crystallization or solution at a plane surface, consider a virtual change where T , $T_{\alpha\beta}$ for the solid, and P for the solution are all held constant. Then

$$\delta G = \delta N \{u - u_L - T(s - s_L) + P(v - v_L)\} = 0 \quad (18)$$

on using 6 and the fact that

$$-T_{\alpha\beta} n_\alpha n_\beta = P \quad (19)$$

u , s , v are the specific quantities for the solid, and u_L , s_L , v_L are the partial quantities for the solution. Hence for equilibrium

$$\mu_L = u - Ts + Pv \quad (20)$$

the well-known Gibbs result¹¹.

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For the α - β quartz transition the equilibrium condition for the coexistence of the two forms at the transition surface is given by

$$\Delta u - T \Delta s - (T_{xx} + T_{yy}) \Delta v_{xx} - T_{zz} \Delta v_{zz} = 0 \quad (21)$$

where

$$\begin{aligned} \Delta v_{zz} &= v \Delta c/c \\ \Delta v_{xx} &= \Delta v_{yy} = v \Delta a/a \end{aligned} \quad (22)$$

From 21 and 22 it is easy to prove that

$$\begin{aligned} \partial T_c / \partial P_x &= +v(\Delta a/a) / \Delta s \\ \partial T_c / \partial P_z &= +v(\Delta c/c) / \Delta s \end{aligned} \quad (23)$$

where e.g. $P_x = -T_{xx}$. From x-ray studies¹⁰

$$\Delta a/a = (2.2 \pm 0.2) \Delta c/c \quad (24)$$

and both quantities in 23 are positive. Since Δs is positive the lefthand expressions in 23 should be and are observed to be positive. Moreover, Coe and Paterson⁹ showed experimentally that

$$(\partial T_c / \partial P_x) : (\partial T_c / \partial P_z) = 2.1 \quad (25)$$

in excellent agreement with 23 and 24.

Finally Thomas and Wooster⁸ studied experimentally the de-twinning (Dauphiné) effect of non-hydrostatic stresses on quartz. Since for the twins 12 holds, the condition for coexistence of twins is

$$\Delta f = 0 \quad (26)$$

where f is the specific Helmholtz free energy, and this is consistent with and justifies the empirical principle that de-twinning occurs best when maximal energy is stored.

Thus, in general, equilibrium conditions for chemical and phase changes may be determined by the Gibbs function, the quantities of the form $v_{\alpha\beta}$ of 13, being thermodynamic 'unknowables' just as are the specific and partial volumes in hydrostatics, and must for a particular process be determined experimentally or from a theoretical model.

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