

The hydrostatic Gibbs function cannot be generalized to produce a potential that defines equilibrium conditions for phase transition when shear stress is present, except in a few special cases of no interest here (Duvall, 1976; Paterson, 1973). The difficulties lie at two levels. In the first place, consider a finite mass of solid material which is systematically brought to the transformation point by application of forces to its outer boundaries. The mass does not transform homogeneously. Nuclei of the new phase begin to grow, transforming the original homogeneous mass into a heterogeneous mass with inhomogeneities in stress distribution produced by the growing nuclei. It is no longer possible to relate stress states in the new and old phases in any simple way and the first and second laws of thermodynamics for the finite mass are no longer satisfied by the simple expedient of setting $E_1 - TS_1 + PV_1 = E_2 - TS_2 + PV_2$, or by an obvious variant thereof.

At the microscopic level the difficulty persists, but in a different way. Consider, for example, only the region in the immediate vicinity of an interface between the nucleus of the new phase and the matrix of the old. The curvature of this interface presents difficulties, so consider a plane interface between the two phases. Is there a simple relation analogous to equality of the hydrostatic Gibbs function in a fluid which relates conditions on the two sides of such an interface? Paterson (1973) reviewed the entire problem. He suggested such a relation for the special case of coherent phase transitions, i.e., transitions in which the new phase can be constructed from the old through imposition of a set of strains $\Delta\eta_{ij}$ across an interface between old and new phases. If $\Delta\eta_{ij}$ is small, he gives the condition of equilibrium as

$$\Delta E - T\Delta S - V_0 \sigma_{ij} \Delta\eta_{ij} = 0. \quad (38)$$

This gives for the analog of the Clausius–Clapeyron equation

$$\partial T / \partial \sigma_{kl} = -V_0 \Delta\eta_{kl} / \Delta S, \quad k, l = 1, 2, 3. \quad (39)$$

Robin (1974) finds even this to be untrue. Instead, equilibrium of the interface depends on its orientation relative to the lattice, so the above equations are not general, even under the very restrictive assumptions made.

It is evident that if experimental data on phase transformations in solids are to be organized, some simple approximation to transformation theory is required, even if it be inexact. In reduction of shock data it is usually assumed that only hydrostatic or mean pressure is significant, and that fluid thermodynamics, including the Clausius–Clapeyron equation, applies. Shock measurements give only values of p_x at which various events occur, including the onset of transformation. Mean pressure \bar{p} is obtained from Eq. (3)

$$\bar{p} = p_x - \frac{4}{3}\tau,$$

where τ is maximum resolved shear stress. In this paper, τ is computed from measured values of the HEL and appropriate values of elastic constants; it is often ignored entirely. Measurement of τ is desirable, but measurement of a second component of stress in shock experiments is not simple. If a phase transition occurs at higher pressure than the HEL, τ may be expected to change from its value at the HEL because of stress re-

laxation, work hardening, temperature increase, and density increase, so that its exact value at the transition point is not determinate without additional stress measurements. A more detailed discussion of difficulties experienced in correcting for shear strength is given by Duvall (1976).

Jones and Graham (1971) have reviewed the shock literature for experimental evidence of the effects of shear stress on phase transitions. They find mean shock pressure for bismuth, corrected for the HEL, in close agreement with statically determined values, but in that case the HEL is small. For germanium the shear correction to p_x is about 15%, and \bar{p} , corrected for the HEL, is within the range of static measurements, though the spread in both cases is rather large. On the basis of one experiment each with CdS and InSb, the value of \bar{p}^{TL} , corrected for the HEL, for the shock transition is lower than the static transition pressure.⁴

The only systematic experimental study of effects of τ on transition pressure has been in iron. The HEL of iron was varied from 0.7 to 1.9 GPa by varying heat treatment and carbon content (Minshall, 1961; Loree *et al.*, 1966a; Jones and Graham, 1971). Their data suggest that the transition is occurring at constant \bar{p} , independent of the resolved shear stress. Supporting evidence is provided by Forbes (1976), who finds \bar{p}^{TL} to be constant in Armco iron when specimen thickness is varied, whereas p_x^{TL} varies as the HEL.

A more extreme case than the one just described exists in heterogeneous rocks and minerals. It has been observed that some brittle materials lose a substantial portion of their shear strength under shock loading (Fowles, 1962; Wackerle, 1962; Graham and Brooks, 1971; Graham, 1974). Grady *et al.* (1975) have recently proposed that this results from heterogeneous melting associated with the yield process (cf. Sec. VI.C). In such a case, correction for strength based on the HEL is totally inappropriate.

On the basis of investigations conducted to this date, there is evidence that in a number of cases the macroscopic shear stress has no effect on the shock initiation pressure of transformation other than the addition of $4\tau/3$ to \bar{p} , as in Eq. (3). Nevertheless, there are some possible exceptions to be noted in Sec. IV, and it appears necessary to give careful consideration to the effects of shear stress on each of the materials under study. A tabulation of HEL is given by Jones and Graham (1971).

F. Finite transformation rates

Time available for a phase transition to occur in a mass element compressed by shock may be only a few nanoseconds and does not normally exceed a few microseconds. If the required time for transition is longer, the transition will not be detected in the usual shock experiment because of sample size limitations. This contrasts so dramatically with time scale in static experi-

⁴Superscript (or subscript) *TL* denotes the pressure of transition determined in compressive loading. *TU* denotes a value obtained in unloading experiments; *T* denotes equilibrium transition values.

ments that validity of comparisons between shock-induced and statically measured transitions has quite properly been questioned (Roy, 1969; Bridgeman, 1956; Bethe, 1942). It is fortunate that experimental manifestations of transition kinetics are quite direct and readily detected in shock experiments, provided the rate lies within a rather broad range defined by geometry of the experiment. Roughly speaking, if the time required to effect a significant fraction of the transition is less than $d/3U_s$ and greater than about 10^{-8} s, the transition rate can be measured in a shock experiment. Here d is diameter of the experimental sample and U_s is shock propagation velocity. For a 90 mm diameter target and a shock speed of 5 km/s, the upper limit is about 6×10^{-6} s. With large explosive systems it is possible to increase this limit several fold (Walsh and Rice, 1957). The lower limit of about 10^{-8} s is determined by electronic response times and inaccuracies of mechanical assembly and impact (Hayes, 1972). Kormer *et al.* (1966) have suggested that index of refraction measurements can detect transformation times as short as 10^{-11} s. (The kinetics of phase transformations in shock-loaded solids has recently been reviewed by Hayes, 1977.)

The amount of material which must be transformed in order to effect a two-wave structure is defined implicitly by the requirement that the effective R-H curve must lie below the Rayleigh line passing through the transition point. This varies with amplitude of the Plastic I wave and relates to detector resolution (Forbes, 1976).

If a transition has been detected, or is thought to have been detected, identification of the new phase is difficult. The new phase may be metastable or it may be a different stable phase than observed statically (Hayes, 1974). In principle it may be possible to make flash x-ray diffraction measurements of the high-pressure phase (Johnson and Mitchell, 1972). The equation of state of the new phase can be estimated by the procedures described in Sec. II.G, but identification of the new phase is normally accomplished through close comparison of shock and complementary static pressure measurements.

Effects of finite transformation rate on shock-wave structure can be described by incorporating a rate function

$$d\alpha/dt = \psi(V, T, \alpha) \quad (40)$$

in a simple model of constitutive relations to be used with the flow equations, Eqs. (5), (6), and (8), where α is mass fraction of the second phase. Solution of these equations for some simple problems suggests experimental procedures to be followed in measuring reaction rates.

Recall that each phase in a two-phase system is represented by a surface in P - V - T space, and that the surfaces do not intersect ("system" here refers to a small mass element). In equilibrium the space between surfaces is bridged by a cylindrical surface with generatrix parallel to the V axis. When the transition is out of equilibrium, the entire range of both surfaces and the entire space between them must be considered momentarily accessible to the system. The exact state path is determined by interactions of the changing stress

and temperature fields and the rate law, Eq. (40). These interactions are calculated by combining constitutive relations of the material with the flow equations. In the simplest case, constitutive relations of the two individual phases are their equations of state. For the mixed phase, they consist of an appropriate mixture of equations of state of the two phases and the transition rate law. Mass exchange then becomes an irreversible process.

Assume that the following conditions apply in a partially transformed state:

1. Shear stresses are negligible.
2. Pressure is common to both phases.
3. Temperature is common to both phases.
4. Particle velocity, U_p , is common to both phases.
5. Interface energy is negligible.

Conditions (2), (3), and (5) are to some extent incompatible since (2) and (3) require the presence of many small islands of the second phase dispersed in the first, whereas this condition is just the one which tends to make interface energy important. Because of the complexity, this difficulty is ignored for the present, but it must be kept in mind for future consideration. Condition (4) is reasonable for solid-solid transitions, perhaps somewhat less reasonable for liquid-solid, and unreasonable for liquid-vapor transitions, which are not considered here.

With the above assumptions, state variables at each point in the continuum are unique. From assumption (5),

$$E(P, T) = (1 - \alpha)E_1(P, T) + \alpha E_2(P, T) \quad (41)$$

and

$$V(P, T) = (1 - \alpha)V_1(P, T) + \alpha V_2(P, T). \quad (42)$$

Subscripts "1" and "2" refer to first and second phases, respectively. Differentiating Eqs. (41) and (42) yields, within the mixed phase region,

$$dV = (1 - \alpha)dV_1 + \alpha dV_2 + (V_2 - V_1)d\alpha, \quad (43)$$

$$dE = (1 - \alpha)dE_1 + \alpha dE_2 + (E_2 - E_1)d\alpha. \quad (44)$$

Equations of state in the two phases are taken in the form

$$V_i = V_i(P, T), \quad (45)$$

$$E_i = E_i(P, T), \quad (46)$$

$$i = 1, 2.$$

Equations (43) and (44) and the differentials of (45) and (46) contain nine variables: dV , dE , dV_1 , dV_2 , dE_1 , dE_2 , $d\alpha$, dP , and dT . When these six equations are combined with the first law in the form

$$dE = -PdV \quad (47)$$

the resulting set of equations can be solved for dP and dT in terms of dV and $d\alpha$ (Horie and Duvall, 1968a, 1968b; Andrews, 1973; Hayes, 1975).

$$dP = a_{11}dV + a_{12}d\alpha, \quad (48)$$

$$dT = a_{21}dV + a_{22}d\alpha, \quad (49)$$

where the a_{ij} 's are functions of α , P , and T .