

FIG. 2. Hugoniot curves for a gas which can dissociate and for a metal which can undergo a polymorphic transition.

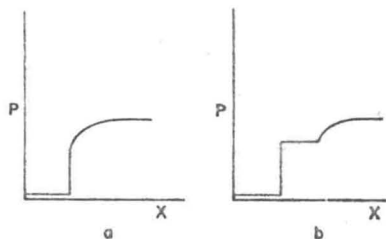


FIG. 3. Pressure profiles of a shock wave in a dissociating gas and of a wave system in a metal undergoing a transformation.

be written as

$$H_B = (1 - \lambda_B)H_1(T_B, p_B) + \lambda_B H_2(T_B, p_B) = H_1 + \lambda_B \Delta H_B,$$

$$v_B = (1 - \lambda_B)v_1(T_B, p_B) + \lambda_B v_2(T_B, p_B) = v_1 + \lambda_B \Delta v_B,$$

where ΔH_B and Δv_B are the changes in specific enthalpy and volume in the transformation at the temperature and pressure corresponding to an arbitrary point B in the region of mixed phases. From the Hugoniot equation, we have a relation between the specific enthalpy and volume at point B and on the coexistence line at point A .

$$H_B = H_A + \frac{1}{2}(p_B - p_A)(v_A + v_B).$$

$H_1(T_B, p_B)$ and $v_1(T_B, p_B)$, quantities associated with phase 1 at a pressure and temperature corresponding to point B , can be represented by the first two terms of a Taylor series in T and p about H_A and v_A . Finally, the Clapeyron equation gives for a first-order transition

$$\Delta H / \Delta v = T dp / dT,$$

where dp/dT is the slope of the coexistence line. From the above equations, one obtains

$$\left(\frac{\Delta H}{\Delta v}\right)_B = \frac{(p_B - p_A)[\frac{1}{2}(v_B + v_A) - (\partial H / \partial p)_T] - C_p(T_B - T_A)}{v_B - v_A - (\partial v / \partial p)_T(p_B - p_A) - (\partial v / \partial T)_p(T_B - T_A)}$$

In the limit as point B approaches point A , that is, in the limit of a very weak second wave, it can be shown that the above equation reduces to

$$\left(\frac{dp}{dT}\right)^2 + \left(\frac{2\alpha}{\kappa_{AB} - \kappa}\right)\frac{dp}{dT} - \frac{C_p}{Tv(\kappa_{AB} - \kappa)} = 0, \quad (1)$$

where $\alpha = (1/v)(\partial v / \partial T)_p$, the thermal expansion coefficient; $\kappa_{AB} = -(1/v) \lim_{B \rightarrow A} [(v_B - v_A) / (p_B - p_A)]$, a shock compressibility directly related to the velocity of the second wave; and $\kappa = -(1/v)(\partial v / \partial T)_p$, the isothermal compressibility of the original phase. All unspecified quantities are evaluated at point A in the original phase. Thus the slope of the coexistence line and the ratio of enthalpy to volume change in the reaction can be determined from careful equation of state experiments and knowledge of the thermal expansion coefficient, specific heat, and compressibility

of the original phase in the vicinity of the transition point. An additional conclusion which can be drawn from this development is that the slope of the Hugoniot curve above the coexistence line in the p - v plane will be nonzero so long as ΔH for the reaction is finite.

If it is assumed that the rate of the crystallographic transformation from one lattice to another is slow compared to the rate at which kinetic energy can be distributed in the lattice, it is possible to gain some insight into the structure of the shock-wave system produced near a transition by noting the similarity to the structure of a shock wave in a reacting gas. In Fig. 2 the Hugoniot curves are shown for a gas which can dissociate and for a metal which exhibits a transformation. In both cases the dashed curves represent the unstable states produced by the shock before reaction has had time to occur.

In the reacting-gas case it is well known that an essentially discontinuous shock process changes the initial state of the gas to one in which only the translational and perhaps the rotational degrees of freedom are fully excited. Then as other degrees of freedom are excited or as chemical reactions proceed, the pressure and volume point moves up the Rayleigh line from point 2 toward the equilibrium point 3 at a rate determined by the kinetics of the reactions involved. The structure of this shock is illustrated by the pressure profile shown in Fig. 3(a).

A similar structure would be expected for the strong shock in a metal represented by line K in Fig. 2(b). An essentially discontinuous shock will carry the metal to point 2 on the extension of the Hugoniot of the low-pressure modification of the material. Then as the transformation occurs, the state point will move from 2 to 3. The shock-wave structure illustrated in Fig. 3(a) persists as the shock in the metal becomes weaker until the velocity represented by Line L in Fig. 2(b) is reached. At still lower shock strengths the wave causing the compression from point 2' to 3' moves at a slower velocity, causing two waves to be produced with a pressure profile as sketched in Fig. 3(b).

The foregoing is concerned only with the steady-state wave system. The transient flow which leads to this steady-state shock configuration is not well understood at the present time; but it probably has the important features discussed below. When a shock first enters the metal, the state produced by the shock must lie on the unstable extension of the first-phase Hugoniot