If the transition occurs under equilibrium conditions, the Clausius–Clapeyron relation with latent heat of transformation, $L$, applies:

$$dP/dT = \Delta S/\Delta V = f(P) = L/T\Delta V, \tag{50}$$

where $f(P)$ is a known function. Divide Eq. (48) by (49), set the ratio equal to $f(P)$, and solve for $d\alpha$. This yields

$$d\alpha = (a_{21}f - a_{11})dV/(a_{12} - a_{22}f). \tag{51}$$

Substitution of Eq. (51) into (48) and (49) yields for the *equilibrium transition*

$$dP = (a_{12}a_{21} - a_{11}a_{22})f\,dV/(a_{12} - a_{22}f) \tag{52}$$

and

$$dT = dP/f(P). \tag{53}$$

Equations (43)–(46) and (51)–(53) comprise the constitutive relations for the mixed phase region when the transformation occurs under equilibrium conditions. For the irreversible case, Eqs. (43)–(46), (48), (49), and (40) comprise the constitutive relations. To use them, divide all differentials by $dt$ to form convective derivatives. These are then combined with the flow equations to form a complete set. Specification of initial and boundary values specifies a problem.

For the equilibrium transition, Eq. (52), the effect of a step increase in pressure at the sample surface is to produce a double shock wave like that shown in Fig. 6; amplitude of the first shock is the transition pressure $p_x^{TL}$.

For the irreversible case, where Eq. (40) applies, application of a step $P_2$ at the sample surface produces a shock wave in which the initial step in pressure decays toward the transition pressure as it propagates into the sample. This is illustrated in Fig. 13. The wave progresses toward the equilibrium form of Fig. 6 at a rate determined by Eq. (40). The simplest procedure for estimating transition rate is to measure the amplitude of the first wave for different specimen thicknesses and compare with calculated decay curves.

If the problem is drastically simplified by assuming that the first shock is a discontinuity propagating *at sound velocity* (Duvall, 1964), with $\Delta V$ = const, $C_{p1} = C_{p2}$, $V_1(P, T)$ independent of $T$, $dV_1/dP$ = const, and if Eq. (40)

is approximated by

$$d\alpha/dt = -(\alpha - \alpha_{eq})/t_0 \tag{54}$$

with $t_0$ constant and $\alpha_{eq}$ defined by Eq. (42) in the mixed phase region, then it follows that amplitude $P_1$ of the first shock varies with propagation distance as (Horie and Duvall, 1968b)

$$P_1 = P_2 - (x\Delta V/2U_s^{(1)}t_0)dP/dV_1 \quad V_1 \leqslant V_{TL} + \Delta V$$
$$= P^{TL} + (P_2 - P^{TL})\exp(-x/2U_s^{(1)}t_0)$$
$$\times V_{TL} + \Delta V \leqslant V_1 \leqslant V_A, \tag{55}$$

where $U_s^{(1)}$ is propagation speed of the first shock and $(P^{TL}, V_{TL})$ is the point at which the R–H curve in phase 1 intersects the mixed phase boundary.

Equation (54) is an oversimplified form of the law for irreversible transformation. An improved form has been given by Andrews (1970, 1971), and an elegant formulation of the entire problem has recently been given by Hayes (1975).

There has been little study of transformation rate effects in shock-induced transitions. Some authors have reported effects of driving pressure on transition pressure (Loree *et al.*, 1966a). According to Eq. (55), this may be a manifestation of finite transformation rate. Novikov *et al.* (1965) have interpreted rise time in the third shock in iron (the Plastic II wave) in terms of reaction rate; but other rate-dependent effects, including viscosity, may enter here, as does also the effective equilibrium R–H curve in the mixed phase region (cf. Sec. II.D). Specific attention to transformation rates has been given by Warnes (1967) for antimony, Hayes (1974) for KCl, Barker and Hollenbach (1974) and Forbes and Duvall (1975) for iron. Their results, discussed in Sec. IV, show that transition kinetics can be significant and can be measured at the boundary of the mixed phase region. This is accomplished by the simple expedient of measuring the rate of decay of the Plastic I wave and deducing the initial transformation rate, from Eq. (55) or some equivalent. Limitations on the technique are provided by time resolution of the measurement and by size of the shock assembly. This measurement does not directly give information about transition rate in the mixed phase region. That must be obtained from comparisons of measured and calculated wave profiles and from the steady profile of the Plastic II wave (Novikov *et al.*, 1965).

## G. Properties of the high-density phase from shock data

The problem is indicated in Fig. 14. The point $H$ has been determined experimentally, so $P^T$ and $V_1^T$ are measured directly; internal energy $E_1^T$ is calculated from the Rankine–Hugoniot relation. The equation of state of phase 1 is presumed known, so temperature $T^T$ and entropy $S_1^T$ can be calculated. A portion of the measured R–H curve, $LM$, has been identified as lying in phase 2. The Clausius–Clapeyron coefficient $dP/dT$ is presumed known. We wish to determine the parameters $V_2^T$ and $S_2^T$ and the equation of state of the high-density phase.

On $LM$, $P_2$, $V_2$, and $E_2$ are known from the jump conditions. The information required to extend our know-


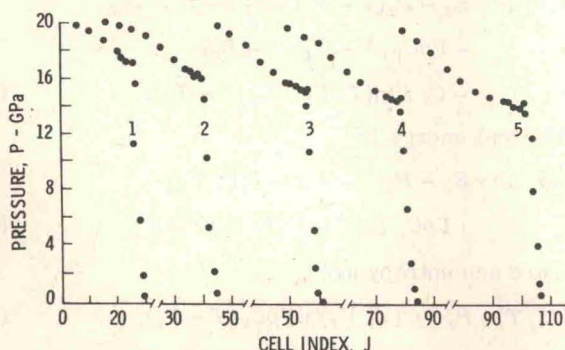
FIG. 13. Pressure profiles for a 20.0 GPa shock wave in iron with rate-dependent phase transition: $t_0 = 1/3\ \mu s$, 1. $t = 0.526\ \mu s$, 2. $t = 0.812\ \mu s$, 3. $t = 1.105\ \mu s$, 4. $t = 1.554\ \mu s$, $\Delta V = -0.004$ cm$^3$/g (Horie and Duvall, 1968a). "Cell index" is a space coordinate in the direction of propagation.
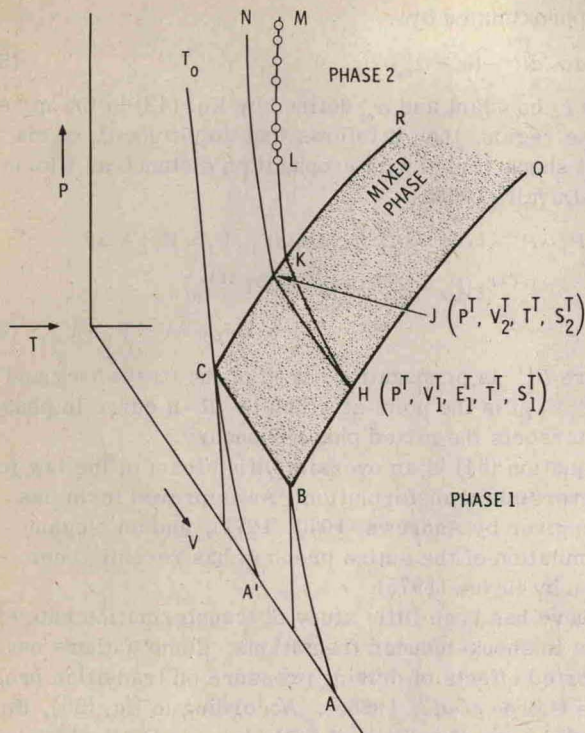
FIG. 14. $ABCD$ is isotherm at temperature $T_0$; $A'C$ is a metastable extrapolation of the phase 2 isotherm at $T_0$; $H$ is the intersection of the R–H curve in phase 1 with the mixed phase boundary, $BQ$; $HJN$ is an isotherm through $H$; $HKLM$ is the R–H curve in the mixed phase and phase 2; $LM$ is a section of the R–H curve in phase 2 determined by measurements.

ledge of these parameters into adjacent regions is defined by the thermodynamic differentials

$$dE = (-P + T\Gamma\rho C_V)dV + C_V dT, \tag{56}$$

$$dP = -(K/V)\,dV + \Gamma\rho C_V dT, \tag{57}$$

$$dS = \Gamma\rho C_V dV + C_V dT/T, \tag{58}$$

where $K$ is the isothermal bulk modulus, $\Gamma$ is the Gruneisen parameter, $C_V$ is the specific heat at constant volume, and $\rho = 1/V$. If $K$, $\Gamma$, and $C_V$ are assumed to be known functions of $V$ and $T$, Eqs. (56)–(58) can, in principle, be integrated, assuming $E$, $P$, $V$, $S$, and $T$ to be known at some reference point, say $L$ on the R–H curve $LM$. Of these five parameters, only two, $S_L$ and $T_L$, are unknown. The result of the integration is three functions:

$$E = E(V, T; S_L, T_L), \tag{59}$$

$$P = P(V, T; S_L, T_L), \tag{60}$$

$$S = S(V, T; S_L, T_L). \tag{61}$$

With attention fixed on the isotherm $T = T^T$, set $P = P^T$, $S = S_2^T, V = V_2^T, E = E_2^T$, and invoke the two additional conditions of equilibrium, assuming the phase change to be first order:

(i) Clausius–Clapeyron equation:

$$S_2^T - S_1^T = (V_2^T - V_1^T)dP/dT. \tag{62}$$

(ii) Equality of the Gibbs functions at the phase boundaries:

$$E_2^T - E_1^T = -P^T(V_2^T - V_1^T) + T^T(S_2^T - S_1^T). \tag{63}$$

Also, from Eq. (60),

$$P(V_2^T, T^T; S_L, T_L) = P^T. \tag{64}$$

Equations (62)–(64) can then, in principle, be solved for the three unknown parameters $S_L, T_L, V_2^T$, where $E_2^T$ and $S_2^T$ have been replaced by the functions on the right-hand sides of Eqs. (59) and (61). With $V_2^T$ determined, the volume change in transition is given by

$$\Delta V = V_2^T - V_1^T.$$

Of the functions $K$, $\Gamma$, and $C_V$, the first is dominant in determining $V_2^T$. The measured section, $LM$, of the R–H curve provides information about $K$. It can be used in the following way. Variations in entropy along the R–H curve are given by the equation (Duvall and Fowles, 1963)

$$2TDS = (V_0 - V)DP + (P - P_0)DV, \tag{65}$$

where capital "$D$" denotes variation along the R–H curve, and $(P_0, V_0)$ is the point at which the R–H curve is centered. Eliminating $DS$ between Eqs. (58) and (65) yields

$$\frac{DT}{DV} + \Gamma\rho T = \frac{V_0 - V}{2C_V}\frac{DP}{DV} + \frac{P - P_0}{2C_V} \equiv f(V). \tag{66}$$

Combining Eqs. (57) and (66) yields an expression for $K/V$

$$\frac{K}{V} = \left[\frac{\rho\Gamma(V_0 - V)}{2} - 1\right]\frac{DP}{DV} + \Gamma\rho\left(\frac{P - P_0}{2} - \Gamma\rho C_V T\right). \tag{67}$$

If $\Gamma$ is known, Eq. (66) can be integrated to give an expression for $T(V)$, along the R–H curve, which contains the reference temperature $T_L$. Except for this constant, Eq. (67) then gives the volume dependence of $K$ along the R–H curve. Its temperature dependence is made explicit by assuming a formula for $C_V$.

Several writers have considered the construction of complete equations of state for use in shock applications (Cowperthwaite, 1966; McQueen et al., 1967; Andrews, 1970, 1973; Hayes, 1972, 1974; Johnson et al., 1974). A particularly simple form is obtained if $\Gamma\rho$ and $C_V$ are assumed constant. Then the Helmholtz energy $A$ has the form

$$A(V, T) = E_L - P_L(V - V_L) - S_L T - f(V; V_L)$$
$$- \Gamma\rho C_V(V - V_L)(T - T_L)$$
$$- C_V T \ln(T/T_L) + C_V(T - T_L). \tag{68}$$

The internal energy is

$$E(V, T) = E_L - P_L(V - V_L) - f(V; V_L)$$
$$+ \Gamma\rho C_V T_L(V - V_L) + C_V(T - T_L). \tag{69}$$

Pressure and entropy are

$$P(V, T) = P_L + f'(V; V_L) + \Gamma\rho C_V(T - T_L), \tag{70}$$

$$S(V, T) = S_L + C_V \ln(T/T_L) + \Gamma\rho C_V(V - V_L). \tag{71}$$

Substitution of these equations into Eqs. (62)–(64) yields the following set to be solved for $T_L$, $S_L$, and $V_2^T$:

$$f'(V_2^T; V_L) + \Gamma\rho C_V(T^T - T_L) = P^T - P_L. \tag{72}$$