JOURNAL OF COMPUTATIONAL PHYSICS 7, 310–326 (1971)

Calculation of Mixed Phases in Continuum Mechanics*

D. J. ANDREWS†

Shock Dynamics Laboratory, Physics Department,
Washington State University, Pullman, Washington 99163

Received August 27, 1970

A general procedure is developed to calculate a phase transformation consistently. The differential forms of the equations constraining a binary mixture to be in equilibrium are inverted to obtain volume and internal energy as independent variables. The set of finite difference equations may be incorporated into a general purpose continuum mechanics program.

INTRODUCTION

The local thermodynamic variables of a material that are related most directly to the partial differential equations of continuum mechanics are pressure, volume, and internal energy. In finite difference methods of the von Neumann–Richtmyer [1] type, volume and internal energy must be the independent variables in the equation of state calculation, and pressure must be calculated from them. However, in the case of mixed phases the formulation of such an equation of state is complicated by constraints of equilibrium between the phases. The constraints of equal pressure and temperature in the two phases for given values of volume and internal energy form a set of simultaneous equations. The differential forms of the constraint equations may be solved more easily, since they are linear in the differentials. Therefore, a numerical integration procedure based on derivatives of the equation of state (specifically, second derivatives of a thermodynamic potential) will be developed. Increments of pressure and temperature will be calculated from given increments of volume and internal energy. The procedure may be incorporated into a general purpose continuum mechanics program. The molar Gibbs potential of each phase will be integrated numerically, in order to treat the phase transforma-

---

* Work done in partial fulfillment of the requirements for the Ph.D. degree at Washington State University. Supported by the Department of the Army, Ballistics Research Laboratory, under Contract No. DA-04-200-AMC-1702X.

† Present address: Department of Earth and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.

tion consistently. The procedure is thermodynamically consistent if the properties of each phase are consistent. Although a solid–solid phase transition is discussed, the method is also applicable to liquid and vapor.

1. MIXED PHASES

The assumptions to be made here regarding a mixture of phases will be identical to those of previous work [2, 3]. The material is assumed to be composed of small grains or crystallites, each of which is a pure phase. It is assumed that each grain is in a thermodynamic equilibrium state at each instant, regardless of whether the mixture is in equilibrium. It is assumed that each grain contains a large number of molecules, so that surface effects are not important, but that the grains are small enough that the material may be considered locally homogeneous on a macroscopic scale. At each point in the material the local macroscopic mass fraction of a phase is defined as the mass fraction of that phase in a neighborhood containing a large number of grains. Local values of molar volume and other extensive variables per mole or unit mass are defined by similar averages. It is assumed that the grains are small enough that pressure and temperature equilibrate to uniform values in each locality at much faster rates than any other rates of interest. In the case of a finite transformation rate the local composition may not be in equilibrium. In a mixture of phases in equilibrium the molar Gibbs potential of the two phases must be equal. If only a single phase exists, it is the phase with the smaller molar Gibbs potential at that pressure and temperature.

Let the mass fraction of the second phase be denoted by x. Then the mass fraction of the first phase is $(1 - x)$. The molar volume of the mixture is

$$V(P, T) = (1 - x)\, V_1(P, T) + x V_2(P, T), \tag{1.1}$$

where V_1 and V_2 are the molar volumes of the first and second phases at the same pressure and temperature. The molar internal energy of the mixture is

$$E(P, T) = (1 - x)\, E_1(P, T) + x E_2(P, T) \tag{1.2}$$

and similar equations hold for other extensive variables for one mole or one unit of mass. In all that follows extensive variables of the mixture will apply to one mole. An extensive variable of an individual phase will apply to one mole of that phase, not to one mole of the mixture. With these understandings, the adjective molar will be dropped from all of the following discussion.

Due to the constraint that pressure and temperature are the same in the two phases of the mixture, these variables are the natural set of independent variables to use when relating properties of the mixture to properties of the individual phases. As an example, consider derivatives of the volume of the mixture. Analogous equations hold for other extensive mixture variables. The differential of Eq. (1.1) is

$$dV = (1 - x)\,dV_1 + x\,dV_2 + (V_2 - V_1)\,dx, \tag{1.3}$$

where the differentials dV_1 and dV_2 satisfy the constraint that pressure and temperature differentials are the same in the two phases. Partial derivatives of volume at constant composition are

$$\left(\frac{\partial V}{\partial P}\right)_{T,x} = (1 - x)\left(\frac{\partial V_1}{\partial P}\right)_T + x\left(\frac{\partial V_2}{\partial P}\right)_T \tag{1.4}$$

and

$$\left(\frac{\partial V}{\partial T}\right)_{P,x} = (1 - x)\left(\frac{\partial V_1}{\partial T}\right)_P + x\left(\frac{\partial V_2}{\partial T}\right)_P. \tag{1.5}$$

Note that derivatives for the frozen mixture can be written as weighted averages of derivatives for the constituents, if pressure and temperature are the independent variables, but not if other variables are independent.

Determination of the mixture properties is most direct if pressure and temperature are the independent variables. Therefore, the properties of the individual phases should be available in the Gibbs representation. It will be assumed that subroutines have been written for each phase to calculate isothermal bulk modulus k_T, heat capacity at constant pressure C_p, and volume thermal expansivity α. These quantities are related simply to the second derivatives of the Gibbs potential:

$$\frac{\partial^2 G}{\partial P^2} = -V/k_T, \tag{1.6}$$

$$\frac{\partial^2 G}{\partial T^2} = -C_p/T, \tag{1.7}$$

$$\frac{\partial^2 G}{\partial P\,\partial T} = V\alpha. \tag{1.8}$$

The requirement of thermodynamic consistency is equivalent to compatibility of these derivatives. A generalized model that is consistent has been presented elsewhere [4]. Any model based on statistical mechanical considerations will be in the Helmholtz representation with volume and temperature as independent variables. Therefore, it will be assumed that the inputs to the lower level subroutines are temperature and volume of each phase, even though the output is in the Gibbs representation.

2. PHASES IN EQUILIBRIUM

In this section a general procedure will be developed to determine all thermodynamic variables for given increments of volume and internal energy. The procedure may be used as an element of a procedure to calculate adiabats and as an element of a general wave propagation program. The thermodynamic equations would appear more elegant if entropy rather than internal energy were chosen as an independent variable. Internal energy is chosen in order to make a straightforward and general connection with the equations of continuum mechanics.

Calculation for General Volume and Energy Increments

In the V–E plane, unlike the P–T plane, phases may coexist in a band with a finite width. All variables change continuously through this band. In a process that traverses this band, pressure and temperature need not be constant. The calculational procedure to be developed for the mixed phase region may also be used in the single phase regions if it is required that the mass fraction of each phase cannot be less than zero nor greater than one.

The first step of the procedure is to evaluate derivatives of volume and internal energy of the individual phases with respect to pressure and temperature. These are

$$\left(\frac{\partial V_i}{\partial P}\right)_T = -V_i/k_{Ti}\,, \tag{2.1}$$

$$\left(\frac{\partial V_i}{\partial T}\right)_P = V_i\alpha_i\,, \tag{2.2}$$

$$\left(\frac{\partial E_i}{\partial P}\right)_T = -P\left(\frac{\partial V_i}{\partial P}\right)_T - T\left(\frac{\partial V_i}{\partial T}\right)_P, \tag{2.3}$$

$$\left(\frac{\partial E_i}{\partial T}\right)_P = -P\left(\frac{\partial V_i}{\partial T}\right)_P + C_{pi}\,, \tag{2.4}$$

where the subscript i takes the values 1 and 2 for the first and second phases.

The next step is to form derivatives for the frozen mixture:

$$\left(\frac{\partial V}{\partial P}\right)_{T,x} = (1-x)\left(\frac{\partial V_1}{\partial P}\right)_T + x\left(\frac{\partial V_2}{\partial P}\right)_T, \tag{2.5}$$

$$\left(\frac{\partial V}{\partial T}\right)_{P,x} = (1-x)\left(\frac{\partial V_1}{\partial T}\right)_P + x\left(\frac{\partial V_2}{\partial T}\right)_P, \tag{2.6}$$

$$\left(\frac{\partial E}{\partial P}\right)_{T,x} = (1-x)\left(\frac{\partial E_1}{\partial P}\right)_T + x\left(\frac{\partial E_2}{\partial P}\right)_T, \tag{2.7}$$

$$\left(\frac{\partial E}{\partial T}\right)_{P,x} = (1-x)\left(\frac{\partial E_1}{\partial T}\right)_P + x\left(\frac{\partial E_2}{\partial T}\right)_P. \tag{2.8}$$

Only three of these derivatives are independent, but the following substitutions will be more straightforward if all four derivatives are evaluated.

The three equations to be satisfied by equilibrium states in the mixed phase region are

$$V = (1 - x)\, V_1(P, T) + xV_2(P, T), \tag{2.9}$$

$$E = (1 - x)\, E_1(P, T) + xE_2(P, T), \tag{2.10}$$

$$0 = G_2(P, T) - G_1(P, T). \tag{2.11}$$

For given values of V and E these equations are to be solved for x, P, and T. In the case of arbitrary equations of state the differential forms of these equations may be solved by a general numerical procedure more easily than the equations themselves. The differential forms of Eqs. (2.9), (2.10), and (2.11) are

$$dV = \left(\frac{\partial V}{\partial P}\right)_{T,x} dP + \left(\frac{\partial V}{\partial T}\right)_{P,x} dT + (V_2 - V_1)\, dx, \tag{2.12}$$

$$dE = \left(\frac{\partial E}{\partial P}\right)_{T,x} dP + \left(\frac{\partial E}{\partial T}\right)_{P,x} dT + (E_2 - E_1)\, dx, \tag{2.13}$$

$$d(G_2 - G_1) = (V_2 - V_1)\, dP - (S_2 - S_1)\, dT. \tag{2.14}$$

Equations (2.12) and (2.13) are the same as Eqs. (3.14) and (3.15) of Ref. [2]. Define $G_{21} = G_2 - G_1$. For mixed phases in equilibrium, $dG_{21} = 0$. In the following paragraphs dG_{21} may be arbitrary so that the relations may also be applied in the case of a finite transformation rate.

Let $\mathscr{X}$ indicate the column matrix with elements V, E, and G_{21}. Let $\mathscr{Y}$ be the column matrix with elements P, T, and x. Let $\mathfrak{A}$ be the square matrix of the coefficients of Eqs. (2.12), (2.13), and (2.14). Then the equations above may be written in the compact form

$$d\mathscr{X} = \mathfrak{A}\, d\mathscr{Y}. \tag{2.15}$$

The problem is to solve for $d\mathscr{Y}$ for given $d\mathscr{X}$. The inverse of the matrix must be calculated. Then

$$d\mathscr{Y} = \mathfrak{A}^{-1}\, d\mathscr{X}. \tag{2.16}$$

The solution for dP and dT will be examined more explicitly. Suppose that the differential of the mass fraction dx has already been determined. Define

$$dV_x = dV - (V_2 - V_1)\, dx \tag{2.17}$$

and

$$dE_x = dE - (E_2 - E_1)\, dx. \tag{2.18}$$

Then the two remaining simultaneous equations to be solved for dP and dT are

$$dV_x = \left(\frac{\partial V}{\partial P}\right)_{T,x} dP + \left(\frac{\partial V}{\partial T}\right)_{P,x} dT \tag{2.19}$$

and

$$dE_x = \left(\frac{\partial E}{\partial P}\right)_{T,x} dP + \left(\frac{\partial E}{\partial T}\right)_{P,x} dT. \tag{2.20}$$

The matrix of coefficients on the right sides is to be inverted. The determinant of the matrix is the Jacobian of volume and internal energy with respect to pressure and temperature at constant composition. The elements of the inverse matrix may be found using properties of Jacobians [5]. Let J be the Jacobian

$$J = \frac{\partial(V, E)}{\partial(P, T)_x}. \tag{2.21}$$

Then

$$\left(\frac{\partial P}{\partial V}\right)_{E,x} = \left(\frac{\partial E}{\partial T}\right)_{P,x} \Big/ J, \tag{2.22}$$

$$\left(\frac{\partial P}{\partial E}\right)_{V,x} = -\left(\frac{\partial V}{\partial T}\right)_{P,x} \Big/ J, \tag{2.23}$$

$$\left(\frac{\partial T}{\partial V}\right)_{E,x} = -\left(\frac{\partial E}{\partial P}\right)_{T,x} \Big/ J, \tag{2.24}$$

$$\left(\frac{\partial T}{\partial E}\right)_{V,x} = \left(\frac{\partial V}{\partial P}\right)_{T,x} \Big/ J. \tag{2.25}$$

The solution for dP and dT is

$$dP = \left(\frac{\partial P}{\partial V}\right)_{E,x} dV_x + \left(\frac{\partial P}{\partial E}\right)_{V,x} dE_x, \tag{2.26}$$

$$dT = \left(\frac{\partial T}{\partial V}\right)_{E,x} dV_x + \left(\frac{\partial T}{\partial E}\right)_{V,x} dE_x. \tag{2.27}$$

This solution for dP and dT is a subset of the solution of three simultaneous equations indicated by Eq. (2.16), if dx is determined from those equations. For arbitrary dx, Eqs. (2.26) and (2.27) give the solution satisfying the constraints of equal pressure and temperature in the two phases.

Given states of the individual phases, the matrix $\mathfrak{A}^{-1}$ may be determined by a sequence of explicit substitutions, starting from Eq. (2.1). This sequence of substitutions may form an algorithm for numerical calculations. For numerical calculation, differentials are to be replaced by finite differences. Values of variables at the beginning of a step are indicated by the superscript o for old, values at the end of a step by an n for new, and values halfway through a step by h. The matrix $\mathfrak{A}^{-1}$ is to be evaluated at the midpoint of the integration step,

$$(\mathfrak{A}^{-1})^h = \mathfrak{A}^{-1}(T^{\mathrm{h}}, V_1^{\mathrm{h}}, V_2^{\mathrm{h}}, E_1^{\mathrm{h}}, E_2^{\mathrm{h}}, S_1^{\mathrm{h}}, S_2^{\mathrm{h}}). \tag{2.28}$$

In the finite difference analog of Eq. (2.16), dV is to be replaced by ΔV, and dE by ΔE. If both the beginning and the end of the step are in the mixed phase region, then G_{21}^{n} and G_{21}^{o} are both zero and ΔG_{21} is zero. Both this case and the case in which the step goes from a single phase region into the mixed phase region are accounted for by the more general expression

$$\Delta G_{21} = -G_{21}^{\mathrm{o}}\,. \tag{2.29}$$

The case in which the step leaves the mixed phase region is accounted for by requiring that x be bounded by zero and one. The finite difference equations for ΔP, ΔT, and Δx are represented formally by

$$\begin{pmatrix} \Delta P \\ \Delta T \\ \Delta x \end{pmatrix} = (\mathfrak{A}^{-1})^{\mathrm{h}} \begin{pmatrix} \Delta V \\ \Delta E \\ -G_{21}^{\mathrm{o}} \end{pmatrix}. \tag{2.30}$$

Only Δx should be calculated from Eq. (2.30). If the new value of x lies outside either bound, it is set equal to that bounding value. If x is adjusted, then Eq. (2.30) does not hold. The adjusted value of Δx is used to determine ΔP and ΔT using finite difference analogs of Eqs. (2.17)–(2.27), which are valid for any Δx. This procedure is efficient, since the determinant (2.21) has already been evaluated as a cofactor of the determinant of $\mathfrak{A}$. By this procedure, the Gibbs potentials of the two phases are equal in the mixed phase region and become unequal in the single phase regions. The single phase that exists is automatically the phase with the smaller Gibbs potential, since use of Eq. (2.29) continually forces x in the direction of stability.

After ΔP and ΔT are determined, increments of volume and internal energy of the individual phases may be found using derivatives that have already been evaluated,

$$\Delta V_i = \left(\frac{\partial V_i}{\partial P}\right)_T^{\mathrm{h}} \Delta P + \left(\frac{\partial V_i}{\partial T}\right)_P^{\mathrm{h}} \Delta T, \tag{2.31}$$

$$\Delta E_i = \left(\frac{\partial E_i}{\partial P}\right)_T^{\mathrm{h}} \Delta P + \left(\frac{\partial E_i}{\partial T}\right)_P^{\mathrm{h}} \Delta T. \tag{2.32}$$

Here the subscript i takes the values 1 and 2 for the two individual phases. Then new values of the extensive variables of each phase are found by

$$V_i^{\mathrm{n}} = V_i^{\mathrm{o}} + \Delta V_i\,, \tag{2.33}$$

$$E_i^{\mathrm{n}} = E_i^{\mathrm{o}} + \Delta E_i\,, \tag{2.34}$$

$$S_i^{\mathrm{n}} = S_i^{\mathrm{o}} + C_{pi}^{\mathrm{h}} \Delta T / T^{\mathrm{h}} - V_i^{\mathrm{h}} \alpha_i^{\mathrm{h}} \Delta P, \tag{2.35}$$

$$G_i^{\mathrm{n}} = G_i^{\mathrm{o}} - S_i^{\mathrm{h}} \Delta T + V_i^{\mathrm{h}} \Delta P. \tag{2.36}$$

Values appropriate to the midpoint of the step are taken to be averages of new and old values. Values of three variables for each phase, V_i, S_i, and E_i or G_i, must be saved from the previous step and must be specified at the beginning of the integration.

The centered finite difference equations developed here are accurate to second order. They are not explicit, for values of variables halfway through the step are needed to calculate the increments. A solution may be found by iteration. Old values of variables may be used to find a first approximation to the matrix $(\mathfrak{A}^{-1})^{\mathrm{h}}$. Then first approximations may be found for the increments and the new values of the unknown variables. Approximate values of variables at the midpoint of the step may be used to re-evaluate the matrix, and the procedure may be repeated. The iteration is done to get correct centering of the finite difference equations; it is not done to solve the set of simultaneous Eqs. (2.12)–(2.14). The solution of the latter is accomplished precisely within each iteration.

The iteration has been described as if both ΔV and ΔE were prescribed before the integration step were taken. In applications to continuum mechanics ΔV will be determined from velocities by the equation of continuity, and will be fixed during the equation of state calculation. However, ΔE depends on the new value of pressure, for, in addition to other possible terms, it always contains the hydrodynamic work. Therefore, the calculation of ΔE must be included within the equation of state iteration. Some special cases will be considered in the succeeding sections.

Integration on an Isentrope

The centered finite difference equation for the internal energy increment on an adiabat is

$$\Delta E = -P^{\mathrm{h}} \Delta V. \tag{2.37}$$

If the phases are required to be in equilibrium the adiabat should be an isentrope. The equation of state iteration consists of this equation followed by Eqs. (2.28)–

(2.36). In the first pass through the procedure, P^h on the right side of Eq. (2.37) is approximated by the old value of pressure. In succeeding iterations the currently available approximation is used.

In order to test the convergence of the iteration, the finite difference equations were programmed and integrated on a computer. The calculations were done in single precision floating point on an IBM 360. Roundoff error for one operation is one part in 10^6. The equation of state parameters used in the test were reasonably representative of the alpha (bcc) and the epsilon (hcp) phases of iron. The initial values were representative of the state at room temperature and zero pressure. The energy difference between the phases was representative, but did not fit the transition pressure accurately. Three iterations were done in each step.

The integrations started at a volume of 7.09264 cm³/mole. In the first test the volume increment was -0.01 cm³/mole for each integration step. Successive approximations to pressure in a step in the mixed phase region are shown in Table I. The values of pressure and volume calculated in the previous step are the zeroth approximation and are listed on the first line. The quantity δP listed in the last column is the difference between each approximation and the final value. In this case the calculation converges to the accuracy of the machine in one iteration.

TABLE I

Convergence of Pressure for $\Delta V = -0.01$ cm³/mole

Iteration Number	V (cm³/mole)	P (megabar)	δP (megabar)
0	6.44264	0.1249712	−0.0000509
1	6.43264	0.1250221	0
2	6.43264	0.1250221	0
3	6.43264	0.1250221	...

In the second test the volume increment was 11 times larger, so that the relative volume step was about one part in 60. The mixed phase region was reached in the fourth step and the transition was complete in the eighth step. Successive approximations to pressure in the sixth step are shown in Table II. The calculation converges to the level of roundoff error in two iterations. Successive values of δP are consistent with a geometrically convergent sequence. The ratios of corresponding δP values in Table I and Table II suggest that the convergence factor is proportional to ΔV. The relative difference in pressure at the same volume in the two tests is about 6×10^{-5}.

In the mixed phase region the calculated molar Gibbs potentials are equal. The entropy of the mixture is constant within the roundoff error. The values of

TABLE II

Convergence of Pressure for $\Delta V = -0.11$ cm³/mole

Iteration Number	V (cm³/mole)	P (megabar)	δP (megabar)
0	6.54264	0.1244478	−0.0005673
1	6.43264	0.1250220	+0.0000069
2	6.43264	0.1250152	+0.0000001
3	6.43264	0.1250151	...

V_1, V_2, E_1, and E_2 are consistent with the values of V, E, and x according to Eqs. (2.9) and (2.10) within the roundoff error. In the interest of precise conservation of mass and energy a corrective procedure was used at first to force Eqs. (2.9) and (2.10) to hold precisely in each iteration. Values of ΔV_1 and ΔV_2 were adjusted while holding the ratio constant, and the same was done with the internal energies. The rate of convergence was the same with and without the corrective procedure. In the interest of simplicity it was abandoned.

Effect of Shear Strength

Up to this point we have considered the material to be a fluid. In the case of an elastic-plastic material, internal energy is a function of entropy and the strain tensor. A generalized Gibbs potential might be formed by Legendre transformations, replacing strain components as independent variables by stress components. Two phases in equilibrium in the same stress state would have equal generalized Gibbs potentials. Such a theoretical formulation is not justified in the real situation. If the grains of each phase have a finite strength, then a mixture of grains in stress equilibrium may not be in a uniform stress state. Local values of stress components might differ from the average or macroscopic values. Therefore, to avoid unwarranted complications, considerations of phase equilibrium will be based on the mean compressive stress, the pressure.

It is assumed that pressure is independent of strain deviators, so that it is uniquely determined by temperature and volume. This assumption is valid for isotropic materials and for cubic crystals but not for hexagonal crystals. Since there is no volume change associated with plastic strain, yielding affects the pressure only indirectly, through an increase in thermal energy.

Calculation of elastic-plastic behavior of stress deviators will follow Wilkins [6]. The internal energy increment should be recalculated in each iteration of the equation of state calculation. In an elastic-plastic material with viscosity it is given by the finite difference equation,

$$\Delta E = \Delta Z - (P^{\mathrm{h}} + Q^{\mathrm{h}})\,\Delta V, \tag{2.38}$$

where ΔZ is the work done against stress deviators in the time step and Q is the contribution to pressure from viscosity. In the case of uniaxial strain

$$\Delta Z = -s^{\mathrm{h}} \Delta V, \tag{2.39}$$

where s^{h} is the stress deviator in the direction of compression halfway through the time step. The change of internal energy due to any form of heat transport could be accounted for by adding a term analogous to ΔZ in Eq. (2.38). The equation of state iteration consists of Eq. (2.38) followed by Eqs. (2.28)–(2.36). In each iteration the currently available approximation to P^{h} is used on the right side of Eq. (2.38).

3. TIME-DEPENDENT PHASE TRANSFORMATION

In this section a finite transformation rate will be considered. A calculational procedure for a time-dependent transformation will be developed and applied to the propagation of a nonsteady shock.

Kinetics of the Phase Change

The transformation rate will be treated according to linear irreversible thermodynamics [7]. Time will be represented by a lower case t, and the upper case will remain temperature. If no interaction between different irreversible processes is considered, then the time rate of change of the mass fraction of the second phase is

$$\frac{dx}{dt} = -L(G_2 - G_1), \tag{3.1}$$

where L is a positive constant [2].

For numerical calculation one could use a finite difference analog of Eq. (3.1) to determine Δx from Δt and finite difference analogous of Eqs. (2.17)–(2.27) to determine ΔP and ΔT from ΔV, ΔE, and Δx. Only the two equations constraining pressure and temperature to be the same in the phases for given volume and internal energy need be inverted. Therefore, the calculation would be simpler than in the case of equilibrium composition.

However, some further analysis is necessary to describe the transition rate in terms of a relaxation time. The relaxation time is defined to be the time interval needed for the mixture to reach equilibrium composition if the transformation continued at its present instantaneous rate. It is necessary for accuracy in the finite difference calculation that the time step be much smaller than the relaxation time. The calculation might be unstable for time steps larger than the relaxation time.

Consider a mixture of phases with given total volume and internal energy.

Define $G_{21} = G_2 - G_1$. The relation between a change in x and the corresponding change in G_{21} at constant volume and internal energy is

$$\begin{pmatrix} 0 \\ 0 \\ dG_{21} \end{pmatrix} = \mathfrak{A} \begin{pmatrix} dP \\ dT \\ dx \end{pmatrix}, \tag{3.2}$$

where $\mathfrak{A}$ is the matrix of coefficients of Eqs. (2.12)–(2.14). The solution for dx is

$$dx = \frac{J}{|\,\mathfrak{A}\,|}\, dG_{21}, \tag{3.3}$$

where J is the Jacobian defined in Eq. (2.21) and the denominator is the determinant of $\mathfrak{A}$. If this linear relationship is used to approximate differences between the present state and equilibrium, then the equilibrium composition, x_{eq}, is given by

$$x_{\mathrm{eq}} - x = (J/|\,\mathfrak{A}\,|)(-G_{21}). \tag{3.4}$$

The differential equation for x in terms of a relaxation time τ is

$$dx = (x_{\mathrm{eq}} - x)\, dt/\tau, \tag{3.5}$$

and expressed in terms of the present state, it is

$$dx = -(J/|\,\mathfrak{A}\,|)\, G_{21}\, dt/\tau. \tag{3.6}$$

The transformation rate given by Eq. (3.6) is proportional to $-G_{21}$, just as it is in Eq. (3.1). By equating these two expressions, the relaxation time may be related to the rate constant L,

$$\tau = J/(|\,\mathfrak{A}\,|\, L). \tag{3.7}$$

The relaxation time may be found more directly by combining Eqs. (3.1) and (3.3) to obtain

$$\frac{dG_{21}}{dt} = -\frac{L\,|\,\mathfrak{A}\,|}{J}\, G_{21}. \tag{3.8}$$

Then the relaxation time may be identified as the quantity given in Eq. (3.7).

If L is constant, then the relaxation time will be a function of pressure and temperature, for it depends on the states of the individual phases. In the case of the alpha–epsilon transition in iron, however, pressure and temperature vary only slightly on an adiabat or Hugoniot curve in the mixed phase region. Therefore, it is not a bad approximation to let τ be constant.

There is no unique definition of the relaxation time. It has been developed here by considering a hypothetical approach to equilibrium at constant volume and internal energy. If a different pair of variables were held constant, a different relaxation time would be found. According to linear irreversible thermodynamics, the differential equation valid in any process is Eq. (3.1). A given value of L will correspond to different values of τ in a given state for different definitions of τ.

In order to describe the demonstration calculation to be done in the next section in terms of a relaxation time, Eq. (3.1) will not be used. There is no reason it could not be used, if care were taken to keep the time step small. Equation (3.6) with a constant τ will be used. The justification is that Eq. (3.6) is equivalent to Eq. (3.1) with an approximately constant value of L.

In the numerical calculational procedure Δx is found from Δt using a finite difference analog of Eq. (3.6). The coefficient of Δt on the right side should be evaluated at the midpoint of the time step. Then ΔP and ΔT may be found from ΔV, ΔE, and Δx using finite difference analogous of Eqs. (2.17)–(2.27). An iteration is necessary to get proper centering of the finite difference equations.

Nonsteady Shock Wave

The scope of this paper is restricted to presenting a general calculational method; it is not intended to be a systematic study of shock-induced phase transitions. To demonstrate the applicability of the method, results of a single problem will be reported here.

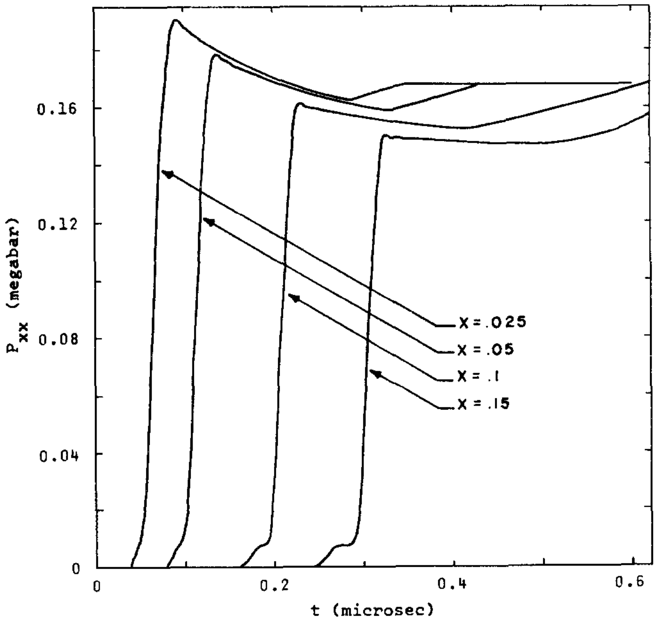

FIG. 1. Shock profiles near the impact surface. Longitudinal compressive stress is plotted as a function of time at points initially at 0.025 cm, 0.05 cm, 0.1 cm, and 0.15 cm from the impact surface.

The calculational procedure discussed above was incorporated into a general purpose finite difference computer program for continuum mechanics problems. The finite difference equations for continuum motion were of the von Neumann–Richtmyer type [1] with one space coordinate and time as independent variables.

The material chosen for the problem is iron, which transforms from the alpha (bcc) phase to the epsilon (hcp) phase at about 130 kilobars. In the model used, the volume change in the transition is -0.33 cm^3/mole and the entropy change is 2.22J/mole–deg on the room temperature isotherm. The entropy change is small compared to that in most phase transitions. The volume change and the entropy change have opposite signs, as in the ice–water transition. On the isentrope starting at standard conditions temperature decreases about 40 deg. in passing through the mixed phase region.

The problem consists of a plane slab of iron initially at rest at standard conditions. Let X represent the spatial coordinate. The left surface of the slab, located initially at $X = 0$, was required to move to the right at a constant velocity of 0.05 cm/μ sec. This boundary condition corresponds to a symmetric impact of two iron slabs at a relative velocity of 0.1 cm/μ sec. The equation of state para-

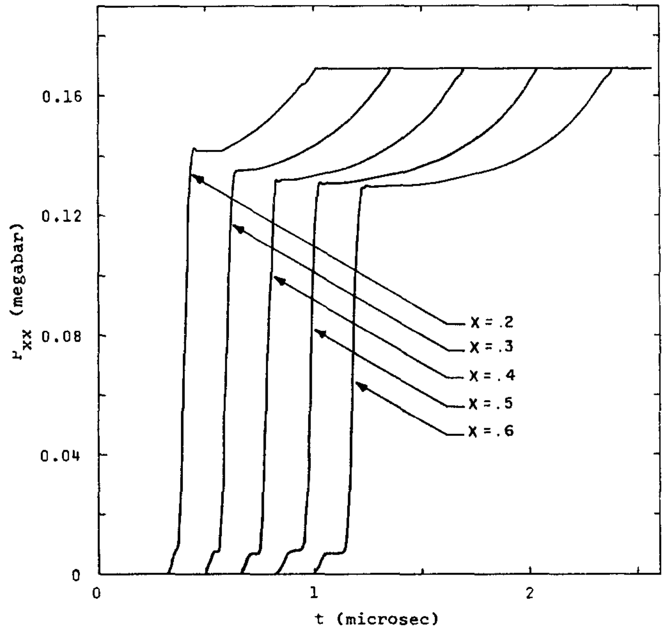

FIG. 2. Shock profiles farther from the impact surface. Longitudinal compressive stress is plotted as a function of time at points initially at 0.2 cm, 0.3 cm, 0.4 cm, 0.5 cm, and 0.6 cm from the impact surface.

meters were from work reported elsewhere [4]. A yield stress of 4.32 kilobars was used, and the relaxation time of the phase transition was chosen to be 0.1 μsec. The time step was restricted so that the relative change of volume of any zone in a time step did not exceed one part in 64. A von Neumann artificial viscosity with a coefficient of 4.0 was used.

In each time step, the equation of state iteration was performed four times for each zone. In the first pair of iterations the work done against stress deviators in that time step was ignored. The reason was to provide the capability of letting the shear modulus and yield stress depend on pressure and temperature even though constant values were used in this calculation. The running time of the program as a whole was eight times longer than with a simple equation of state calculation. If the stress deviator calculation were incorporated into the equation of state iteration, then only two iterations would be necessary to get second-order accuracy, and the calculation time could be cut roughly in half.

To look at the early relaxation of the step wave input, a problem was run with the iron divided spatial zones 0.0025 cm thick. Plots were obtained of longitudinal compressive stress as a function of time in zones that were initially at the positions

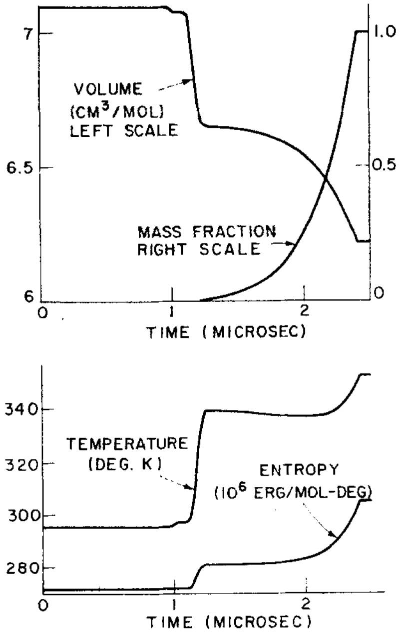

FIG. 3. Volume, mass fraction, temperature, and entropy as a function of time at the point initially at 0.6 cm from the impact surface.

0.025, 0.05, 0.1, and 0.15 cm from the impact surface. These curves are shown in Fig. 1. As the iron relaxes toward the denser phase, its shock impedance decreases. Since the velocity at the boundary is held constant, pressure at points near the boundary decreases after the jump at the wavefront. The pressure jump at the wavefront decreases with increasing propagation distance and approaches the equilibrium transition pressure. The separation between the plastic and the transition waves gradually becomes evident. The elastic precursor of 7.3 kilobars is also evident in the plots.

To look at the approach of the transition wave to a steady profile, the problem was rerun for a longer time with zones 0.005 cm thick. Plots of longitudinal compressive stress as a function of time at points initially at 0.2, 0.3, 0.4, 0.5, and 0.6 cm are shown in Fig. 2.

Other thermodynamic variables at the point initially at 0.6 cm are plotted as a function of time in Fig. 3. At this point the transition wave has almost reached a steady state. Entropy increases in both the plastic and the transition waves, since the material goes through nonequilibrium states. When the transition begins temperature decreases initially, as it does in the isentropic case, and then increases due to the increase in entropy.

The time scale of the problem is determined by the relaxation time of 0.1 μsec. Results for a different relaxation time may be found by scaling both time and distance by the same factor as the relaxation time. Stress, volume, and velocity will be the same at scaled space–time points.

ACKNOWLEDGMENT

Professor George E. Duvall's prior and continuing work on solid–solid phase changes has been an important basis of this work. His advice is gratefully acknowledged.

The calculational method of this paper was incorporated into Physics International Company's POD code to do the shock wave calculation.

REFERENCES

1. J. von Neumann and R. D. Richtmyer, *J. Appl. Phys.* **21** (1950), 232.
2. Y. Horie, "The Kinetics of Phase Change in Solids by Shock Wave Compression," unpublished Ph.D. thesis, Washington State University, Pullman, Washington, 1966.
3. Y. Horie and G. E. Duvall, Shock-induced phase transition in iron, in "Behavior of Dense Media under High Dynamic Pressure: Proceedings of the Symposium on High Dynamic Pressure," International Union of Theoretical and Applied Mechanics, Paris, September 1967, Gordon and Breach, New York, 1968.
4. D. J. Andrews, "Equation of State of the Alpha and Epsilon Phases of Iron," unpublished Ph.D. thesis, Washington State University, Pullman, Washington, 1970.

5. H. B. Callen, "Thermodynamics," Wiley and Sons, p. 128, New York, 1960.
6. M. L. Wilkins, Calculation of elastic-plastic flow, in "Methods in Computational Physics" (B. Alder, S. Fernbach, and M. Rotenberg, Eds.), Vol. III, Academic Press, New York, 1964.
7. S. R. De Groot, "Thermodynamics of Irreversible Processes," North-Holland Publishing Company, Amsterdam, 1966.