Explosive Phase Transitions

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Contents

I. Introduction

There are two types of solid phase transition kinetics, characterized by an interphase boundary movement either independent of temperature or occurring at a rate exponentially related to the temperature and with an activation energy approaching that of self-diffusion.[1] Within the former category a variety of phase transformations from metastable states in condensed systems are accompanied by sound phenomena and in some cases by explosive effects. Such rapidly phase transforming systems, which may be regarded as explosives with energy yields very low compared with chemical explosives, have aroused interest as a possible source of seismic activity. Although these explosives would be geologically small in volume, they would be of course large from a chemical point of view ($\sim$1 km^3).

Chemical explosives are of two kinds: *high or detonating* explosives in which the reaction is propagated directly behind a shock wave with a rate greater than the sound velocity in the original material, and *low or deflagrating* explosives in which the reaction rate is governed by heat and mass flow in the reaction front and is subsonic. In the same way one may describe rapid phase transformations in condensed materials as detonative or as deflagrative. Detonation of a chemical explosive involves initiation by a shock which raises the temperature locally to the ignition point. Phase transformations from metastable states, on the other hand, need not be thermally activated and could be propagated by weak shocks.

A brief description of basic shock theory equations and a statement of the general requirements for detonative processes precedes the review of specific types of rapid phase transformation.

II. Shock Theory

A. Basic Relations

The basic "classical" laws governing normal discontinuities in hydrodynamics are well established and have been described in detail by a number of authors.[2-8] It should be noted that the relations stated below are based on an idealized system with the following assumptions: a steady state process in a fluid system, with one-dimensional flow and the discontinuity perpendicular to the direction of flow, neglect of radiation, and assumption of Newtonian (nonrelativistic) mechanics. A stationary

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(1) A. L. Roitburd, *Zh. Eksp. Teor. Fiz., Pis'ma Red.*, **13**, 95 (1971); *JETP Lett.*, **13**, 66 (1971).

(2) R. Courant and K. O. Friedrichs, "Supersonic Flow and Shock Waves," Interscience, New York, N. Y., 1948.

(3) H. Eyring, R. E. Powell, G. H. Duffey, and R. B. Parlin, *Chem. Rev.*, **45**, 69 (1949).

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(6) G. E. Duvall and G. R. Fowles, in "High Pressure Physics and Chemistry," Vol. 2, R. S. Bradley, Ed., Academic Press, London, 1963, p 209.

(7) Y. B. Zel'dovich and Y. P. Raizer, "Physics of Shock Waves and High Temperature Hydrodynamic Phenomena," W. D. Hayes and R. F. Probstein, Translators, Academic Press, New York, N. Y., 1966; G. E. Duvall, *Proc. Int. Sch. Phys. Enrico Fermi*, 7 (1971).

(8) J. N. Bradley, "Flame and Combustion Phenomena," Methuen, London, 1969.

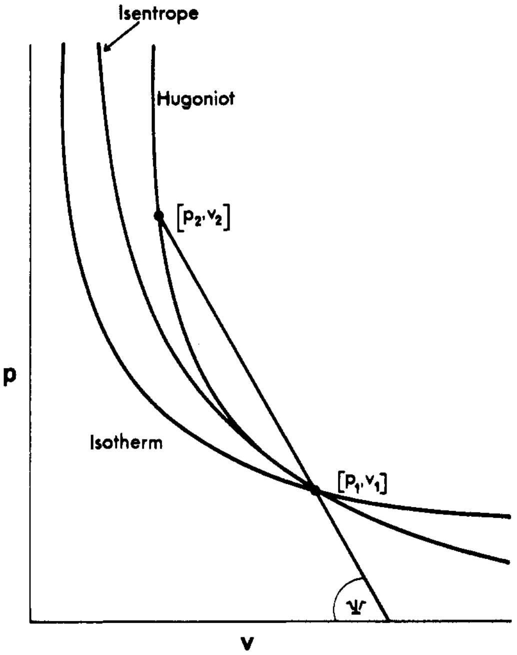

Figure 1. Schematic diagram showing relative positions of Hugoniot (shock adiabat), isentrope (reversible adiabat), and isotherm.

shock is considered (*i.e.*, the observer moves with the discontinuity), and the material on each side of the discontinuity is assumed to obey a known equation of state.

p_1, ρ_1, h_1, T_1	p_2, ρ_2, h_2, T_2
$\rightarrow$	$\rightarrow$
u_1	u_2

stationary
discontinuity

The notation is as follows: p, pressure; ρ, density; u, velocity relative to discontinuity; h, specific enthalpy; e, specific internal energy; and v, specific volume ($1/\rho$). Subscripts 1 and 2 denote unshocked ("upstream," ahead of the shock) and shocked ("downstream," behind the shock) states.

Conservation considerations yield the following equations.

Conservation of mass (continuity)

$$\text{mass flow } m = \rho_1 u_1 = \rho_2 u_2 = u_1/v_1 = u_2/v_2 \quad (1)$$

Conservation of momentum

$$p_0 = p_1 + \rho_1 u_1^2 = p_2 + \rho_2 u_2^2 \quad (2)$$

Conservation of energy

$$h_0 = h_1 + \tfrac{1}{2}u_1^2 = h_2 + \tfrac{1}{2}u_2^2 \quad (3)$$

From eq 1 and 2

$$p_2 - p_1 = m(u_1 - u_2) = m^2(v_1 - v_2) \quad (4)$$

If the terms in eq 4 are positive, *i.e.*, there is a decrease in flow velocity, increase in pressure, and increase in density, there is a *compression* or *deceleration* discontinuity. On the other hand, if ($p_2 - p_1$) is negative, there is an *expansion* or *acceleration* discontinuity.

From

$$h = e + pv \quad (5)$$

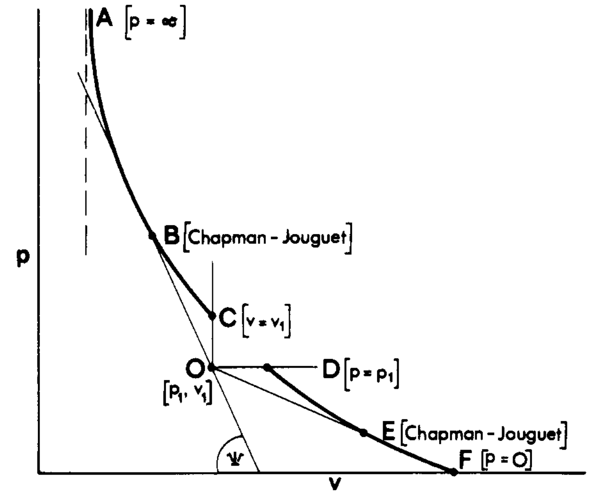

Figure 2. Schematic Hugoniot curve. Case I: transition from point (p_1, v_1) below the curve to point (p_2, v_2).

and eq 1–3

$$h_2 - h_1 = \tfrac{1}{2}(p_2 - p_1)(v_1 + v_2) \quad (6)$$

$$e_2 - e_1 = \tfrac{1}{2}(p_2 + p_1)(v_1 - v_2) \quad (7)$$

These are called *Rankine–Hugoniot* or simply *Hugoniot* relations; they have the advantage of being purely thermodynamic and not involving the flow velocity. In order to plot p_2 against v_2 for a given (p_1, v_1), *i.e.*, in order to construct a Hugoniot curve, one requires an equation of state such as

$$e = f(\rho, T) \quad (8)$$

If the material on both sides of the discontinuity has the same equation of state, *i.e.*, if no reaction or phase change occurs, (p_1, v_1) lies on the Hugoniot curve. A typical Hugoniot is shown in Figure 1, which includes for comparison the isentrope (reversible adiabat) and isotherm. The three curves are the loci of points attainable by shock, isentropic, and isothermal transitions, respectively, from (p_1, v_1). (Below p_1, v_1, the Hugoniot and isentrope are coincident).

The line connecting the points describing the initial (p_1, v_1) and final (p_2, v_2) states is called the *Rayleigh* line, and the slope of this line gives a measure of the velocity. From eq 1 and 4

$$m = [(p_2 - p_1)/(v_1 - v_2)]^{1/2} = u_1/v_1 \quad (9)$$

so

$$u_1 = v_1[(p_2 - p_1)/(v_1 - v_2)]^{1/2} = v_1(\tan\psi)^{1/2} \quad (10)$$

and

$$u_1 - u_2 = (v_1 - v_2)m = (v_1 - v_2)(\tan\psi)^{1/2} \quad (11)$$

It is helpful to consider also the velocities relative to a stationary observer in state 1 (in front of the shock) rather than relative to a stationary shock. The *shock velocity*, u_s, is given by eq 10, and the *particle* or *flow velocity*, u_{fl}, behind the shock front is given by eq 11.

State 1 (unshocked)	State 2 $\leftarrow$ $u_{fl} = u_s - u_2 = (v_1 - v_2)(\tan\psi)^{1/2}$

shock
front
$\leftarrow$
$u_s = v_1(\tan\psi)^{1/2}$

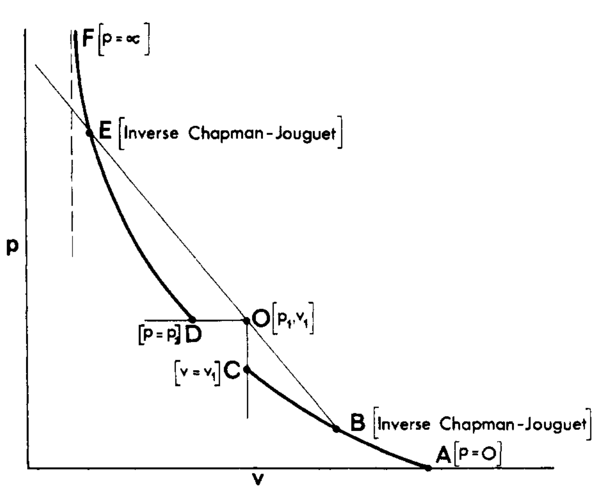

Figure 3. Schematic Hugoniot curve. Case II: transition from point (p_1, v_1) above the curve to point (p_2, v_2).

B. Change of State

It is not necessary for (p_1, v_1) to lie on the (p_2, v_2) Hugoniot curve; *i.e.*, the material may undergo a chemical reaction or phase transformation such that the initial and final states have different equations of state. The processes may be divided into those for which the initial point (p_1, v_1) lies below the (p_2, v_2) curve (case I, Figure 2) and those for which (p_1, v_1) lies above the curve (case II, Figure 3).

Hayes[4] described case I as "exothermic": not necessarily associated with the release of heat but corresponding to a pressure increase in a constant volume, constant internal energy reaction, or a volume increase in a constant pressure, constant enthalpy reaction. An alternative description is "expansive." This is the situation in the explosion of all chemical explosives, in which gaseous products are formed. The so-called "endothermic" or "contractive" case II (Figure 3) involving a volume decrease in a constant pressure, constant enthalpy reaction in general cannot yield a stable shock wave.

C. Detonations and Deflagrations

From eq 6 and 7 it can be seen that ($p_2 - p_1$) and ($v_1 - v_2$) must have the same sign. If one takes (p_1, v_1) as the origin, only the upper left and lower right quadrants are of physical interest (see Figures 2 and 3). The upper left quadrant corresponds to *compression* solutions, *i.e.*, $v_2 < v_1$, across the shock front, and these are called *detonations*. The lower right quadrant is the *expansion* solution, $v_2 > v_1$, corresponding to *deflagration* which literally means "fast burning," "explosion," or "flare."

In Figure 2 the tangents through (p_1, v_1) to the Hugoniot correspond to a sonic particle velocity behind the discontinuity, *i.e.*, $u_2 = a_2$. At the "Chapman-Jouguet" points, B and E

$$-dp/dv = -(\partial p/\partial v)_S = \rho_2^2 a_2^2 = (p_2 - p_1)/(v_2 - v_1) = m^2 = \rho_2^2 u_2^2 \qquad (12)$$

(In Figure 3, a line drawn through (p_1, v_1) with slope $-\rho_1^2 a_1^2$ intersects the Hugoniot in two "inverse Chapman-Jouguet" points B and E[4].)

It may be shown (the Chapman-Jouguet postulate) that a stable detonation has a velocity u_D equal to the sum of the flow velocity u_{fl} and the sound speed a_2 behind the shock front.

$$u_D = u_{fl} + a_2 \qquad (13)$$

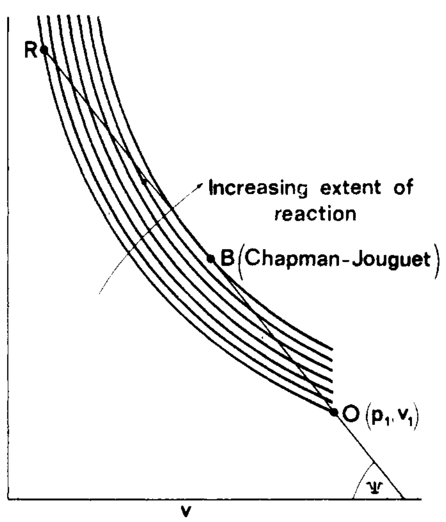

Figure 4. Family of Hugoniot curves depicting transition from point O to point B accompanied by reaction.

TABLE I. Features of Various Solutions of Case I Hugoniot Curves

Region	Velocity characteristics		Description
AB	$u_1 > a_1$	$u_2 < a_2$	Strong detonation Over-driven detonation
B	$u_1 > a_1$	$u_2 = a_2$	Stable detonation (Chapman-Jouguet detonation)
BC	$u_1 > a_1$	$u_2 > a_2$	Weak detonation
DE	$u_1 < a_1$	$u_2 < a_2$	Weak deflagration
E	$u_1 < a_1$	$u_2 = a_2$	Chapman-Jouguet deflagration
EF	$u_1 < a_1$	$u_2 > a_2$	Strong deflagration

D. Case I Shock Transition

Values of the velocities u_1 and u_2 relative to a_2 define various solutions of the Hugoniot equation; these are described in Figure 2 and Table I. Overdriven detonations are observed when detonation is initiated by a strong shock wave, but the velocity decays to that of a stable detonation. There is a solution to the flow equations for detonations above Chapman-Jouguet detonations and for deflagrations with speeds up to Chapman-Jouguet deflagrations. Weak detonations and strong deflagrations which require high reaction velocities ($u_2 > a_2$) are not observed.

It is helpful in visualizing a detonation with a slow reaction rate (*i.e.*, with a finite reaction zone behind the shock front) to consider a family of Hugoniot curves (Figure 4) corresponding to successive stages of reaction. The initial transition at the shock front is to the point R of intersection of the Hugoniot and Rayleigh lines: a simple shock transition. In a steady state process, all states must lie on a simple Rayleigh line corresponding to the detonation velocity, so the state of the system changes along the Rayleigh line until it reaches the Chapman-Jouguet point B on the fully reacted Hugoniot. From point O to point B there is a net *increase* in pressure. A typical detonation pressure profile is illustrated in Figure 5a.

In the case of a *deflagration*, a precompression shock precedes the reaction zone at a greater velocity, so across the reaction zone there is *decrease* in pressure (Figure 5b).

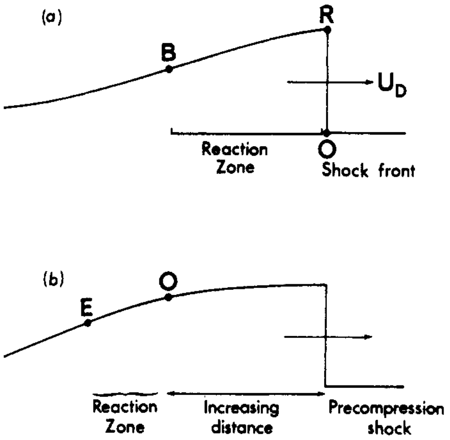

Figure 5. Schematic pressure profiles of (a) a detonation, and (b) a deflagration. Letters refer to points on Figures 2 and 4.

E. Case II Shock Transition

When (p_1, v_1) lies above the Hugoniot curve, so that there are no Chapman–Jouguet points (Figure 3), a formal classification of processes can also be made (Table II), but such processes are in general not physically realizable. The terms "detonation" and "deflagration" for regions ED and CB now correspond to compression and expansion of material rather than to velocity conditions.

F. Shock Pressure

The conservation equations 1 and 2 may be rearranged to yield an expression for the *shock pressure*, p_2, in terms of velocities. As p_2 is generally much greater than p_1, $p_1 - p_2 \approx p_1$.

$$p_2 = \rho_1 u_1^2 - \rho_2 u_2^2 = \rho_1 u_1 (u_1 - u_2)$$

In terms of the shock velocity u_s and the particle flow velocity u_{fl}, the shock pressure is

$$p_2 = \rho_1 u_s u_{fl} \tag{14}$$

This equation is used in section IV.D.

III. Phase Transitions Associated with Shock Waves

A. Feasibility

In order for a detonative or deflagrative phase transition to be observed, it is necessary that a "case I" situation exist. Kuznetsov[9] considered the location of shock adiabats relative to the equilibrium phase transition line in the following way. At the initial pressure p_1 let the enthalpy of phase a on the equilibrium transition line of phases a and b be H^*, and let the material be in a metastable state of phase a for the same pressure p, and for $H_1 = H^* + \delta H$. The volumes V_1 and V^* of phase a at the points (p_1, H_1) and (p_1, H^*) are related by the expression

$$V_1 = V^* + (\partial V/\partial H)_{p,a}\delta H = V^* + (1/T)(\delta T/\delta p)_{S,a}\delta H$$

where the subscript a denotes phase a and S denotes constant entropy so $(\partial T/\partial p)_{S,a}$ is the isentropic value of $(\partial T/\partial p)$ or the adiabatic gradient for phase a. The volume of the equilibrium state of the material at the same pressure p_1 and for the same enthalpy increment δH is (by the Clapeyron equation)

TABLE II. Features of Various Solutions of Case II Hugoniot Curves

Region	Velocity characteristics		Description
FE	$u_1 > a_1$	$u_2 < a_2$	Strong detonation
E	$u_1 = a_1$	$u_2 < a_2$	
ED	$u_1 < a_1$	$u_2 < a_2$	"Slow detonation"
CB	$u_1 > a_1$	$u_2 > a_2$	"Fast deflagration"
B	$u_1 = a_1$	$u_2 > a_2$	
BA	$u_1 < a_1$	$u_2 > a_2$	Strong deflagration

$$V_p = V^* + (\delta H/T)\,(dT/dp)$$

where $dT/dp = T\Delta V/\Delta H$ is the derivative of the pressure–temperature phase equilibrium line at pressure p, and ΔH is the enthalpy change for the process (to be distinguished from the shock enthalpy change $h_2 - h_1$ of eq 5). It follows from the above equations that for an isobaric ($p = p_1$) and isenthalpic (involving the same increment δH) transition from a metastable state to a stable state, the volume change is given by

$$V_p - V_1 = (\delta H/T)[(dT/dp) - (\partial T/\partial p)_{S,a}]$$

(The change in volume with simultaneous satisfaction of the conditions of constant pressure and constant enthalpy is made possible by the change of phase). Also

$$\delta H = \alpha \Delta H$$

where α is the relative concentration of phase b, so it follows that the isenthalpic, isobaric transition from the metastable state of phase a to the two-phase state in thermodynamic equilibrium is accompanied by a volume change which has the same sign as

$$\Delta H[(dT/dp) - (\partial T/\partial p)_{S,a}] \text{ or } L[(\partial T/\partial p)_{S,a} - (dT/dp)] \tag{15}$$

If this quantity is positive, a case I situation exists and a phase change associated with a shock wave is feasible. Whether or not the analysis of Kuznetsov is correct in detail for the phase transformations being considered, it is apparent that the general conclusion is sound: an exothermic process with a volume increase accompanying the phase change (ΔH negative, ΔV positive) could produce a shock wave. On the other hand, an endothermic process with a volume decrease (ΔH positive, ΔV negative) could not produce a shock wave whatever the values of ΔH and ΔV. The other cases (ΔH positive, ΔV positive, and ΔH negative, ΔV negative) depend on the particular values of dT/dp and $(\partial T/\partial p)_{S,a}$. Other aspects of this problem are discussed in section IV.D.

B. Spherical Detonations and Deflagrations

The relations quoted in section II.A refer to discontinuities in a one-dimensional system. The emphasis in experimental work on chemical detonations has been to obtain an "ideal" detonation in a cylindrical system, with a rate independent of the radius of the explosive.[3] With regard to possible geophysical applications, it would seem necessary to obtain information about spherical systems, but in fact the problem may be simpler than it appears. Formally, spherical detonation waves in which the detonation front expands with constant speed according to the Chapman–Jouguet condition are possible only if the rates of change of pressure and other quantities are infinite immediately behind the detonation front. In practice, the front *is* propagated, but with a speed lower than that de-

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(9) N. M. Kuznetsov, *Zh. Eksp. Teor. Fiz.*, **49**, 1526 (1965); *Sov. Phys. JETP*, **22**, 1047 (1966).

rived on the Chapman–Jouguet hypothesis as the rarefaction process interferes with the internal mechanism of the detonation process.[2,10]

In solids, the "internal burning" theory of detonation initiation by hammer blows indicates that detonation commences in the interior of the explosive. If the wave front is not too strongly curved (radius of curvature considerably greater than the reaction zone length), conditions for detonation on a spherical front approximate to those for a planar detonation.[3]

If as is proposed in section III.D the reaction zone is in fact narrow in phase transitions, there is no theoretical objection to detonation. It is probably useful to consider that a discontinuity which is expanding spherically is in fact a completely "confined" explosive charge, so there is no lateral rarefaction. In a cylindrical charge of solid chemical explosive a conical shape in the detonation head corresponds to steady state detonation in which lateral rarefactions "eat away" at the shock wave.[8] It is easy to intuitively extend this model to a spherical detonation free of lateral rarefaction.

A spherical *deflagration* wave may be described as a deflagration front preceded by a precompression wave of the same type as the wave produced by an expanding sphere.[2]

C. Elastic-Plastic Behavior of Solids

In solids a complication exists which is not encountered in fluids. The stress system in a fluid may be described by a hydrostatic pressure if dissipative processes are neglected, but solids can withstand shear stress and consequently stress systems in solids are anisotropic. The Rankine–Hugoniot relations remain valid, if the hydrostatic pressure is replaced by the stress component normal to the wave front. However, when an elastic solid is subjected to a shock wave with a pressure exceeding a certain critical value, the deformation no longer follows Hooke's law. The solid becomes plastic, and the slope of the pressure–volume line changes. This causes a compression wave of sufficient intensity to split into two waves, an elastic wave followed by a slower "plastic" wave. On the other hand, if the shock wave has a sufficiently high velocity, no splitting occurs because the plastic wave propagates faster than the elastic wave and merges with it.[7,11] In phase transformation *detonations*, a solid may be considered to be "plastic" in the narrow reaction zone which is propagating at the same velocity as the shock front, but in phase change *deflagrations*, it is unlikely that the elastic limit is exceeded.

D. Reaction Zone Thickness and Critical Size

Ubbelohde[12] considered that a system undergoing a "weak" detonation would require a wide reaction zone to complete the energy release so that a large mass would be necessary to show the effect. Our proposal is that a very *narrow* reaction zone is involved because there is little or no "activation energy" in such processes; they are cooperative and take place across a narrow molecular-scale reaction zone. A similar argument holds for the critical size of the sample; a geological scale sample is not necessary for an explosive phase transition to occur. These explosive transitions are distinct from chemical explosions involving materials such as ammonium nitrate which are thermally activated and may well involve a broad reaction zone. In a chemical detonation the shock wave raises the temperature to the ignition point, but the shock front in addition subjects materials to intense shearing stresses[6,11,13,14,14a] which may be more effective in bringing about a phase transformation. Transition velocities are discussed further in section IV.A.

TABLE III. Undercooling Limits of Metals

Metal	Exptl undercooling limit[a] ($\Delta T_{\max}$, K)	Reduced undercooling limit[b] ($\Delta T_{\max}/T_m$)	Calculated under-cooling limit[c] ($\Delta T^c_{\max}$, K)	Reduced calcd under-cooling limit ($\Delta T^c_{\max}/T_m$)
Bismuth	90	0.166	370	0.68
Nickel	319	0.185	470	0.27
Cobalt	330	0.187	570	0.33
Iron	332	0.182	600	0.33
Silver	227	0.185	420	0.34

[a] Turnbull and Cech, ref 25. [b] T_m is the normal melting point. [c] Evaluated from $\Delta T^c_{\max} = L/C_p$ (eq 17).

E. Heat and Mass Transfer Requirements

In order that the condition of a narrow reaction front be met, and in any case because the high temperatures and consequent high thermal reaction rates of chemical detonations do not occur, there are two further requirements for rapid phase transformation accompanied by shock waves: (i) no heat flow limitation, *i.e.*, adiabatic or shock adiabatic (Hugoniot) processes only; (ii) no mass transfer limitation, *i.e.*, "shear" or "diffusionless" processes only.

1. Heat Transfer Limitation

If phase transformation and crystallization processes are to occur rapidly, the processes must be adiabatic and not isothermal. At first sight this indicates that the initial phase must be in a state of metastability such that the local temperature increase on transformation does not exceed the difference between the initial temperature and the equilibrium transition temperature. This is in contrast with the so-called "combustion waves" in solids (reaction of a solid to give a solid product) where heat transfer is the limiting factor.[15] The rate of crystallization from supersaturated solutions and undercooled melts usually increases with the extent of metastability but, in general, is limited by the rate of heat transfer. This is illustrated by an increase in solidification rate in the presence of a wire to assist heat flow.[16] The ratio of the enthalpy change ("latent heat") of transformation to the heat capacity which provides an estimate of the degree of undercooling required is of the order of 400 to 600° for the solidification of supercooled metals (see Table III) and ~60° for the martensite transformation of iron.

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(10) G. I. Taylor and R. S. Tankin in ref 4, p 622.

(11) D. G. Doran and R. K. Linde, *Solid State Phys.*, **19**, 229 (1966).

(12) A. R. Ubbelohde, *Proc. Roy. Soc., Ser. A*, **204**, 25 (1950); "Chemistry of the Solid State," W. E. Garner, Ed., Butterworths, London, 1955, p 268.

(13) L. D. Livshits, Y. N. Ryabinin, L. V. Larionov, and A. S. Zverev, *Zh. Eksp. Teor. Fiz.*, **55**, 1173, (1968); *Sov. Phys. JETP*, **28**, 612 (1969).

(14) P. W. Bridgman, *Phys. Rev.*, **48**, 825 (1935).

(14a) A. A. Petrov, *Fiz. Tverd. Tela*, **13**, 1816 (1971); *Sov. Phys. Solid State*, **13**, 1519 (1971).

(15) R. A. W. Hill and T. L. Cottrell, Fourth International Symposium on Combustion (Combustion and Detonation Waves), MIT, 1952, Williams and Wilkins, Baltimore, Md., 1953, p 349.

(16) W. Borodowsky, *J. Russ. Chem. Soc.*, **35**, 128 (1903); *Z. Phys. Chem. (Leipzig)*, **43**, 75 (1903); *J. Chem. Soc.*, 84 (ii), 357 (1903).

However, if the transformation generates a shock wave, energy may be transferred from the reaction front by this mechanism, permitting a rapid reaction with a smaller degree of undercooling. Evidence for the removal of energy in this way is provided by the absence of melting in the high pressure polymerization reaction of acrylamide.[17]

2. Mass Transfer Limitations

In martensite transformations it is well established[18,19] that individual atoms undergo correlated movements which are less than one interatomic distance, in contrast to diffusion controlled solid-solid transformations in which the atoms undergo random diffusional movements which are long range compared with the interatomic distance. Roitburd[1] has discussed from the point of view of continuity of phase boundaries and diffusion of vacancies the existence of these two qualitatively different kinetic types of phase transformations. This review will be concerned with the "shear" or essentially "diffusionless" transformations.

F. Initiation

The way in which nucleation or initiation of detonative phase transformations occur is discussed in section IV. In fact, because one is dealing with nucleation control rather than diffusion control, the initiation process is the most important feature from a practical point of view. The subject of initiation of detonation of solid and liquid chemical explosives, reviewed recently by Lin and Eyring,[20] has proved extremely difficult but may be of significance in discussing phase transitions. Some progress has been made in the consideration of the nucleation of martensite transformations.[19]

G. Rarefaction Shocks due to Phase Transitions

A phenomenon associated with rapid phase transitions is observed on some occasions when pressure is *released* from a sample. It has been shown[7] that when material that has previously been compressed by a shock wave is unloaded during the following rarefaction, a rarefaction shock can develop if a phase transition occurs. In a rarefaction shock not associated with a reaction, the decrease in pressure implies an unacceptable decrease in entropy, but in a reactive discontinuity the increase in entropy due to the reaction can compensate for the loss due to dynamic effects.

It is also observed[21] that explosions may result on release of *static* high pressure. Although this has been attributed to the samples becoming mechanically unstable, a possible alternative explanation is a rapid phase charge associated with a rarefaction shock.

IV. Undercooled Metal Systems

A. Transition Velocity Profiles

Late last century Tammann[22] described a relationship between the transition velocity of a crystallizing undercooled organic melt and the extent of undercooling. He observed that the transition velocity reached a maximum at some undercooling characteristic of the material. From the normal melting point to this maximum the transition velocity was a direct function of the extent of undercooling and the thermal conductivity of the medium, and an inverse function of the latent heat of crystallization. Such profiles were earlier noted by Bogojawlensky,[23] but he found that some liquids showed a plateau in their transition velocity-undercooling profile rather than a maximum. Tammann[24] subsequently considered these differences in profile as being due to variations in the molecular complexity of the liquid and solid phases.

More recently such studies have been extended to include undercooled metal melts. Turnbull and Cech[25] noted that profiles with maxima were obtained with these systems, although they gave no quantitative estimates of the transition velocities. Colligan and Bayles[26] demonstrated that the relationship between the transition velocity and the extent of undercooling could be fitted to the empirical eq 16 (the Jackson relation[26a])

$$R_{\mathrm{T}} = A(\Delta T)^n \tag{16}$$

In this equation R_{T} is the transition velocity, ΔT is the extent of undercooling, and A and n are constants. Horvay and Cahn[27] noted that A was approximately 0.2 and n was approximately 2. From what has been said so far, such a relation would be expected to apply only to that portion of the velocity-undercooling profile from the melting point to the maximum in the curve. However, recent work by Colligan and coworkers[28] has cast doubt on the existence of such maxima, and this suggests that the Jackson relation is valid at all undercoolings. The ramifications of this are considered further when aspects of mechanism are discussed.

B. Undercooling Limits

Before considering specific transitions, some consideration needs to be given to the maximum extent of undercooling that can be achieved. Turnbull and Cech, in studies of metal droplets,[25] found that the maximum extent of undercooling was 0.18 times the normal melting temperature. Colligan and coworkers[28] found more recently that undercooling is possible below the previously suggested limit. They proposed that the limit observed by Turnbull and Cech may be due to experimental inadequacies rather than a physical law and gave a thermodynamic relationship for the maximum attainable undercooling

$$\Delta T_{\max} = \Delta T^{\mathrm{c}}_{\max} = L/C_{\mathrm{p}} \tag{17}$$

where L is the latent heat, C_{p} is the heat capacity at constant pressure, and the superscript c indicates that this is a calculated parameter. From Table III where data for the undercooling limits of selected metals are presented,

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(17) I. M. Barkalov, V. I. Gol'danskii, V. L. Tal'roze, and P. A. Yampol'ski, *Zh. Eksp. Teor. Fiz., Pis'ma Red.*, **3**, 309 (1966); *JETP Lett.*, **3**, 200 (1966).

(18) C. M. Wayman, "Introduction to the Crystallography of Martensitic Transformations," Macmillan, New York, N. Y., 1964.

(19) J. W. Christian, "The Theory of Transformations in Metals and Alloys," Pergamon, Oxford, 1965.

(20) S. H. Lin and H. Eyring, *Annu. Rev. Phys. Chem.*, **21**, 225 (1970).

(21) For example, S. Malmrud and S. Claesson, *Ark. Kemi*, **25**, 201 (1966).

(22) G. Tammann, *Z. Phys. Chem. (Leipzig)*, **20**, 51 (1899).

(23) A. Bogojawlensky, *Z. Phys. Chem. (Leipzig)*, **27**, 585 (1898).

(24) G. Tammann, *Gedenboek aangeboden aan J. M. van Bemmelen*, 297 (1910).

(25) D. Turnbull and R. E. Cech, *J. Appl. Phys.*, **21**, 804 (1950).

(26) G. A. Colligan and B. J. Bayles, *Acta Met.*, **10**, 895 (1962).

(26a) K. A. Jackson, "Liquid Metals and Solidification," Seminar, 39th National Metal Congress, Chicago, 1957; American Society for Metals, Cleveland, Ohio, 1958, pp 174-186.

(27) G. Horvay and J. W. Cahn, *Acta Met.*, **9**, 695 (1961).

(28) G. A. Colligan, W. T. Loomis, and V. A. Suprenant, *J. Aust. Inst. Metals*, **10**, 89 (1965).

it can be seen that the quantity $(L/C_p)/T_m$ depends on the system under consideration.

C. Rapid Solidification of Undercooled Metal Melts

There are several undercooled metals whose solidification may be accompanied by acoustic disturbances or "audible clicks" and others which show evidence of the generation of a shock wave within the transforming system. These effects are most apparent for certain of the transition metals, in particular iron, cobalt, and nickel as well as their alloys with silver; and also silver and bismuth.

The best documented solidification of this type is that in nickel. Walker[29] noted that there was a significant increase in acoustic disturbance accompanying solidification of liquid nickel undercooled by 140 K. At this temperature there was a marked decrease in the grain size of the crystalline product. Similar changes in grain size have also been noted at comparable undercoolings of copper and silver and their alloys, particularly where oxygen is present.[30,31]

Walker found that crystallization could be induced in a container undercooled by an amount comparable to but different from an adjacent one that was currently transforming, and this suggested that a shock wave was propagated under these conditions. Walker did not give a quantitative estimate of the magnitude of this pressure pulse, but Glicksman,[32] who observed a similar effect in bismuth, gave a figure of 10^5 to 10^6 Pa for the pressure pulse. Further evidence for the production of shock waves in such solidifications was provided by the pit-like structures observed by Colligan[33] in cobalt at an undercooling of some 266 K. This pitting markedly resembled the effects observed by Ivanov[34] on the surface of metals (for example, iron) by subjecting them to shock waves from the detonation of adjacent explosives.

The undercoolings at which shock effects are noticed in nickel, cobalt, and bismuth, and silver are given in Table IV. The data suggest an almost linear relationship between the undercooling corresponding to the onset of shock effects and the maximum undercooling limit calculated previously in Table III. This relationship is shown graphically in Figure 6 and suggests that the onset of disturbance is dependent upon the latent heat of transformation. This dependence will be developed further in the next section.

The speeds of solidification at the onset of acoustic disturbance and the speeds of sound in the liquid metals are also given in Table IV. For a detonation the transition velocity from state 1 to state 2 equals or exceeds the speed of sound in state 1. On the other hand, for a deflagration there is a precompression shock followed by a subsonic transition from state 1 to state 2. The ratio of transition velocity to sound velocity therefore indicates the detonative or deflagrative character of the process: if it approaches or exceeds unity, the process may be considered detonative; if less, then the process is deflagra-

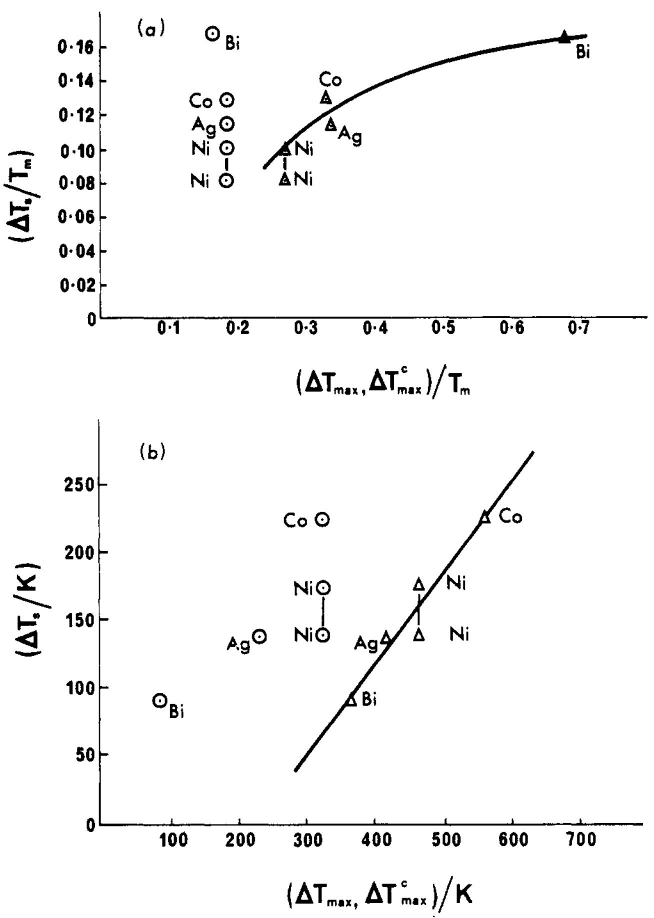

Figure 6. Acoustic effects in undercooled metal melts. (a) Reduced undercooling at onset of shock effects as a function of maximum undercooling. (b) Undercooling at onset of shock effects as a function of maximum undercooling. Experimental undercooling limits are represented by circles and calculated limits by triangles.

TABLE IV. Acoustic Effects in Undercooled Metals

	Undercooled metal			
	Bismuth	Nickel	Cobalt	Silver
Undercooling on onset of shock effects $(\Delta T_s/K)$	90[a]	170[b] 140[e]	226[c]	~140[d]
Reduced undercooling $(\Delta T_s/T_m)$	0.166	0.099 0.081	0.128	0.113
$\Delta T_s/\Delta T_{max}$[f]	1.0	0.53 0.44	0.69	0.62
$\Delta T_s/\Delta T^c_{max}$[g]	0.243	0.36 0.30	0.40	0.33
Transition velocity at onset of shock effects (u, m sec^{-1})	8.1[h] 5[i]	20.4[h] 50[i]	50[i]	
Sound velocity (a, m sec^{-1})	1650[j]	1830[k]	1500[l]	
u/a, mean	0.003	0.02	0.03	

[a] Glicksman, ref 32. [b] Colligan, *et al.*, ref 28. [c] Colligan, cited in ref 32. [d] Powell, ref 30. [e] Walker, ref 29. [f] Values of experimental maximum undercooling (ΔT_{max}) given in Table III. [g] Values of calculated maximum undercooling (ΔT^c_{max}) given in Table III. [h] From calculations by Glicksman, ref 32. [i] From data reported by Glicksman, ref 32. [j] J. E. Hill and A. L. Ruoff, *J. Chem. Phys.*, **43**, 2150 (1965). [k] Calculated on the basis of that in mercury allowing for a difference in the bulk moduli of the two liquid metals. [l] Taken as that for mercury: G. W. C. Kaye and T. H. Laby, "Tables of Physical and Chemical Constants," 13th ed, Longmans, London, 1966, p 65.

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(29) J. L. Walker, *Metal Soc. Conf. (Pittsburgh)*, **8** (1959); "Physical Chemistry of Process Metallurgy," Part 2, Interscience, 1961, p 845.

(30) G. L. F. Powell, *J. Aust. Inst. Metals*, **10**, 1 (1965).

(31) G. L. F. Powell and L. M. Hogan, *Trans. Met. Soc. AIME*, **242**, 2133 (1968); **245**, *407 (1969)*.

(32) M. E. Glicksman, *Acta Met.*, **13**, 1231 (1965).

(33) G. A. Colligan, quoted in ref 32.

(34) A. G. Ivanov and S. A. Novikov, *Fiz. Tverd. Tela*, **4**, 249 (1962); *Sov. Phys. Solid State*, **4**, 177 (1962).

TABLE V. Thermodynamic Parameters for Deflagrative Solidification

	Undercooled metals				Martensite[a] $Fe_{70\%}Ni_{30\%}$
	Bismuth	Cobalt	Nickel	Silver	
Shock pressure (p, GPa)[b]	0.12	0.58	0.71	. . .[c]	41.5
Increase in internal energy across shock front[d] (Δe, J kg^{-1})	1800	5000	1800	. . .	19,000
Increase in enthalpy across shock front[e] (Δh, J kg^{-1})	1.14×10^4	6.7×10^4	8.7×10^4	. . .	5.2×10^6
$C_p \Delta T_s$, J kg^{-1} [f]	1.3×10^4	1.6×10^5	9.2×10^4	4.4×10^4	. . .[g]
$\Delta e/L$[h]	0.034	0.019	0.058	. . .	0.36
$\Delta h/L$	0.22	0.30	0.28	. . .	100
$C_p \Delta T_s/L$	0.25	0.61	0.28	0.25	. . .

[a] Included for comparison; see section V.E. [b] As derived in section II.F. [c] Transition velocity data not available. [d] Equation 7. [e] Equation 6. [f] Values of ΔT_s from Table IV; values of C_p from Table VII. [g] Not applicable. [h] Values of L, latent heat of transition, from Table VII.

tive. On this basis the shock solidifications described above are clearly deflagrative.

D. Thermodynamics of Shock Solidification

If the crystallization processes described in the previous section are associated with shock effects, then the thermodynamic relationships of shock theory can be applied to them. Accordingly, the shock enthalpies (calculated on the basis of eq 6) and internal energies (eq 7) for these transitions are given in Table V. Also shown are the values of the shock pressure calculated from eq 14 (1 GPa = 10^9 N m^{-2} = 10^4 bars). For this calculation the shock front is considered as being propagated at the speed of sound ($u_S = a$), and the transition velocity (u) is taken to be a measure of the flow velocity (u_{fl}). Also shown in Table V are the values of the product of the undercooling at the onset of shock effects (ΔT_S) and the specific heat of the liquid metal ($C_{p,l}$). In all cases this value is very close to that of the shock enthalpy. This suggests that the temperature of the solidifying melt is raised to the melting point, a suggestion that is confirmed by Powell's experiments with silver.[30] Ratios of the shock enthalpy to latent heat and shock internal energy to latent heat suggest that about 30% of the latent heat of transformation is transferred to the shock wave's enthalpy and that 5% appears as internal energy. Thus by the thermodynamic eq 5 the shock compression term absorbs about 25% of the latent heat of transition. This result makes an interesting comparison with polymerization studies. Adadurov and Barkalov[35] noted that the passage of a shock wave (generated outside the system) caused a 60% polymerization of acrylamide. Barkalov and coworkers[17] subsequently identified the polymerization "energy" with the internal energy of shock compression.

Finally, consideration should be given to the Kuznetsov expression 15 presented in section III.A. The partial derivative in that expression may be written

$$(\partial T/\partial p)_{S,a} = \alpha_l v_l T/C_{p,l} \qquad (18)$$

The other derivative in the expression by use of the Clapeyron–Clausius relation becomes

$$dT/dp = T(v_l - v_s)/L \qquad (19)$$

TABLE VI. The Kuznetsov Condition

Undercooled metal	Kuznetsov factor $(\{v_l[\alpha L/C_p] - 1\} + v_s)$, m^3 kg^{-1}	Equilibrium volume change $(v_s - v_l)$, m^3 kg^{-1}
Nickel	$+0.02 \times 10^{-4}$	-0.06×10^{-4}
Bismuth	$+0.09 \times 10^{-4}$	$+0.05 \times 10^{-4}$
Cobalt	$+0.01 \times 10^{-4}$	-0.12×10^{-4}
Silver	-0.03×10^{-4}	-0.07×10^{-4}

As a result of these substitutions, the Kuznetsov expression is

$$T[\alpha_l v_l L/C_{p,l}) + (v_s - v_l)] \qquad (20)$$

The volume change given by the expression $[(\alpha_l v_l L/C_{p,l}) + (v_s - v_l)]$ and the equilibrium volume change $(v_s - v_l)$ are listed for undercooled bismuth, nickel, cobalt, and silver in Table VI. The constants used in the calculations for these metals are listed in Table VII. From Table VI it may be seen that the volume change under shock conditions is not necessarily of the same magnitude or sign as that under equilibrium conditions. Bismuth, nickel, and cobalt give positive values for the Kuznetsov expression in spite of their different equilibrium volume changes. Thus, on the basis of the criterion suggested in section III.A, a phase transition accompanied by the production of a shock wave is feasible for these metals. On the other hand, for silver the Kuznetsov expression is negative; inaccuracy of data is a possible cause, as experimentally this system is similar to the others.

E. Mechanistic Aspects

The type of transition discussed above is usually described as proceeding by a nucleation and growth mechanism. The growth part of the process, being essentially diffusion, is generally described by the Arrhenius equation

$$R_G = A_G \exp(-Q/RT) \qquad (21)$$

where R_G is the rate of growth, Q is the activation energy for growth, T is the temperature, and A_G and R are constants. Such an equation with Q constant indicates that the rate increases exponentially with temperature. When the temperature is such that the viscosity becomes high, the rate expression is no longer exponential. The rate

(35) G. A. Adadurov, I. M. Barkalov, V. I. Gol'danskii, A. N. Dremin, T. N. Ignatovich, A. N. Mikhailov, V. L. Tal'roze, and P. A. Yampol'skii, *Dokl. Akad. Nauk SSSR*, **165**, 851 (1965).

TABLE VII. Constants for Undercooled Metal Systems

	Bismuth	Nickel	Cobalt	Silver
Latent heat of transition (L, J kg^{-1})	5.2×10^4 [a]	3.1×10^5 [a]	2.7×10^5 [b]	1.1×10^5 [b]
Heat capacity ($C_{p,l}$, J kg^{-1} K^{-1})	1.4×10^2 [a]	6.6×10^2 [a]	7.1×10^2 [c]	3.2×10^2 [d]
$L/C_{p,l}$	368	470	375	351
Coefficient of expansion[e] (α, K^{-1})	1.2×10^{-4}	5×10^{-4}	2×10^{-4}	1×10^{-4}
Specific volume of liquid at onset of shock effects (v_l, m^3 kg^{-1})	9.85×10^{-5} [a]	1.26×10^{-4} [a]	1.25×10^{-4} [f]	1.25×10^{-4} [f]
Specific volume of solid at temperature of onset of shock effects in liquid (v_s, m^3 kg^{-1})	1.03×10^{-4} [a]	1.20×10^{-4} [a]	1.13×10^{-4} [g]	9.6×10^{-5} [g]

[a] Glicksman, ref 32. [b] U. S. Atomic Energy Commission Report ANL-5750, cited in "Handbook of Chemistry and Physics," 50th ed, Chemical Rubber Co., 1969–1970, p D-56. [c] Assumed the same as iron; value from reference in footnote *d*. [d] O. Kubaschewski, *Trans. Faraday Soc.*, **45**, 931 (1949). [e] Evaluated from the expansion formula $v = v_0(1 + \alpha(T - T_0))$, where v and v_0 are the final and initial specific volumes, T and T_0 are the final and initial temperatures, and α is the volume coefficient of thermal expansion. Data for specific volume as a function of temperature from "Handbook of Chemistry and Physics," 50th ed, 1969–1970, p B-255. [f] Extrapolated to the temperature corresponding to the onset of shock effects; data for specific volume as a function of temperature as in footnote *e*. [g] G. W. C. Kaye and T. H. Laby, "Tables of Physical and Chemical Constants," 13th ed, Longmans, London, 1966, p 118.

nevertheless still increases with rising temperature. Since the solidifications previously described have rates which increase with increasing undercooling (that is, with decreasing temperature), they would not appear to be growth controlled. Consequently the limiting process may be considered to be nucleation.

MacDowell[36] gave the rate expression for nucleation as

$$R_N = A_N \exp[-(F^* + Q)/RT] \qquad (22)$$

where F^* is an energy term corresponding to a "critical" radius for nucleation, and all other symbols are analogous to those in the growth expression. The energy F^* is not an activation energy in the usual sense in that it is temperature dependent. It decreases with increasing temperature such that the rate increases with increased undercooling. There are, in fact, a number of expressions for the rate of nucleation processes,[37] but all have a temperature-dependent factor. This factor frequently appears in the exponent, as in the example above. MacDowell[36] proposed that the overall exponent could go through a minimum. It seems reasonable that such a minimum could occur at the onset of acoustic disturbances and shock effects. This explanation would suffice for systems that showed a maximum or steepening in their transition velocity-undercooling profiles.

Other workers have suggested that the deflagrative solidification in undercooled metals may be due to the onset of cavitation. In an elegant experiment involving the crystallization of ice from undercooled water, Hunt and Jackson[38] demonstrated that nucleation can be associated with the collapse of cavities within the liquid. In a mathematical treatment Horvay[39] suggested that there was a change in rate-determining mechanism from homogeneous nucleation to cavitation-induced nucleation at an undercooling for which the critical radii for nucleation and cavitation are the same. Such an interpretation does not necessitate a maximum in the velocity-undercooling profile, and is thus a satisfactory explanation for deflagrative solidifications which do not show maxima in their profiles.

A rather similar conclusion in respect of nucleation and cavitation controlled processes has been reached by Glicksman.[32] His analysis of the "kinetics and dynamics of dendritic freezing" indicated that the hydrostatic pressure in the melt is reduced as undercooling increases; when this reduction is such that the pressure is less than the hydrostatic tension between the container and the melt, cavitation occurs. In order to reach this conclusion, Glicksman applied non-rigid-body mechanics to a cylindrically confined system that is nucleated at the base and grows as an expanding spherically capped zone. The model initially yields equations expressing "dimensionless" velocity and acceleration in terms of phase densities, temperature, and thermal constants. The equation for acceleration may be written

$$\mathrm{d}^2Z/\mathrm{d}t^2 = A\mathrm{U}(k)C_\mathrm{p}(1 - \rho_1/\rho_\mathrm{s})T^{2n+1}/Lh_0) \qquad (23)$$

where $\mathrm{d}^2Z/\mathrm{d}t^2$ is the "dimensionless center of mass acceleration," A and n are constants (the same as in the empirical relation eq 16), $\mathrm{U}(k)$ is a function depending solely on the geometrical details of crystal growth, h_0 is the height of the cylindrical ingot constraining the melt, and the other symbols have their usual meanings.

More useful than this quantity is the "terminal center of mass velocity," which is more akin to the experimental rate. This quantity results from a consideration of Newton's dynamical law, yielding the impulse equation

$$v_\mathrm{t} = \int_0^{t_\mathrm{f} \approx h_0/v_\mathrm{d}} (\mathrm{d}^2Z/\mathrm{d}t^2)\,\mathrm{d}t \qquad (24)$$

In this equation v_t is the "terminal center of mass velocity," v_d is the "dendrite tip velocity," and t_f is the total time of recalescence.

When values of v_t are plotted against the extent of undercooling, the function increases to a peak at the undercooling associated with the marked changes in crystal size and acoustic effects earlier described. This is of significance in that since the impulse imparted to the melt

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(36) J. F. MacDowell, *Ind. Eng. Chem.*, **58** (3), 38 (1966).

(37) For example, D. R. Uhlmann and B. Chalmers, *Ind. Eng. Chem.*, **57** (9), 19 (1965); ref 19, p 368.

(38) J. D. Hunt and K. A. Jackson, *J. Appl. Phys.*, **37**, 254 (1966).

(39) G. Horvay, *Proc. Nat. Congr. Appl. Mech., Berkeley, Calif., 1962*, **4**, 1315 (1963).

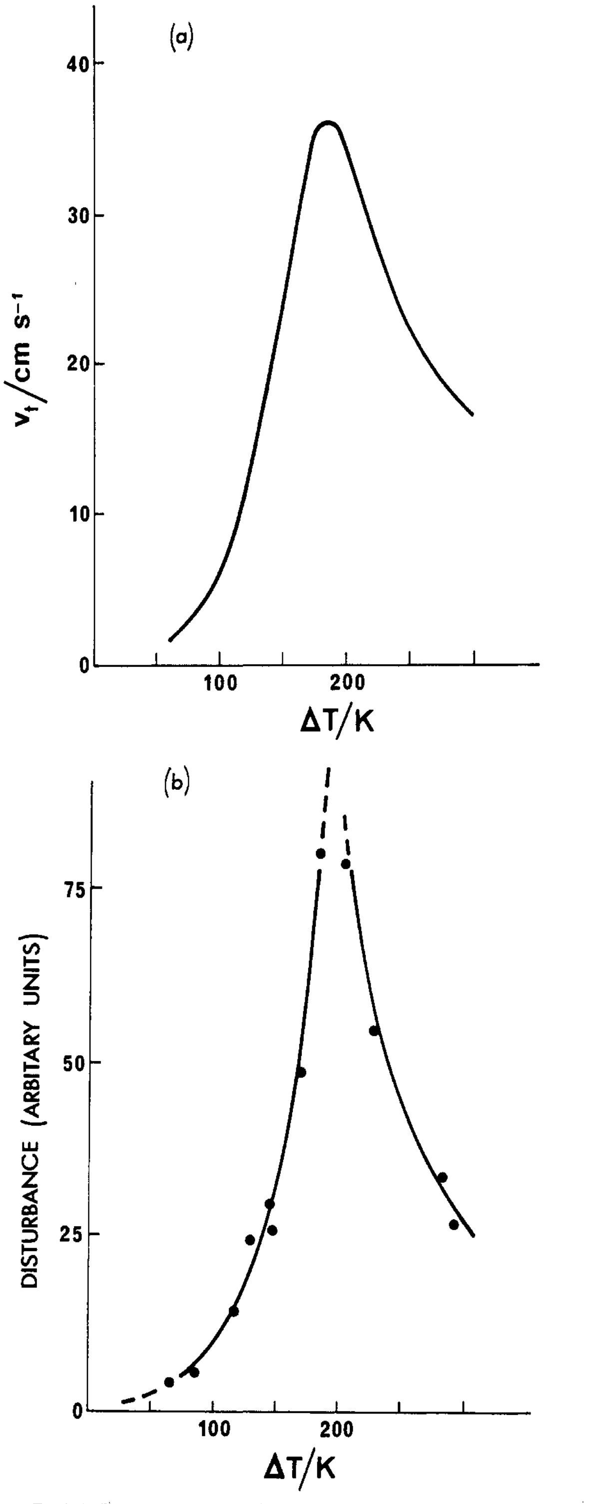

Figure 7. (a) Typical curve of terminal center of mass velocity (v_t) as a function of degree of undercooling (ΔT) for nickel, after Glicksman.[32] (b) Disturbance amplitude (arbitrary units) as a function of degree of undercooling (ΔT) for nickel, after Walker.[29]

and container is a linear and direct function of the terminal velocity, a plot of acoustic disturbance *vs.* undercooling should have the same shape as the terminal velocity–undercooling plot. This comparison is made for nickel in Figure 7.

Another, more empirical, approach is based on a suggestion by Walker.[29] He gave an expression for "nucleation pressure" as a function of temperature

$$p_N = \Delta F/\Delta V - (dp/dT)\Delta T \qquad (25)$$

where ΔF is the free energy change for nucleation, and has the significance of an activation energy.[19] Values of ΔF have been estimated[19] for bismuth and nickel, and the function 25 is plotted in Figure 8. The line intersects the shock pressure line (eq 14) at undercoolings which may provide estimates of the extent of undercooling necessary for deflagrative solidification.

All of the above treatments effectively propose that nucleation is the rate-controlling step in deflagrative solidification. In this they differ from a proposal by Christian[19] that in condensed phases nucleation was invariably surpassed in importance by growth.

V. The Martensite Transformation

A. General Features and Occurrence in Metals

In iron containing a small amount of carbon there is observed a characteristic transition from austenite to martensite, and similar transformations occur in other transition metals (transformation twinning[39a] is a related phenomenon). Although there is an extensive literature on the martensite transformation, only those aspects concerned with structural changes, kinetics, and the application of shock theory will be considered here.

The transition involves the shear of one or more planes through short distances (less than interatomic) to form small plates. In principle, any transformation that can be effected by shear movement is capable of being martensitic, the classical case being the transformation from body-centered cubic to hexagonal close-packed. These transitions are not reversible in the strict thermodynamic sense since the reverse transition occurs with hysteresis. Addison[40] indicated that the transition from hexagonal close packing to body-centered cubic in titanium, zirconium, hafnium, and cobalt are martensitic, as are the reverse transitions in lithium and sodium. A similar phenomenon is observed in the sodium chloride–cesium chloride polymorphism (see next section).

The martensite transformation is characterized by extremely fast propagation rates. Whereas the ratio of the transition velocity to the velocity of sound in the transforming medium is very small (about 0.002) for the deflagrative transitions described earlier, the ratio is of the order of unity for the martensite transformation.[41,42] This suggests that the martensite transformation might be considered a detonation and implies a low activation energy for the process. Both of these aspects of the transition will be considered below.

B. Martensitic Transitions in Halides

The near equivalence of the transition and sound velocities, which is characteristic of the martensite transition, has been used predictively. Thus, Kuz'min[43] has suggested that the transformation in ammonium bromide from undercooled crystals of cesium chloride structure to a sodium chloride lattice is martensitic. Similarly, the hysteresis effects, sound phenomena (discussed in section V.D), and the surface relief of the crystals have been used by Livshits and coworkers[13] to propose a martensit-

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(39a) F. E. Wang, *J. Appl. Phys.*, **43**, 92 (1972).

(40) W. E. Addison, "The Allotropy of the Elements," Oldbourne Press, London, 1964.

(41) R. F. Bunshah and R. F. Mehl, *J. Metals*, **5**, 1251 (1953).

(42) F. Dusek, *Sb. Ved. Pr., Vys. Sk. Banske Ostrave*, **13**, 525 (1967); *Chem. Abstr.*, **71**, 5793 (1969).

(43) S. V. Kuz'min, *Rab. Fiz. Tverd. Tela*, **No. 2**, 155 (1967); *Chem. Abstr.*, **71**, 117241 (1969).

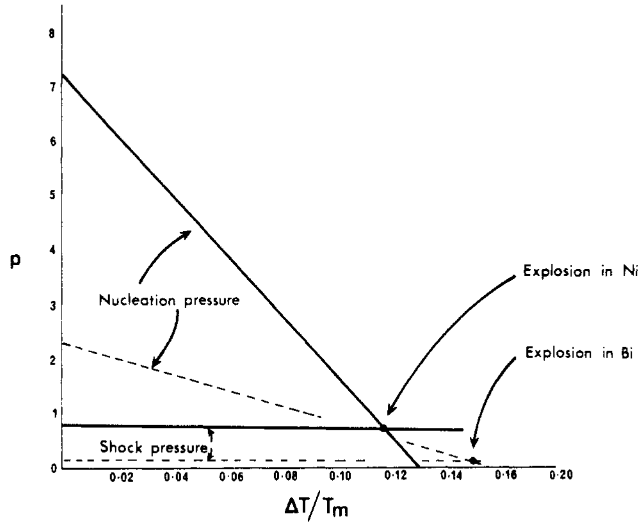

Figure 8. Shock pressures (eq 14) and nucleation pressures (eq 25) as a function of reduced undercooling, with solid lines for nickel and broken lines for bismuth. An "explosion" is proposed at the intersection of nucleation and shock pressure lines. Experimental values (Table IV) of $\Delta T_s/T_m$ (reduced undercooling at onset of acoustic effects) are: bismuth 0.166, nickel 0.09. p values are in units of GPa.

ic character for the sodium chloride–cesium chloride transition in potassium chloride.

C. Kinetic Aspects

While some mechanistic considerations of the martensite transformation have involved the application of nucleation and growth kinetics,[44] the speed of the transition is such that the activation energy must be very small. Accordingly, Scheil[45] suggested that the transition was nucleation-controlled. Nucleation was envisaged as being followed by very rapid propagation of martensite into the surrounding austenite as a strain wave. Propagation as a strain wave eliminated the high activation energy associated with diffusional (normal growth) propagation. This idea was developed further by Machlin and Cohen[46] in their "reaction path concept" which involved the application of transition state theory to the process. They considered that the activation energy for nucleation was supplied by the formation of internal strains by internal deformation, this energy being lower in regions of localized existing strain. Once the activated complex at which nucleation had just occurred had formed, there followed a "spontaneous increase in strain and volume to yield a full-sized martensite plate." This model suggests that the martensite transformation has at least formal analogy to the nucleation-controlled deflagrative solidifications described earlier.

More recently, terminology has been proposed that distinguishes between those transformations that involve diffusion and those which require movement of less than an interatomic distance.[47] This is tantamount to recognizing that all transformations involve both nucleation and growth, those involving diffusion being growth controlled and others nucleation controlled.

D. Further Evidence for Detonative Character

There is additional evidence, apart from the near-equivalence of the transition and sound velocities, to suggest that the martensitic transformation is detonative. Machlin and Cohen[48] from their study of the crystallographic habit of both the original austenite and the resulting martensite considered that the transformation strain was propagated as a wave. The same authors,[49] in showing that the reaction could autocatalytically produce bursts of martensite, noted that the transformation was accompanied by audible clicks. The container was also occasionally shattered and the toluene column of the thermometer separated, in spite of the specimen being freely suspended in the refrigerating liquid. Clearly, a shock wave was propagated through the liquid from the transforming crystals. Magee[50] has found that in cold stage electron microscopy experiments elastic waves generated by bursts of martensite formation caused spall fracture and severe bending at the thin edges of iron–nickel alloy samples. Bunshah and Mehl[41] calculated the velocity of elastic waves in an iron–nickel alloy, and noted that it was of the same order of magnitude as both the velocity of sound and the martensite transition velocity.

E. Shock Parameters for the Martensite Transition

Using the previously derived equations for shock pressure (eq 14), shock internal energy change (eq 7), and shock enthalpy change (eq 6), shock parameters may be calculated for the martensite transformation. Bunshah and Mehl[41] give the initial density of the alloy as 8.3×10^3 kg m^{-3} and the speed of transition as about 10^3 m sec^{-1}. Taking the speed of sound as 5×10^3 m sec^{-1}, a shock pressure of 41.4 GPa is obtained. A smaller value of 8 GPa is obtained if the calculated elastic wave velocity of Bunshah and Mehl[41] is used instead of the sound velocity. The increases in enthalpy and internal energy across the shock wave are 5×10^6 and 2×10^4 J kg^{-1}, respectively. The first of these far exceeds the latent heat of transformation of this alloy, given by Smithells[51] as 5.3×10^4 J kg^{-1}. By analogy with the undercooled metals, these results suggest that about 30% of the latent heat is appearing in the internal energy of the shock wave. The comparison of the martensite transition with the crystallization of undercooled metal melts is set out in Table V.

VI. Polymorphic Transitions

A. "Metallic" Transitions

Transitions are known that involve metastable amorphous phases undergoing transformation to stable metallic polymorphs. The best documented of these is "explosive antimony," an amorphous deposit obtained from the electrolysis of antimony trichloride solution. Steinwehr and Schulze[52] noted that this deposit exploded when an electric current greater than "some critical value" was passed through it. Coffin and Johnston[53] described how the material could explode with sufficient violence to shatter the copper on which it had been deposited, and

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(44) For example, J. C. Fisher, J. H. Holloman, and D. Turnbull, *J. Metals*, **1** 691 (1949); Z. S. Basinski and J. W. Christian, *Acta Met.*, **2**, 101 (1954).

(45) E. Scheil, *Z. Anorg. Chem.*, **183**, 98, (1929).

(46) E. S. Machlin and M. Cohen, *J. Metals*, **4**, 489 (1952).

(47) D. S. Lieberman in "Phase Transformations," American Society for Metals, Chapman and Hall, London, 1970, p 1.

(48) E. S. Machlin and M. Cohen, *J. Metals*, **3**, 1019 (1951).

(49) E. S. Machlin and M. Cohen, *J. Metals*, **3**, 746 (1951).

(50) C. L. Magee in ref 47, p 115.

(51) C. J. Smithells, Ed., "Metals Reference Book," Butterworths, London, 1949, pp 418–21, cited in ref 41.

(52) H. von Steinwehr and A. Schulze, *Z. Phys.*, **63**, 815 (1930).

(53) C. C. Coffin and S. Johnston, *Proc. Roy. Soc., Ser. A*, **146**, 564 (1934).

TABLE VIII. Metallic Transitions in Pseudo-Metals

	Explosive antimony	Amorphous arsenic
"Slow" transformation temp[a] (T_s, K)	373[b]	523[c]
"Rapid" transformation temp (T_r, K)	383[b]	538[d]
$(T_r - T_s)/T_s$[e]	0.026	0.028

[a] Equilibrium transformation after prolonged heating. [b] Coffin, ref 55. [c] Richter and Gommel, ref 60. [d] Geiling and Richter, ref 62. [e] This quantity is analogous to the reduced undercooling at which shock effects occur in undercooled metals but is of much smaller magnitude.

according to Glazunov and Lazarev[54] liberation of heat during the transformation was accompanied by the evolution of a white smoke.

There has been sustained interest in the nature of this transformation. Coffin[55] found that the deposit could be transformed to crystalline antimony by slow heating, and further ascertained that the first-order kinetics observed under these conditions yielded an activation energy of 114 kJ mol^{-1}. Observing this to be of the same magnitude as an ionization potential, he considered that the transformation proceeded by a "sort of ionisation." Subsequent reports have proposed the formation of new phases. Hendus,[56] for example, carried out X-ray diffraction studies on the amorphous material and reported explosive antimony as having a liquid-like structure with the atomic spacings similar to those in ordinary crystalline antimony. A more recent study by Krebs and coworkers[57] envisaged a layer structure for the lower ordered explosive polymorph.

There has been some interest as to which of the polymorphic modifications was the more metallic. Coffin[58] studied the magnetic susceptibility and electrical properties and concluded that the explosive form, being less diamagnetic than ordinary antimony, could be compared to the glass of an undercooled liquid.

Investigation of analogous transitions in other amorphous metals has not proceeded to the same extent although amorphous phases have been recognized in a large number of semimetals.[59] Of these, the transition that appears to show the closest analogy to antimony is the "metallic" transition in arsenic.

Amorphous arsenic can be synthesized as a sublimation product of ordinary arsenic.[60] X-Ray and electron diffraction studies were carried out on the amorphous and crystalline modifications by Breitling and Richter,[61] and these showed similar structures but with a rather wider lattice spacing for the amorphous allotrope. This may be taken to suggest that the metastable phase may be of low order in this system. The similarity between the transitions of explosive antimony and amorphous arsenic is shown in Table VIII, although it should be pointed out that whereas there is an explosion with obvious shock effects in the case of antimony, the phenomenon in arsenic is merely an unexpected increase in the transition velocity under certain conditions.[62] In addition, the case of antimony is a little different in that it is commonly believed to contain an appreciable amount of halogen.[55,57] Thus the transition in antimony may possibly be better considered pseudo-polymorphic. It is of interest that the martensite transformation in metals and the crystallization of silver and silver alloys from undercooled melts also involve "impure" phases.

Another possible explosive amorphous-crystalline transition which may be mentioned here is that of lead disulfide. Duncan and Ott[63] reported the isolation of an unstable amorphous lead disulfide, but synthesis by Silverman[64] at 2 GPa resulted in an explosion and a small yield of a crystalline material. The explosion may have been due to a rapid transition from the metastable amorphous state.

B. Lead Azide. Crystallization from Aqueous Solution

Bowden and Yoffe[65] have reviewed the explosion of β-lead azide in its crystallization from aqueous mixtures of lead nitrate and sodium azide. The solutions were so arranged as to be separated by a layer of sodium nitrate solution, and it was in this last layer that the crystals grew. The process was accompanied by audible clicks and flashes of light, eventually (generally after some hours) culminating in a (chemical) explosion. Although β-lead azide tends to revert under equilibrium conditions to the more thermodynamically stable α form, the explosion appears to be caused not by this polymorphic change but rather by the crystallization from solution. This is because the same explosion phenomenon has been observed when α-lead azide is crystallized from solution. Exactly the same behavior has been recorded for β-mercuric azide. Curiously, cadmium azide does not explode under the conditions outlined above, but can be made to explode when formed by the action of cadmium metal on hydrazoic acid.

Because the concentration of azide in the solution surrounding the growing crystal is just supersaturated, these systems have some similarity to the "explosive crystallization" described many years ago by Weston.[66]

The nature of the transformation is rather uncertain. Bowden and Yoffe[65] stated that it was known that the explosion was not due to a phase change but gave no evidence as to how they reached this conclusion. They also implied growth control, which would render this case different from all others thus far described. It is not feasible to apply the concepts of shock theory to this system because of the uncertainty of the initial state.

C. Polymerization Processes

The shock thermodynamic approach to fast transitions was originally developed for application to phase transitions and polymerization processes in organic compounds.[17] One convincing example of polymerization occurring with an accompanying shock wave appears to be the polymerization of maleic anhydride. Hamann[67] observed that solid maleic anhydride underwent a "sponta-

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(54) A. Glazunov and N. Lazarev, *Chem. Listy,* **34,** *89 (1940).*

(55) C. C. Coffin, *Proc. Roy. Soc., Ser. A,* **152,** 47 (1935).

(56) H. Hendus, *Z. Phys.,* **119,** 265 (1942).

(57) H. Krebs, F. Schultze-Gebhardt, and R. Thees, *Z. Anorg. Chem.,* **282,** 177 (1965).

(58) C. C. Coffin, *Can. J. Res.,* Sect. A, **13,** 120 (1935).

(59) H. Richter, *Phys. Z.,* **44,** 406 (1943).

(60) H. Richter and G. Gommel, *Z. Naturforsch. A,* **12,** 996 (1957).

(61) G. Breitling and H. Richter, *Mater. Res. Bull.,* **4,** 19 (1969).

(62) S. Geiling and H. Richter, *Acta Crystallogr.,* **2,** 305 (1949).

(63) W. E. Duncan and E. Ott, *J. Amer. Chem. Soc.,* **53,** 3940 (1931).

(64) M. S. Silverman, *Inorg. Chem.,* **5,** 2067 (1966).

(65) F. P. Bowden and A. D. Yoffe, "Fast Reactions in Solids," Butterworths, London, 1958, p 123.

(66) F. E. Weston, *Chem. News,* **98,** 27 (1908).

(67) S. D. Hamann, *Aust. J. Chem.,* **20,** 605 (1967).

neous polymerization" when heated to 370–440 K at pressures above 2 GPa. Hamann considered that the process was due not to the transfer of heat of polymerization to the shock wave in the manner proposed by Barkalov[17] but to the transfer of enthalpy of a polymorphic transition. This polymorphic transition was envisaged as occurring from the monomer to a new crystalline state in which the molecules were better arranged to polymerize than in the original monomer. This type of transition has also been suggested for low-temperature polymerization; Semenov[68] saw it as reminiscent of the martensite transformation. Petrov[14a] has recently reviewed such explosive solid reactions, polymerizations, and phase transformations induced by strong shearing stresses in "Bridgman anvils."

VII. Seismogenesis

The possibility of rapid solid–solid phase transitions (*e.g.*, olivine–spinel) as sources of seismic energy has been suggested by several authors.[69-71] Although one current geophysical view[72] is that earthquake sources are characterized by shear phenomena, and that solid–solid transitions with volume change do not appear to be an important factor in seismogenesis, the existence of a number of explosive phase transitions in chemical systems suggests that this process should not be dismissed as a possible earthquake source mechanism. Modern theories of continental drift and plate tectonics involve the sinking of material at continental margins,[73] providing a potential mechanism for the attainment of a metastable state prior to explosive transformation to a denser phase. An explosive transition to a less dense phase is also possible, associated with upward convection. Indeed, some earthquakes occur at a depth of 700 km where the temperature and pressure conditions are such that earthquakes caused by shear phenomena are difficult to imagine.

From the point of view of seismogenesis, it should be noted that explosive shocks produce transverse waves as well as compressional waves, both in laboratory-scale solid samples[74] and in geologic systems.[71,75]

In conclusion, it is interesting to consider a quotation from an account of the sudden crystallization of undercooled seawater in Siberia, as recorded by Welzl[76]: "An icy pulp was forming, the chunks of ice were growing, getting wider, the pulp was up to a foot thick, it was getting clotted, chunks of ice shifted closer and closer, until they formed large irregular bundles of pulp—and then suddenly, almost in the same second—bang! it all froze and the icy covering was whisked across the sea farther than the eye could reach."[77]

VIII. Glossary of Symbols

Numbers refer to equations in which the symbols first appear.

A, A_G, A_N	empirical constants
C_p	heat capacity at constant pressure
F^*	activation energy corresponding to critical nucleation radius (22)
ΔF	free energy change for nucleation (25)
ΔH	enthalpy change during phase transition (15)
L	latent heat of phase transformation $(= -\Delta H)$ (15)
Q	activation energy (21)
R	gas constant
R_G	rate of growth (21)
R_N	rate of nucleation (22)
R_T	rate of transition (16)
S	(subscript) isentropic
T	temperature
T_m	melting temperature
ΔT	extent of undercooling (16)
ΔT_{max}	maximum attainable extent of undercooling (17)
ΔT_s	undercooling at onset of shock effects
a	sound velocity
c	(superscript) calculated quantity
e	specific internal energy (5)
h	specific enthalpy (3)
l	(subscript) liquid
m	mass flow (1)
n	empirical constant
p	pressure
p_N	nucleation pressure (25)
p_2	shock pressure (14)
s	(subscript) solid
u	velocity relative to shock discontinuity (1)
u_D	detonation velocity (relative to unshocked material) (13)
u_S	shock velocity (relative to unshocked material)
u_{fl}	flow velocity (relative to unshocked material)
v	specific volume (ρ^{-1})
v_t	terminal center of mass velocity (24)
Δv	volume change during phase transition
α	coefficient of volume thermal expansion
ρ	density
ψ	angle between Rayleigh line and volume axis (10)
1	(subscript) unshocked, ahead of discontinuity
2	(subscript) shocked, behind discontinuity

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(68) N. N. Semenov, *J. Polym. Sci.*, **55**, 563 (1961).

(69) A. R. Ubbelohde in ref 15, p 349; A. R. Ubbelohde, *Nature (London)*, **224**, 895 (1969); F. F. Evison, *Bull. Seismol. Soc. Amer.*, **53**, 873 (1963); **57**, 9 (1967); F. F. Evison, Vesiac Report on Source Mechanism of Shallow Seismic Events, University of Michigan, 1967, No. 12, p 173; J. G. Dennis and C. T. Walker, *Tectonophysics*, **2**, 401 (1965); C. T. Walker and J. G. Dennis, *Nature (London)*, **209**, 182 (1966); R. E. Riecker and T. P. Rooney, *Geol. Soc. Amer. Bull.*, **78**, 1045 (1967); A. R. Ritsema in "Phase Transformations and the Earth's Interior," A. E. Ringwood and D. H. Green, Ed., Proceedings of Symposium, Canberra, Australia, 1969, Upper Mantle Scientific Report No. 26, North-Holland, Amsterdam, 1970, reprinted from *Phys. Earth Planet, Interiors*, **3**, 503 (1970); L. D. Livshits and Y. N. Ryabinin, *Fiz. Osn. Poiskov Metod. Prognoza Zemletryasenii*, 28 (1970); *Chem. Abstr.* **76**, 115966 (1972); A. F. M. Barton, A. P. W. Hodder, and A. T. Wilson, *Nature (London)*, **234**, 293 (1971). J. Kasahara and H. Tsukara, *J. Phys. Earth*, **19**, 79 (1971); A. E. Ringwood, *Earth Planet. Sci. Lett.*, **14**, 233 (1972).

(70) M. J. Randall, *Bull. Seismol. Soc. Amer.*, **54**, 1291 (1964).

(71) M. J. Randall, *J. Geophys. Res.*, **67**, 4956 (1962); **71**, 5297 (1966).

(72) F. F. Evison, *Tectonophysics*, **9**, 113 (1970).

(73) For example, O. M. Phillips, "The Heart of the Earth," W. A. Freeman, San Francisco, Calif., 1968, p 163.

(74) J. S. Rinehart and J. Pearson, "Behaviour of Metals Under Impulsive Loads," American Society for Metals, Cleveland, Ohio, 1954.

(75) F. Press and C. Archambeau, *J. Geophys. Res.*, **67**, 337 (1962).

(76) J. Welzl, "Thirty Years in the Golden North," P. Selver, Translator, Allen and Unwin, London, 1932.

(77) *Note Added in Proof.* Elastic shocks have been observed accompanying the phase change between the wurtzite (low pressure) and NaCl (high pressure) structures of ammonium fluoride: J. Kasahara, I. Ohno, and K. Iida, *J. Phys. Earth*, **19**, 47 (1971).