RESEARCH ARTICLE | FEBRUARY 01 1990

A thermochemical model for shock-induced reactions (heat detonations) in solids

Mark B. Boslough

J. Chem. Phys. 92, 1839–1848 (1990)
https://doi.org/10.1063/1.458066

A thermochemical model for shock-induced reactions (heat detonations) in solids

Mark B. Boslough
Sandia National Laboratories, Albuquerque, New Mexico 87185

(Received 18 May 1989; accepted 20 October 1989)

Recent advances in studies of shock-induced chemistry in reactive solids have led to the recognition of a new class of energetic materials which are unique in their response to shock waves. Experimental work has shown that chemical energy can be released on a time scale shorter than shock-transit times in laboratory samples. However, for many compositions, the reaction products remain in the condensed state upon release from high pressure, and no sudden expansion takes place. Nevertheless, if such a reaction is sufficiently rapid, it can be modeled as a type of detonation, termed "heat detonation" in the present paper. It is shown that unlike an explosive detonation, an unsupported heat detonation will decay to zero unless certain conditions are met. An example of such a reaction is $Fe_2O_3 + 2Al + \text{shock} \rightarrow Al_2O_3 + 2Fe$ (the standard thermite reaction). A shock-wave equation of state is determined from a mixture theory for reacted and unreacted porous thermite. The calculated shock temperatures are compared to experimentally measured shock temperatures, demonstrating that a shock-induced reaction takes place. Interpretation of the measured temperature history in the context of the thermochemical model implies that the principal rate-controlling kinetic mechanism is dynamic mixing at the shock front. Despite the similarity in thermochemical modeling of heat detonations to explosive detonations, the two processes are qualitatively very different in reaction mechanism as well as in the form the energy takes upon release, with explosives producing mostly work and heat detonations producing mostly heat.

I. INTRODUCTION

There has been a resurgence of interest in shock-induced chemical reactions in solids, culminating in the recent recognition of a new class of energetic materials, in which thermochemical energy is controlled by high pressure shock compression.[1] Much of the recent work has been concerned with chemical synthesis,[2–4] building on the earlier work which was dominated by the Soviets.[5–7] Shock-induced chemical reactions in solids have been studied experimentally by postshock analysis, as well as by time-resolved measurements, leading to a number of theoretical efforts to explain the mechanisms by which such rapid reactions can take place.

The present paper is devoted to the development of a description of such reactions based on fundamental thermochemical and shock wave principles. Unlike the other theoretical developments to date, the present model ignores the kinetic aspects of the reactions entirely, and assumes only that the reaction proceeds rapidly enough that an equilibrium state can be defined behind the shock wave. The purpose of this effort is to provide a conceptual framework to which the more advanced models can be related, and the subject is approached in much the same manner as the earliest attempts to describe explosive detonations without regard for chemical mechanisms. Shock temperature data are also presented to the extent that they provide experimental support for the model.

II. BACKGROUND

The growing interest in the problem of shock initiation of chemical reactions in solids is reflected in the large number of experimental and theoretical papers published since the 1983 bibliography of Graham *et al.*[8] An example is the recent work concerned with materials that exhibit exothermic reactions under shock, forming intermetallic compounds. These reactions have been studied extensively by examining samples recovered from explosive-loading experiments.[9–10] These recovery experiments were instrumental in demonstrating that the shock environment is unique in its ability to rapidly mix and activate the components, thereby initiating a fast reaction.

Strongly exothermic reactions, such as intermetallics, thermites, and other pyrotechnic mixtures, are currently of particular interest. The earliest work in the U.S. on such materials was a series of exploratory experiments in which the estimated internal energy increase due to a shock was compared to the statically measured autoignition energy for a number of heat powders.[11] These experiments were not designed to provide evidence for chemical reactions at or behind the shock front; time-resolved experiments have been required to make that observation. Sheffield and Schwarz[12] observed possible evidence that reactions can take place on a microsecond time scale by measuring wave profiles in shocked titanium subhydride/potassium perchlorate mixtures. They proposed that the reaction front moves through the reactive material at the same velocity as the shock, and pointed out the similarities to initiation of high explosives. Kovalenko and Ivanov[13] performed Hugoniot measurements as well as recovery experiments on lead nitrate/aluminum mixtures, finding that the reactions that led to the products they observed in postshock analysis were apparent in the Hugoniot data. Their work provided further evidence that shock-induced chemical reactions can take place at a rate commensurate with that of shock wave propagation.

0021-9606/90/031839-10$03.00

Batsanov *et al.*[14] compared Hugoniot measurements on stoichiometric mixtures of tin and sulfur to those on tin sulfide in an attempt to determine the extent of reaction as a function of shock pressure. However, because the uncertainties in the measured Hugoniots are large relative to their difference in pressure at a given specific volume, their determination of the quantity of reacted material was effectively only an estimate.

To provide a more sensitive time-resolved method for observing shock-induced chemical reactions, shock-temperature measurements have also been applied. Boslough and Graham[15] used time-resolved radiation pyrometry to show that shock-induced reactions in nickel/aluminum mixtures take place on a submicrosecond time scale. Hornig *et al.*[16] applied a similar technique to an aluminum/ferric oxide (thermite) mixture, and concluded that ignition occurred in less than 100 ns. These temperature measurements provided more support for the view that the reactions occur immediately behind the shock front, but both studies were complicated by thermal radiation from the heterogeneously heated powders. This potential problem was overcome by making use of fine-grained powders for rapid thermal equilibration, and by comparing time-resolved shock temperatures in nickel/aluminum mixtures to those in inert pure nickel under similar conditions.[17] The measured temperatures were consistent with prompt shock-induced reaction of at least 45% of the reactants in the mixture.

Experimental observations of shock-induced chemical reactions have encouraged attempts to model the process. Maiden and Nutt[18] developed a heterogeneous model for calculating shock initiation thresholds by assuming that the reaction is ignited when the surface temperature of a pore meets a hot-spot ignition criterion. They assumed that the initiation process is very similar to that for high explosives, and adapted an explosive initiation theory to determine criticality conditions. By contrast, Enikolpyan *et al.*[19] believe that observed explosive-like reactions in powder mixtures under low strain-rate pressure-shear loading is due to unique chemical processes having nothing to do with thermal activation. They based their argument on the observation of extremely rapid reactions for both strongly and weakly exothermic systems, independent of starting temperature. Instead, they proposed that the reactions are initiated through mechanisms of mechanical "disintegration" and mixing of the substituents by a shock wave.

Horie and Kipp[20] formulated two mathematical models, one homogeneous and one heterogeneous, within the context of the "catastrophic" shock approach of Graham.[21] The models assume that the shock generates a nonequilibrium mixture by high-speed relative mass motion, plastic flow, fracture, and mass mixing through processes such as Helmholtz instabilities and microjetting. Taylor *et al.*[22] extended this model by considering chemical reactivity that proceeds at various rates due to a heterogeneous temperature field.

Graham[1] has now pointed out that shock-induced reactions in nonexplosive energetic solids are fundamentally different from either high explosive detonations or pyrotechnic reactions. Controlling features appear to be: shock-induced mixing, shock activation, configuration change and heating.[4] The distinctive nature of this process allows recognition of such reactive solids as a new class of energetic materials.

III. SHOCK THERMODYNAMICS

When an inert, homogeneous substance is compressed by a steady, one-dimensional shock wave to another state in thermodynamic equilibrium, the specific internal energy increase across the shock is

$$E_H - E_0 = \tfrac{1}{2}(P_H + P_0)(V_0 - V_H), \tag{1}$$

where E is the specific internal energy, P is the pressure and V is the specific volume. The variables subscripted by 0 and H refer to the initial state and the state behind the shock front, respectively. This equation is often referred to as the Rankine–Hugoniot equation, and comes directly from the conservation of mass, momentum, and energy across the shock front.[23] In general, it is the normal stress in the direction of shock propagation that is used in Eq. (1) rather than the pressure. However, for a stress much greater than the yield strength of the solid, the difference between stress and pressure is small and can be ignored. The range of Hugoniot elastic limits for various aluminum alloys is 0.02 to 0.7 GPa.[24] This range is well within the peak shock stresses under discussion, so for simplicity we will assume that the strength of thermite is negligible. By ignoring strength, the details of the calculated shock compression at low stresses are inaccurate, but the conclusions of the paper are not affected.

In addition to Eq. (1) the specific internal energy of any material in thermodynamic equilibrium can be written as a function of P and V, as the equation of state $E(P,V)$. By combining the equation of state with the Rankine–Hugoniot equation, E can be eliminated and P can be written as a function of V. This P–V relationship is the material-dependent shock wave equation of state, and is called the Hugoniot. It should be emphasized that the Hugoniot is not a thermodynamic path followed by the material, but is a locus of end states achieved by shock waves of varying intensity.

The shock process is rapid and adiabatic, but in general it is irreversible and therefore not isentropic. The irreversibility comes from dissipative mechanisms within the shock front which convert mechanical (and sometimes chemical) energy to heat. Thus, for a given material, the principal Hugoniot curve will lie above the isentrope centered on the same initial state in the P,V plane. The difference in pressure at a given specific volume is due entirely to the greater thermal energy, and can be related by using the Mie-Grüneisen approximation,

$$E_H - E_S = (V/\gamma)(P_H - P_S), \tag{2}$$

where the subscript S refers to states on the isentrope, and γ is the Grüneisen parameter:

$$\gamma(V) = V\left(\frac{\partial P}{\partial E}\right)_V = \alpha V K_T / C_V, \tag{3}$$

where α is the volume coefficient of thermal expansion, K_T is the isothermal bulk modulus, and C_V is the specific heat at constant volume. Use of the Mie–Grüneisen approximation

[Eq. (2)], requires the assumption that the Grüneisen parameter is a function only of volume, and has no pressure dependence.

The energy along the isentrope is determined simply by integrating the differential expression for the first law of thermodynamics, holding entropy constant:

$$E_S - E_0 = -\int_{V_0}^{V} P_S \, dV. \tag{4}$$

Combining Eqs. (1), (2), and (4) allows the Hugoniot pressure to be written as a function of V, if the isentrope $P_S(V)$ is known,

$$P_H(V) = \left(\int_{V_0}^{V} P_S \, dV + \left[\frac{V}{\gamma}\right] P_S\right) \Big/ \left(\left[\frac{V}{\gamma}\right] - \frac{1}{2}(V_0 - V)\right), \tag{5}$$

where it has been assumed that $P_0 = 0$.

For a reactive material, $P_H(V)$ can be determined similarly. If a material undergoes a chemical reaction during the shock process, the energy of the Hugoniot state is different by an amount equal to the heat of reaction Q and Eq. (1) becomes

$$E_H - E_0 = -Q + \tfrac{1}{2} P_H (V_0 - V), \tag{6}$$

where V_0 refers to the initial specific volume of the reactant. The thermal energy between the Hugoniot and isentrope of the product is related to the thermal pressure by Eq. (2), where γ is now that of the product. If the specific volume of the product at standard conditions is $V_0' < V_0$, the energy along the principal isentrope of the product is

$$E_S - E_0 = -\int_{V_0'}^{V} P_S \, dV. \tag{7}$$

The integral of P_S from V_0 to V_0' is zero because it corresponds to the isentropic compression of the product from a porous zero-strength solid with specific volume equal to V_0. In the general case, the initial state has some specific volume $V_{00} \neq V_0$, corresponding to the initial porosity $p = (1 - V_0 / V_{00})$. In this case V_0 is replaced by V_{00} in Eq. (6). Thus, the general Hugoniot pressure of a porous, reactive material is

$$P_H(V) = \left(-Q - \int_{V_0'}^{V} P_S \, dV - \left[\frac{V}{\gamma}\right] P_S\right) \Big/ \left(\frac{1}{2}(V_{00} - V) - \frac{V}{\gamma}\right), \tag{8}$$

where $Q = 0$ and $V_0' = V_0$ for nonreacting material. By inserting known material properties into Eq. (8), the theoretical pressure–volume Hugoniot of an unreacted material (reactant Hugoniot) can be compared to that of the same material if it reacts during the shock process (product Hugoniot).

IV. THERMITE EQUATION OF STATE

The thermite reaction,

$$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe, \tag{9}$$

is an example of a reaction for which the heat is large in comparison to the heat generated by a shock wave for shocks of 10 GPa or less. The heat of reaction per unit mass of reactant in Eq. (9) is -0.95 kcal/gm (-3.97×10^6 J/kg).[25]

TABLE I. Thermite reactant parameters.

Parameter	Aluminum	Hematite	Mixture
Mass fraction (m_i)	0.253	0.747	1.000
Initial density (ρ_0, g/cm^3)	2.700	5.274	4.249
Initial specific volume (V_0, cm^3/g)	0.3704	0.1896	0.2353
Initial volume fraction (v_i)	0.398	0.602	1.000
Zero pressure bulk modulus (K_{0S}, GPa)	76.4	202.7	122
Pressure derivative of K_{0S} (K_{0S}')	5.32	4.53	6.65
Zero pressure Grüneisen parameter (γ_0)	2.35	1.99	2.08

The reactant Hugoniot of the unreacted left-hand side of Eq. (9) was determined using Eq. (5) and the parameters listed in Table I, which have been taken from published data for aluminum and hematite. To calculate the isentropic pressure and its volume integral, the Bridgman quadratic equation[26] was used;

$$\frac{V}{V_0} = 1 - (P_S/K_{0S}) + \tfrac{1}{2}(1 + K_{0S}')(P_S/K_{0S})^2, \tag{10}$$

where K_{0S} is the zero-pressure isentropic bulk modulus, and K_{0S}' is its first pressure derivative. For aluminum, these constants were determined from ultrasonic data by Anderson.[26] For hematite, the ultrasonic data of Lieberman and Schreiber[27] were used. It should be noted that Eq. (10) is valid only for strains less than a few percent. For the present study, in which pressures are less than about 10 GPa, the Bridgman equation provides a reasonable approximation. For higher shock pressures (and larger strains) a higher-order finite strain theory is necessary. For substances consisting of more that one component, however, the higher-order finite strain calculations introduce complications into the mixture theory, so the quadratic equation is used for simplicity.

For a multicomponent system with a uniform stress distribution, Eq. (10) is summed over all components i:

$$V = \sum_i m_i V_i, \tag{11}$$

where m_i and V_i are the mass fraction and specific volume of the ith component, respectively. For a two-component system such as thermite, the composite bulk modulus (assuming zero porosity) is

$$K_{0S} = [(v_1/K_{0S1}) + (v_2/K_{0S2})]^{-1}, \tag{12}$$

where the initial volume fraction of component i has been written as v_i. Equation (12) is the Reuss average, and assumes that the stress is constant throughout the aggregate.[28]

Similarly, the bulk modulus derivative for the two component system is

$$K'_{0S} = K^2_{0S}[v_1(1+K'_{0S1})/K^2_{0S1} + v_2(1+K'_{0S2})/K^2_{0S2}] - 1, \qquad (13)$$

where K_{0Si} and K'_{0Si} are the bulk modulus and its pressure derivative at zero pressure, respectively. Substituting the bulk moduli and derivatives from Table I gives $K_{0S} = 122$ GPa and $K'_{0S} = 6.65$ for the thermite reactant. A composite Grüneisen parameter can also be determined from the component values. Duvall and Taylor[29] showed that there is no simple way of calculating γ analogous to Eqs. (12) or (13). A simple mass-fraction-weighted average, while inaccurate, is a reasonable approximation for present purposes. Substituting the appropriate values into Eq. (8), the isentrope and a family of Hugoniots for various initial porosities were calculated for the thermite reactant. These curves are plotted in the pressure–volume plane in Fig. 1. For an initial porosity of 50%, the thermal pressure is so great that the final state densities are below standard density ($V > V_0$). Such "anomalous Hugoniots" are discussed in detail by Zel'dovich and Raizer.[30]

In the same manner, we can calculate the Hugoniot for which the end state is the right-hand side of Eq. (9), (the thermite product). It is impractical to use the principal isentrope (centered at standard conditions) as the reference curve in Eq. (8), because the Hugoniot for the thermite product lies in the melt region of stability of both components, and Eq. (2) is only appropriate where there are no phase boundaries between the reference isentrope and the Hugoniot. It is therefore necessary to construct a reference isentrope centered above the melting point of both components. Since Al_2O_3 has the higher melting point (2312 K), we center the isentrope on the liquid side of that temperature. The densities of liquid alumina[31] and liquid iron[32] at 2312 K and one atmosphere are well known from experiment and are included in Table II. The elastic and anharmonic constants, unfortunately, are not well known for the liquid phases. For liquid iron the values were taken from the shock wave data of Brown and McQueen,[33] and for alumina it was necessary to use the values measured ultrasonically for the solid phase (Anderson[26]; see Table II). Fortunately, for small strains, the Hugoniots are most sensitive to Q and V_0, both of which are well known.

Since a reference curve other than the principal isentrope is used, the appropriate value of Q is the difference between the heat of reaction of thermite at standard conditions and the enthalpy required to heat the reacted mixture from standard conditions to the state at which the reference isentrope is centered, namely the liquid side of the Al_2O_3 melting temperature at 2312 K. According to published enthalpy tables,[34] the enthalpy difference between iron at standard conditions and liquid iron at 2312 K is $\Delta H^{2312}_{298} = 23.01$ kcal/g mole. Similarly, for liquid Al_2O_3, $\Delta H^{2312}_{298} = 59.74$ kcal/g mole. For the thermite products, $\Delta H^{2312}_{298} = 105.76$ kcal/g mole. Subtracting this from the thermite heat of reaction gives the excess enthalpy due to the reaction, which, in consistent units, is -1.9×10^6 J/kg. The reference isentrope and a family of porous Hugoniots for the thermite products are plotted in Fig. 2.

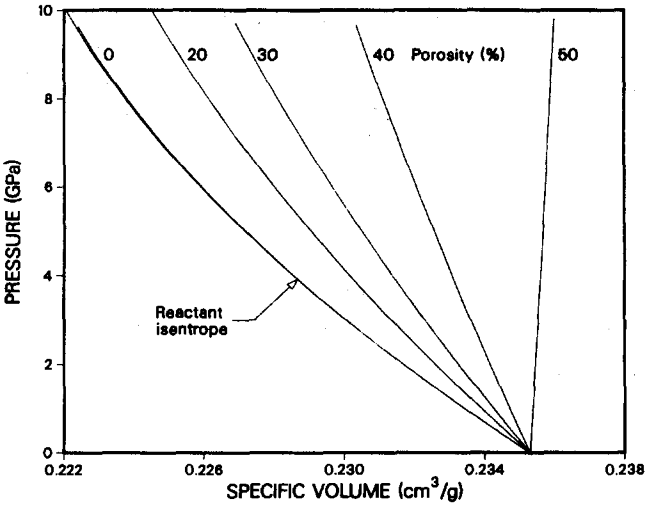

FIG. 1. Calculated thermite reactant isentrope and family of thermite reactant Hugoniots for various initial porosities centered on standard conditions.

V. HEAT DETONATION MODEL

The calculated Hugoniots depicted in Figs. 1 and 2 are representations of the end states that are achieved by shocking thermite without and with the chemical reaction taking place, respectively. In this sense they are two extreme end states. The reactant Hugoniot is that for which the reaction is not initiated, or proceeds at a rate much slower than rates associated with the shock wave. The product Hugoniot corresponds to final states that have undergone 100% reaction. These states can only be reached if the reaction is fast compared to shock wave transit times (i.e., the sample size is large compared to the dimension associated with the shock front). Methods of calculating intermediate states are not addressed in this paper.

TABLE II. Thermite product parameters.

Parameter	Iron	Alumina	Mixture
Mass fraction (m_i)	0.523	0.477	1.000
Reference density (ρ_0, g/cm^3)	6.59	2.96	4.154
Reference specific volume (V_0, cm^3/g)	0.152	0.338	0.241
Reference volume fraction (v_i)	0.330	0.670	1.000
Zero pressure bulk modulus (K_{0S}, GPa)	136	252	197
Pressure derivative of K_{0S} (K'_{0S})	5.0	3.97	5.2
Zero pressure Grüneisen parameter (γ_0)	2.1	1.32	1.7

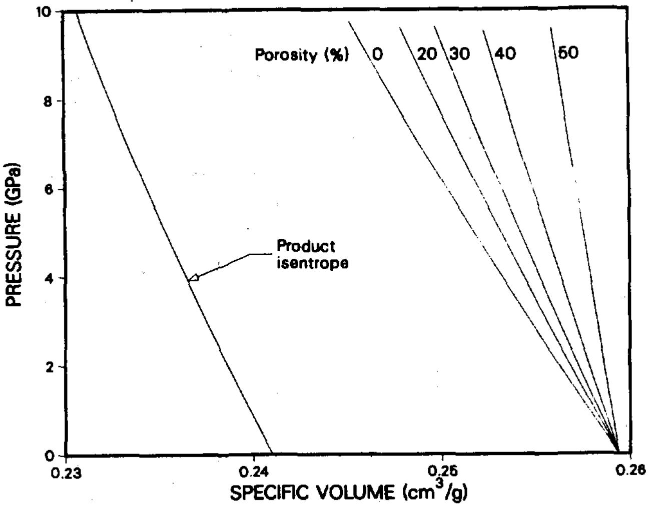

FIG. 2. Calculated thermite product isentrope centered on the liquid side of the alumina melting point and family of thermite product Hugoniots for various initial porosities centered on state with initial internal energy equal to standard conditions plus heat of thermite reaction.

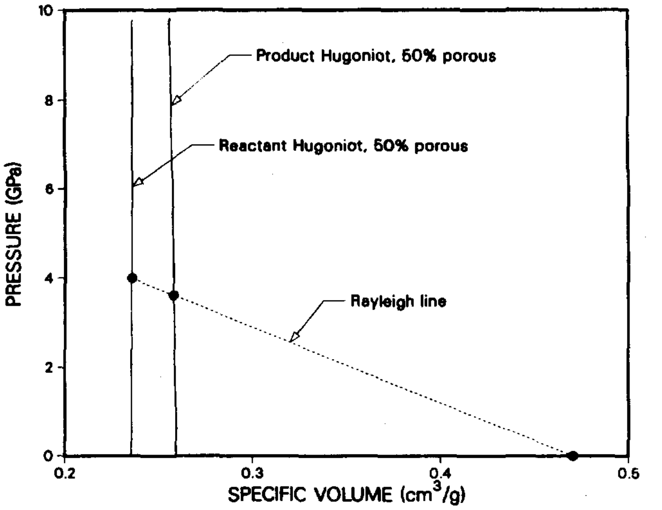

FIG. 3. Relationship between 50% porous thermite reactant and product Hugoniots to Rayleigh line in P–V plane.

If the reaction rate is finite but rapid enough to go to completion, the initial shock will achieve a state on the reactant Hugoniot. At some later time, the final state must lie on the product Hugoniot. The case of a steady wave (in which the profile does not change with time) is illustrated in Fig. 3 for 50% porous thermite. The initial shock takes the material to the state on the reactant Hugoniot. It can be shown (see, e.g., Courant and Friedrichs[35]) that a steady wave can only reach states intersected by the Rayleigh line, so the final state is that on the product Hugoniot.

When a shock-induced exothermic reaction is achieved in this way it is a "strong" or "overdriven detonation" in the terminology of Fickett and Davis.[36] The following argument shows that for nonexplosive energetic solids, a reaction shock will decay unless it is supported. If the reacted material is unsupported from the rear, rarefactions will follow the detonation wave. From the Rankine–Hugoniot equations[23] the velocity of the reaction (or detonation) wave is

$$U = V_{00}\sqrt{P_H/(V_{00}-V)}. \tag{14}$$

The sound velocity in a medium (with respect to the material into which it is propagating) is

$$c = V\sqrt{-(\partial P/\partial V)_S}, \tag{15}$$

so, if the particle velocity of the shocked material is u, the rarefactions will catch up with and decay the detonation wave if the inequality

$$c > U - u \tag{16}$$

is true. One can use the Rankine–Hugoniot equations to write u in terms of V and P_H,

$$u = \sqrt{P_H(V_{00}-V)}, \tag{17}$$

together with Eq. (14) to get the right-hand side of inequality (16)

$$U - u = V\sqrt{P_H/(V_{00}-V)}. \tag{18}$$

Equation (6) can be generalized for a porous solid, differentiated, and combined with the differential form of the first law of thermodynamics to get

$$TdS = \tfrac{1}{2}(V_{00}-V)dP + \tfrac{1}{2}PdV \tag{19}$$

along the Hugoniot. The total differential of $S(P,V)$ can be written as

$$TdS = \left(\frac{V}{\gamma}\right)dP - V\left(\frac{1}{\gamma}\right)\left[\frac{\partial P}{\partial V}\right]_S dV, \tag{20}$$

using Eq. (3), the thermodynamic identity $\gamma = V(\partial P/\partial E)_V$. Equating Eqs. (19) and (20), and using Eq. (15) gives the sound speed in terms of the slope of the Hugoniot:

$$c = V\left(\left[-1 - \frac{\gamma}{2V}(V_{00}-V)\right]\frac{dP}{dV}\bigg|_H + \left(\frac{\gamma P_H}{2V}\right)\right)^{1/2}. \tag{21}$$

When the slope of the Hugoniot is steeper than that of the Rayleigh line, we have

$$-\frac{dP}{dV}\bigg|_H > \frac{P_H}{V_{00}-V}. \tag{22}$$

Substituting inequality (22) into Eq. (21) gives

$$c > V\sqrt{P/(V_{00}-V)}. \tag{23}$$

Comparing this inequality to Eq. (18) demonstrates that inequality (16) is true, therefore an unsupported strong detonation decays.

Inspection of Fig. 3 shows that a situation analogous to a Chapman–Jouguet detonation (see Ref. 36) in a high explosive is unattainable in a shock-induced reaction (heat detonation), when the zero-pressure density of the reaction products is greater than the initial density of the solid reactants. In a high explosive, the reaction products contain gas, and the zero-pressure density will always be less than the initial density of the explosive. Thus, an unsupported strong detonation will decay until the Rayleigh line becomes tangent to the Hugoniot of the reaction products at some non-zero pressure, at which time a steady, Chapman–Jouguet detonation ensues if kinetically permitted. An unsupported reaction shock such as described by Fig. 3 will eventually decay to zero.

In the case of a reactive solid for which the initial density is greater than the final density of the product, another possibility arises. In this situation, a Rayleigh line can be found that has a point tangent to the reacted Hugoniot, analogous to the Chapman–Jouguet point. It is theoretically possible that a sustained, steady heat detonation could exist corresponding to this solution of the shock equations. However, most models and observations indicate that energetic solids are more sensitive at lower densities (higher porosities), and it is not clear whether any mixture exists that would be sufficiently sensitive to undergo a shock-induced reaction while still satisfying the density restrictions required for a sustained reaction. In the absence of vapor-phase products, an unsupported heat detonation is possible only if a dense sample could be made in which shock-induced substituent mixing is sufficient for rapid chemical reaction, The possibility of a sustained detonation controlled by volatile impurities in energetic solids also exists, and is discussed elsewhere.[37]

The present discussion has been limited to heat detonations in exothermically reacting powder mixtures, but a very similar model was proposed in 1965 by Kuznetsov,[38] which described a detonation caused by a material undergoing a first-order phase transformation. The conclusions of that study were that: (1) no detonation is possible if the initial state is in equilibrium (i.e., the initial phase must be metastable under the initial conditions), (2) the condition that the transformation be exothermic is neither sufficient nor necessary to allow a detonation, and (3) the detonation is allowed only if the specific volume increases under an isobaric and isenthalpic transformation. Such a detonation was invoked by Barkalov, Gol'danskii and co-workers[39] to explain the rapid polymerization of acrylamide under shock. The Kuznetsov[38] model was applied to a single-component phase transformation, but none of its assumptions preclude its application to mixtures of reactive powders. Thus, Kuznetsov's conclusions also apply to thermite.

It is important to make the fundamental distinction between shock-initiated reactions and gasless combustion (e.g., Merzhanov[40]). The process of gasless combustion relies on the thermal and mass transport properties of the reacting material; consequently the velocity of the reaction front is much slower than that of a heat detonation, which relies on processes proceeding at the rate of the shock wave. This difference is reflected quantitatively as the rate of chemical energy conversion. For example, a gasless combustion wave in 50% porous thermite travels at a velocity of about 1 cm/s into material with density 2.15 g/cm^3, liberating 8.5 kJ/cm^3 of chemical energy in the process, for a net power conversion of about 8.5 kW/cm.[2] A heat detonation, travelling at 1 km/s, operates at a power level of 0.85 GW/cm, which is 5 orders of magnitude higher. The gasless combustion and heat detonation processes are further distinguished by the temperatures achieved. In the former, pressures are low and adiabatic temperatures are limited by vaporization of the substituents. In the latter, the high pressures increase the vaporization temperature, so the adiabatic temperature can reach higher values. For applications in which a large amount of thermal energy is required as quickly as possible, shock-induced heat detonations are clearly more useful than either gasless combustion or high explosive detonation.

TABLE III. Work and heat efficiencies.

	High explosive (RDX)	Shocked pyrotechnic ($2Al/NH_4NO_3$)	50% porous thermite (10 GPa) ($2Al/Fe_2O_3$)
Work efficiency	98%	75%	$-29\%^a$
Heat efficiency	2%	25%	$129\%^a$
Postshock temperature (K)	374	1694	4600

[a] See the text.

The thermal nature of heat detonations can further be demonstrated by comparison to explosive detonations. Fickett and Davis[36] discuss the concept of "useful work" of Jacobs[41] which describes the net amount of work per unit mass that can ideally be obtained from a detonating high explosive:

$$W = \int_V^{V_F} P_S\, dV - \tfrac{1}{2}u^2. \qquad (24)$$

The work efficiency is $-W/Q$, where Q is the heat of reaction. V_F refers to the final specific volume of the release isentrope of the reaction products. To perform the calculations for porous thermite, we can approximate the release isentrope with the calculated Hugoniot for the reaction products.

Similarly, we can define "useful heat" to be $H = -(Q + W)$, which is the amount of heat that can ideally be derived from the detonation. The heating efficiency of the detonation is then $-H/Q$. Table III compares these values for 50% porous thermite shocked to 10 GPa to those tabulated by Fickett and Davis[36] for two explosives. The fact that useful work for thermite is negative signifies that the heat detonation actually requires that the surroundings do a net amount of work on the system, while the heating efficiency greater than 100% means that, in addition to the conversion of chemical energy to heat, some work is also converted to heat.

While calculations of Hugoniots in the pressure-volume plane are useful for energy comparisons, the pressure-particle velocity plane is more useful for making comparisons to most experimental shock wave data. Eq. (17) was used to transform the reacted and unreacted 50% porous thermite Hugoniots to this plane. Inspection of Fig. 4 demonstrates that, at a given particle velocity, the pressure on the reacted Hugoniot is about 10% higher (and at a given shock pressure, the unreacted Hugoniot has a 5% greater particle velocity). Experimental attempts to measure the reaction threshold by a series of Hugoniot measurements are destined to be frustrated by large uncertainties (which are typical for porous solids) that are as big as the difference between the Hugoniots. It is for this reason that, according to Batsanov *et*

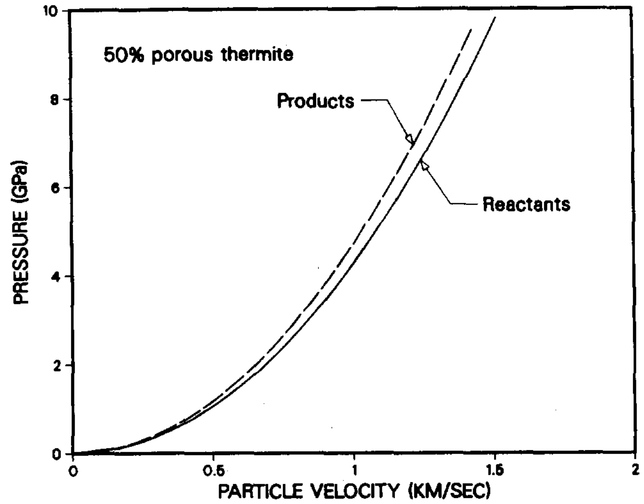

FIG. 4. Calculated Hugoniots for initially 50% porous thermite reactant and product in P–u_p plane

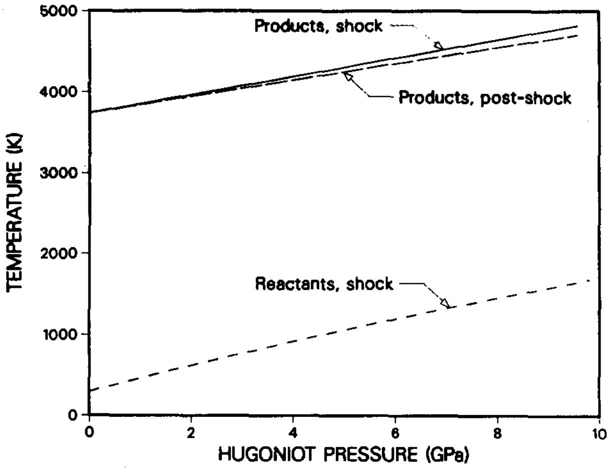

FIG. 5. Calculated shock temperatures for 50% porous thermite reactant and product, and calculated postshock temperatures for product.

al.,[14] their determination of the fraction of shock-reacted tin sulfide by this experimental strategy "has the character of an estimate."

Another experimental approach would be to measure time-resolved stress with *in situ* stress gauges or the particle velocity with laser velocity interferometry (VISAR). The latter technique was chosen by Sheffield and Schwarz,[12] who observed small ($\approx 10\%$) increases in particle velocity in titanium subhydride/potassium perchlorate mixtures 1 to 2 μs after being shocked. However, the growth they observed in particle velocity is extremely small compared to that observed in shocked explosives (e.g., Setchell[42]) and experiments of this type should not be expected to yield accurate data on heat detonation reactions.

VI. SHOCK TEMPERATURES

A. Temperature calculations

Despite the small differences between reactant and product Hugoniots, the difference in internal energy is extremely large. The $> 100\%$ heating efficiency implies that, for large heats of reaction, the temperature on the product Hugoniot will be much higher than on the reactant Hugoniot. The shock temperature can be calculated by writing down the total differential

$$T\,dS = C_v\,dT + \left(\frac{\partial P}{\partial T}\right)_V T\,dV \qquad (25)$$

and integrating along an isentrope ($dS = 0$) with the definition of the specific heat at constant volume (C_V) and the definition of the Grüneisen parameter [Eq. (3)] to get the temperature as a function of specific volume along an isentrope centered on a reference state with temperature T_{ref} and volume V_{ref}:

$$T_S = T_{\text{ref}} \exp\left[\int_V^{V_{\text{ref}}} \frac{\gamma}{V}\,dV\right]. \qquad (26)$$

Substituting Eq. (25) into the differential expression for the first law of thermodynamics, integrating along an isochore ($dV = 0$) between the isentrope and Hugoniot, and using the Mie–Grüneisen approximation (Eq. 2) yields

$$\int_{T_S}^{T_H} C_V\,dT = \frac{V}{\gamma}(P_H - P_S). \qquad (27)$$

By assuming that C_V and γ/V are both constant, the equation for shock temperature reduces to the relatively simple form:

$$T_H = \frac{1}{C_V}\frac{V_0}{\gamma_0}(P_H - P_S) + T_{\text{ref}} \exp\left[\frac{\gamma_0}{V_0}(V_{\text{ref}} - V)\right]. \qquad (28)$$

Shock temperatures calculated in this manner are plotted in Fig. 5 as a function of shock pressure for 50% porous thermite with reacted and unreacted final states.

The residual (postshock) temperature can also be calculated by making use of Eq. (26), if the release of pressure is an isentropic process. Making no further assumptions, the postshock temperature can be calculated using the equation:

$$T_F = T_H \exp\left[\frac{\gamma_0}{V_0}(V - V_F)\right] \qquad (29)$$

along with Eq. (28), where V_F is the final specific volume of the product after release to zero (or atmospheric) pressure. The calculated postshock temperatures are also plotted in Fig. 5, as a function of shock pressure, and listed in Table III for a 10 GPa shock.

B. Temperature measurements

Figure 5 shows that, for shock pressures up to 10 GPa, the shock temperature of 50% porous thermite is at least 3000 K hotter if it reacts than if it does not react. Thus, the experimental measurement of shock temperatures is an extremely sensitive probe of the chemical state of shocked porous thermite. We have carried out two planar impact experiments on porous thermite to measure shock temperatures using a four-channel radiation pyrometer.[43] The pyrometer measures time-resolved absolute intensity (spectral radiance) of light radiated from the impact interface between a thermite pellet and a transparent lithium fluoride window (Fig. 6). A two-parameter least-squares fit to the spectral radiances determines a time-resolved temperature and effective emissivity of the interface.

The sample pellets used in the impact experiments were approximately stoichiometric mixtures of aluminum and hematite, hot pressed to a porosity of about 50% by Mound Facility, Miamisburg, Ohio (see Table IV for exact porosity values). The aluminum was CERAC A-1183, with a mean particle size of $\leqslant 1\ \mu$m, and the hematite was Phizer R-1599 with a mean size of $\leqslant 0.3\ \mu$m. The pellets were mounted on aluminum projectiles and fired from Sandia's 25 m long, compressed-gas gun[44] at velocities of 1.183 and 1.292 km/s for experiments 2279 and 2274, respectively. Shock pressures (Table IV) were determined by the impedance matching technique[23] using the known shock properties of lithium fluoride[45] and the calculated properties of porous thermite.

The measured shock temperatures for the two experiments are plotted in Fig. 6. Both measurements exhibit similar features: a sudden increase at the time of impact, followed by a gradual decay over a period on the microsecond time scale, and another large increase after several microseconds. The initial increase in temperature is ubiquitously observed when porous solids are shocked, and is apparently due to the collapse of pores and generation of local temperature heterogeneities. The brightness temperature measurements of Matytsin and Popov[46] provide strong evidence that the brief high temperatures they observed upon the emergence of a shock wave from a powder onto the boundary with a transparent window are due to hot spots that form when surface layers of particles are deformed more than the inner layers. Their measurements also demonstrate that the observed high temperatures are not caused by residual gas filling the pores of the solid. Since radiation pyrometry measurements are sensitive only to the highest temperatures in the field of view, it is the hot spot temperatures that are measured immediately after impact. For a fine-grained pellet such as we used, thermal conduction within the sample allows the temperature field to become uniform within a few hundred nanoseconds. The temperature upon thermal equilibrium is the "mean-bulk shock temperature." For an unreacted mixture of aluminum and hematite shocked to 5 GPa, this should be about equal to the 1000 K calculated in the previous section and plotted in Fig. 5. It is clear from Fig. 7 that the actual shock temperature is significantly higher, indicating that a shock-induced reaction has taken place. The measured temperatures are well below the 4000 K calculated for fully reacted shocked thermite, however, suggesting that only a partial reaction has taken place.

TABLE IV. Experiments.

Experiment number	Sample porosity (%)	Sample density (g/cm^3)	Sample thickness (mm)	Impact velocity (km/s)	Shock pressure[a] (GPa)
2274	48	2.22	4.33	1.292	4.4–4.7
2279	49	2.20	4.37	1.183	3.9–4.1

[a] Shock pressures from impedance match to calculated Hugoniots; lower pressure is for unreacted state (thermite reactant); higher pressure is for fully reacted state (thermite product).

Since the shock temperature of lithium fluoride is much lower than that of the thermite, there is a temperature discontinuity at the interface, and heat is both conducted and radiated away from the shocked thermite. This results in a gradual cooling of the interface (relative to the timescale of the experiment). A rigorous treatment of the temperature evolution of an interface after the arrival of a shock wave is beyond the scope of the present paper, but is discussed in some detail by Grover and Urtiew.[47] This cooling is evident in the 2274 data, but ends after about 1 μs in experiment 2279. The constant temperature suggests that the reaction is continuing at a nonzero rate in experiment 2279, offsetting the cooling effects of heat transport.

After 2.5 to 3 μs, there is another sharp increase in tem-

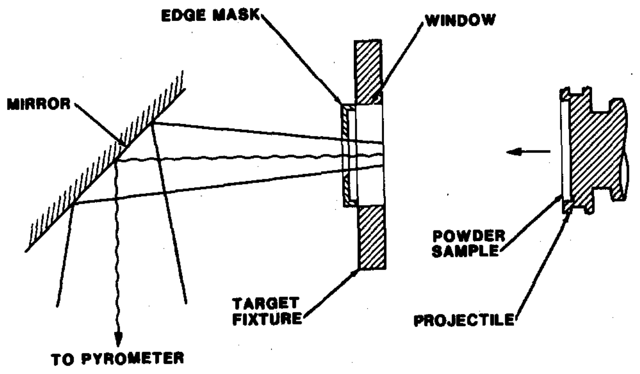

FIG. 6. Target configuration of shock temperature experiments.

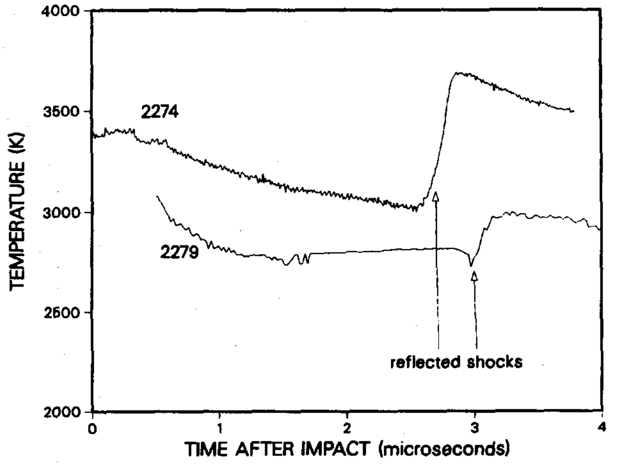

FIG. 7. Measured time-resolved temperatures for shocked 50% porous thermite.

perature for both experiments, caused by the arrival of the shock that reflected from the rear surface of the pellet, which was in contact with the aluminum projectile. When the reflected shock arrives at the lithium fluoride interface, it is again reflected. The second reflection is a rarefaction, since the shock impedance of the compressed thermite product is higher than that of the lithium fluoride. The pressure of this third (second observed) state is no higher than the directly impedance-matched state between lithium fluoride and aluminum at the impact velocity, which is 10.6 and 9.2 GPa for experiments 2274 and 2279, respectively.

The temperature of this second-observed state can be estimated by approximating the second Hugoniot by an isentrope and using Eq. (26) with the first Hugoniot state as the reference. This is a reasonable approximation, since the volume change due to the second shock is relatively small. When the pressure releases to the third (second observed) state, Eq. (26) is also used. Combining the two steps is equivalent to a single isentropic step. Since the Hugoniot must be steeper than the reference isentrope, the volume change (ΔV) associated with a pressure increase of 6 GPa can be used as an upper bound. From Eq. (26), the temperature increase from a reflected shock should be

$$\Delta T = T_H - T_R = T_H\left[1 - \left(\frac{\gamma_0}{V_0}\Delta V\right)\right]. \tag{30}$$

Substituting in the approximate shock temperature of 3000 K and the volume change, -0.008 cm^3/g, as estimated above, the expected temperature increase upon arrival of the reflected shock is about 170 K. While the temperature increase exhibited in experiment 2279 is close to the expected value, that of experiment 2274 is about four times greater, suggesting that the reflected shock releases additional chemical energy.

A number of inferences about the reaction mechanism can be drawn from the temperature history. The following hypothesis is consistent with the observations thus far. Since the reaction does not go to completion after the first shock, there must be a kinetic inhibition to continued reaction. If the rate of the reaction is controlled by the mixing due to differential flow of the heterogeneous solid at the shock front as suggested by Graham,[1] then incomplete mixing will lead to a partial reaction. Once the front has passed, the kinetics are limited by diffusion, and the rate slows down until, at best, it offsets the flow of heat out of the sample. Upon arrival of the reflected shock, the large increase in temperature of experiment 2274 implies a sudden increase in reaction rate. Since the partially reacted first shock state is a hot, heterogeneous mixture of reactants and products, with fluid inclusions, it is reasonable that the passage of another shock would cause another stage of turbulent, dynamic mixing, resulting in another stage of reaction at the second shock front. Thus, the temperature measurements are consistent with reaction kinetics that are controlled by dynamic mixing at the shock front.

VI. SUMMARY

To better understand shock-induced chemical reactions in porous solids, we have used equilibrium thermodynamics along with conservation equations across the shock front to develop a simple thermochemical model. A number of assumptions were made to simplify the equation of state calculations, none of which alter the conclusions that: (1) a solution to the equations exists for a shock-induced reaction with condensed products that is fundamentally different from a combustion wave, (2) for a steady wave to exist, the reaction is fully analogous to a detonation in the P–V plane, (3) for an initial density below a threshold value, an unsustained reaction shock will decay to zero and (4) such a reaction shock generates heat rather than work upon expansion, so it can be called a heat detonation. The thermochemical model ignores the details of the reaction mechanism, and assumes only that the kinetics are fast enough that the final state is uniform and in equilibrium. Nevertheless, further insight can be gained by treating experimental measurements and kinetic modeling within the context of this model.

Since the shock wave equations of state of the reactants are so similar to those of the products of these energetic solids, most shock wave experimental probes are insensitive to the reaction. One exception is the measurement of shock temperature, which has demonstrated that thermite undergoes a partial reaction when shocked to pressures above 4 GPa. Measured temperatures are in the range 2700–3400 K, compared to calculated temperatures of about 1000 K on the reactant and 4000 K on the product Hugoniots. Since, for porous solids, the temperature field is heterogeneous immediately behind the shock front, the shock temperature is poorly defined until thermal equilibrium is attained. For the fine grained powders that we used, the thermal equilibration time is about 100 ns, which gives an upper bound to the time it takes for the reaction to take place. The fact that the temperature becomes uniform and relatively constant after this time interval implies that a quasiequilibrium, uniform state has been reached behind the shock front, and that our assumptions for the thermochemical model are valid.

ACKNOWLEDGMENTS

This work was performed at Sandia National Laboratories supported by the U. S. Dept. of Energy under Contract No. DE-AC04-76DP00789. Mark Anderson, Merri Lewis, and Dave Wackerbarth provided expert technical assistance. The careful reviews by Bob Graham and Paul Taylor are appreciated.

[1] R. A. Graham (private communication, 1989).

[2] R. A. Graham, B. Morosin, Y. Horie, E. L. Venturini, M. Boslough, M. J. Carr, and D. L. Williamson, in *Shock Waves in Condensed Matter*, edited by Y. M. Gupta (Plenum, New York, 1986), p. 693.

[3] R. A. Graham, B. Morosin, E. L. Venturini, and M. J. Carr, Annu. Rev. Mater. Sci. **16**, 315 (1986).

[4] R. A. Graham, in *Shock Waves in Condensed Matter—1987*, edited by S. C. Schmidt and N. C. Holmes (North-Holland, Amsterdam, 1988), p. 11.

[5] A. N. Dremin and O. N. Breusov, Russian Chem. Rev. **37**, 392 (1968).

[6] G. A. Adadurov and V. I. Gol'danskii, Russian Chem. Rev. **50**, 948 (1981).

[7] S. S. Batsanov, Russian J. Inorganic Chem. **28**, 1545 (1983).

[8] R. A. Graham, B. Morosin, and B. Dodson, Sandia Report SAND83-1887 (Sandia National Laboratories, Albuquerque, 1983).

[9] Y. Horie, R. A. Graham, and I. K. Simonsen, Mat. Lett. **3**, 354 (1985).

[10] Y. Horie, D. E. P. Hoy, I. Simonsen, R. A. Graham, and B. Morosin, in *Shock Waves in Condensed Matter*, edited by Y. M. Gupta (Plenum, New York, 1986), p. 749.

[11]A. P. Hardt and R. H. Martinson, in *Proceedings of the Eighth Symposium on Explosives and Pyrotechnics* (Franklin Institute Research Laboratories, Philadelphia, 1974), p. 53-1.

[12]S. A. Sheffield and A. C. Schwarz, in *Proceedings of the Eighth International Pyrotechnics Symposium*, edited by A. J. Tulis (IIT Research Institute, Chicago, 1982), p. 972.

[13]A. N. Kovalenko and G. V. Ivanov, Combustion, Explosion, and Shock Waves **19**, 481 (1981).

[14]S. S. Batsanov, G. S. Doronin, S. V. Klochkov, and A. I. Teut, Combustion, Explosion, and Shock Waves **22**, 765 (1986).

[15]M. B. Boslough and R. A. Graham, Chem. Phys. Lett. **121**, 446 (1985).

[16]H. Hornig, J. Kury, R. Simpson, F. Helm, and W. von Holle, in Proceedings of the Eleventh International Pyrotechnics Seminar, Vail, Colorado (1986), p. 699.

[17]M. B. Boslough, Phys. Chem. Lett. **160**, 618 (1989).

[18]D. E. Maiden and G. L. Nutt, in Proceedings of the Eleventh International Pyrotechnics Seminar, Vail, Colorado (1986), p. 813.

[19]N. S. Enikolopyan, A. A. Khzardzhyan, E. E. Gasparyan, and V. B. Vol'eva, Academy Nauk, USSR, Procs. Phys. Chem. **294**, 567 (1987).

[20]Y. Horie and M. E. Kipp, J. Appl. Phys. **63**, 5718 (1988).

[21]R. A. Graham, J. Chem. Phys. **83**, 3048 (1979).

[22]P. A. Taylor, M. B. Boslough, and Y. Horie, in *Shock Waves in Condensed Matter—1987*, edited by S. C. Schmidt and N. C. Holmes (North-Holland, Amsterdam, 1988), p. 395.

[23]M. H. Rice, R. G. McQueen, and J. M. Walsh, *Solid State Physics, Vol. 16*, edited by F. Seitz and D. Turnbull (Academic, New York, 1958), p. 1.

[24]R. A. Graham and O. E. Jones, Sandia Report SC-R-68-1857 (Sandia National Laboratories, Albuquerque, 1968).

[25]H. Ellern, *Military and Civilian Pyrotechnics* (Chemical Publishing Company, New York, 1968).

[26]O. L. Anderson, J. Phys. Chem. Solids **27**, 547 (1966).

[27]R. C. Lieberman and E. Schreiber, J. Geophys. Res. **73**, 6585 (1968).

[28]J. P. Watt, G. F. Davies and R. J. O'Connell, Rev. Geophys. Space Phys. **14**, 541 (1976).

[29]G. E. Duvall and S. M. Taylor, J. Composite Mater. **5**, 130 (1971).

[30]Ya. B. Zel'dovich and Yu. P. Raizer, *Physics of Shock Waves and High-Temperature Hydrodynamic Phenomena* (Academic, New York, 1967).

[31]H. Schins and F. S. Gunnerson, High Temp. High Pressures **18**, 249 (1986).

[32]A. D. Kirshenbaum and J. A. Cahill, Trans. Metall. Soc. AIME **224**, 816 (1962).

[33]J. M. Brown and R. G. McQueen, J. Geophys. Res. **91**, 7485 (1986).

[34]*CRC Handbook of Chemistry and Physics*, edited by R. C. Weast (CRC, Boca Raton, Florida, 1980).

[35]R. Courant and K. O. Friedrichs, *Supersonic Flow and Shock Waves* (Springer, New York, 1976).

[36]W. Fickett and W. C. Davis, *Detonation* (University of California, Berkeley, 1979).

[37]M. B. Boslough, in Proceedings of the Ninth Symposium (International) on Detonation (in press, 1990).

[38]N. M. Kuznetsov, Soviet Phys. JETP **22**, 1047 (1966).

[39]I. M. Barkalov, V. I. Gol'danskii, V. L. Tal'roze, and P. A. Yampol'skii, JETP Lett. **3**, 200 (1966).

[40]A. Merzhanov, Arch. Combustion Proc. **5** (1974).

[41]S. J. Jacobs, United States Naval Ordnance Laboratory Report NAVORD-4366, 1956.

[42]R. E. Setchell, Comb. Flame **43**, 255 (1981).

[43]M. B. Boslough and T. J. Ahrens, Rev. Sci. Instrum. **60**, 3711 (1989).

[44]R. E. Setchell, in *Shock Waves in Condensed Matter—1981*, edited by W. J. Nellis, L. Seaman and R. A. Graham (American Institute of Physics, New York, 1981), p.657.

[45]W. J. Carter, High Temp. High Pressures **5**, 313 (1973).

[46]A. I. Matytsin and S. T. Popov, Combustion, Explosion and Shock Waves **23**, 364 (1987).

[47]R. Grover and P. A. Urtiew, J. Appl. Phys. **45**, 146 (1974).