Assessment of Gasless Detonations in Mixtures of Reactive Powders

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Abstract

A methodology to assess the detonability of heterogeneous powder mixtures that react exothermically without significant gas production is presented. First, a thermodynamic analysis was performed to demonstrate that many compositions of this class are unable to support detonation wave propagation, as the volumetric expansion of the product is too small to support a shock front in the reactants since the product density is larger than the reactant density. Certain mixtures of nickel and aluminium, manganese and sulfur, zinc and sulfur, and zinc and tellurium were found to satisfy the thermodynamic requirements for detonation when initial reactant densities are sufficiently large (i.e., porosity sufficiently low). In those mixtures, self-sustained detonation would be possible only if the reaction time, which depends on the reaction rate, is less than the characteristic time for the shocked material to expand laterally, which depends on the charge diameter and sound speed in the shock-compressed reactants. This condition ensures that the volumetric expansion due to the reaction occurs mainly in the direction of shock propagation. Therefore, a quasi-one-dimensional model of the reaction zone was developed to account for the competition between the energy release rate and momentum and energy losses due to lateral expansion. Using this model with an empirically derived, state-independent relation for the reaction rate, the smallest charge radius in which a self-sustained, supersonic reactive compression wave could be observed in micrometric powder mixtures of Mn+S confined in steel was predicted to be on the order of tens of meters.

Keywords: Gasless Detonation, Charge Diameter, CJ, ZND, Khariton, Volumetric Expansion

Background

Despite several attempts to experimentally observe detonation in mixtures of reactive powders whose products contain little or no gas at the equilibrium state [1-7], no unambiguous evidence has yet been obtained that such detonations are possible. In mechanically activated mixtures of Al-Teflon and Mg-Teflon whose products contain a relatively small amount of gas in comparison to conventional explosives, Dolgoborodov et al. [8-11] have observed quasi-steady fronts propagating at velocities up to approximately 1300 m/s (i.e., supersonic with respect to the initial sound velocity in the porous reactants) when the mixture was subjected to a shock wave produced by a high explosive charge of approximately 10 g. The authors of these studies have interpreted the fast, quasi-steady propagation as a type of detonation. On the other hand, the peak pressures they measured at the bottom of columns at least 100 mm long were on the order of only hundreds of MPa, and the patterns of imprint on witness plates placed at the end of the columns suggested that the reaction propagation took place via jetting of gaseous and liquid reaction intermediates caused by rapid pressure buildup, i.e., convective burning. Thus, the coupling between a leading shock wave and the release of reaction energy via chemical reaction that is required for detonations did not appear to have been realized. Similar fast convective deflagrations have been observed in mixtures of nanometric powders of aluminum and metal oxide or teflon, which propagated at velocities on the order of 1000 m/s and yielded pressure fronts on the order of 15-20 MPa [12-16]. Gur'ev et al. [3] reported self-sustained waves traveling at velocities near 2.2 km/s in mixtures of zinc and sulfur that were initiated with charges of high explosive, however, attempts by Jetté et al. [7] to reproduce this result using even larger diameter charges produced only decaying shock waves and no evidence of coupling between the shock and reaction.

In order to achieve a gasless detonation, if possible at all, mixtures that may lend themselves to supporting detonation propagation in charge dimensions that can be practically tested must be identified. Therefore, proper mixture selection criteria must be specified, and experimental effort should be focused on those mixtures that fulfill these criteria. In this work, two such criteria will be considered: the volumetric expansion of the products and the rate of conversion of reactants to products.

The first criterion that must be considered is the thermodynamic one. A mixture can support detonation propagation if its reaction products expand sufficiently to support a shock in the reactants. This expansion could occur as a result of the products having a less dense phase or crystal structure than the reactants and/or due to thermal expansion resulting from the chemical heat release [17]. In high explosives, the products are less dense than the shock-compressed reactants due to the large heat release of the reaction and the composition of the products, consisting of numerous low molecular weight compounds instead of the larger molecular weight reactants, so that this condition can usually be satisfied. In the case of gasless products, thermal expansion of the product due to energy release may be sufficient for detonation propagation only if the conversion from reactants to products does not result in significant volumetric contraction at ambient temperature. Thus, the composition and density of the products resulting from reactions in the shocked reactants must be calculated to determine whether the thermal expansion of the products yields a density less than that of the reactants. Chapman and Jouguet's criterion for determining the detonation velocity and thermodynamic state of the products of an explosive provides a necessary (but not sufficient) condition that must be satisfied in order for a detonation wave to be obtained in a given reactive material. They treated detonation waves as a transition between two equilibrium states using the steady one-dimensional conservation laws for mass, momentum, and energy [18]. By including the effect of the chemical heat release in the internal energy via the heats of formation of the various products and reactants and by neglecting heat conduction, viscosity, and stiffness effects, they obtained Rankine-Hugoniot (RH) relations for a "reactive shock." The three RH equations can be combined with an equation of state relating internal energy to pressure and volume to yield a single equation describing the detonation Hugoniot, or the locus of all possible end states in the products for the given initial state in the reactants.[1]

The final equilibrium state can theoretically fall anywhere along the detonation Hugoniot, depending upon the detonation velocity. Chapman and Jouguet noted that unsupported detonations have a unique velocity and that their equilibrium product state corresponds to the point reached from the initial state via a straight line that is tangent to the detonation Hugoniot in the pressure-volume plane.

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[1] Note that for a non-reactive shock wave the initial state lies on the Hugoniot curve, while for a shock accompanied by exothermic energy release and volumetric expansion, as in explosives, the detonation Hugoniot generally lies above the initial state on the P-v plane.

Jouguet showed that at the tangency point (also called the Chapman-Jouguet (CJ) point) the material velocity of the products relative to the shock is equal to the sound speed in the products. Physically, the sonic condition is equivalent to requiring that no disturbance originating in the products can travel upstream toward the shock wave. Thus, a self-sustained detonation is independent of the rear boundary conditions, hence the unique solution.

According to the CJ theory therefore, if the detonation Hugoniot is convex and lies above the initial unshocked state on the pressure-specific volume plane, the tangency condition can be met at the CJ point, which provides a steady detonation solution to the governing equations of mass, momentum and energy conservation. The possibility of detonations in energetic (or metastable) materials whose reaction products (or final phase) are gasless in the equilibrium state has been investigated using the CJ theory, or methods that are essentially equivalent to it. Kuznetsov [19], Boslough [20], Yu and Meyers [21], Bennett and Horie [22], Merzhanov et al. [23], Dobler et al. [24], Torunov and Trofimov [25-26] and Gur'ev et al. [4] have proposed similar methods of estimating the detonation Hugoniot for such mixtures and their methods can be used to show that CJ detonations could be achieved in certain mixtures if the initial porosity of the powder mixture is not too large. Some of these authors conducted preliminary investigations into the ability of such detonations to be realized in experiments using gasless reactive systems but did not observe self-sustained waves.

The second criterion that needs to be considered was first formulated by Khariton [27]: the slower the exothermic chemical transformation, the larger the sample must be in order to detonate. Indeed, when the charge diameter is small and/or the reaction rate is slow, lateral rarefactions can penetrate deep into the reaction zone before reactions are complete, which results in quenching of the reactions and failure of the detonation to propagate. Therefore, the assumptions of the CJ theory that the flow is one-dimensional and that chemical equilibrium is reached when the product material velocity becomes sonic only apply if the charge is infinite in diameter or when reaction rate is infinitely fast (or when reaction zone is infinitely thin).

To account for the competition between the rate of the exothermic chemical transformation (a volume effect) and the rate of lateral momentum loss (a surface/edge effect, which is dependent on charge size), the reaction zone structure of the detonation must be resolved. Zeldovich, von Neumann, and Doering [28-29] developed a theory that describes the states between the shock and the sonic plane of a detonation. In this theory, referred to as the ZND theory, the three conservation equations are complemented with a reaction rate equation. The shock is assumed inert (i.e., reactions begin downstream of the shock, not in the shock) and at every point downstream of the shock thermodynamic equilibrium is assumed to be achieved for pressure, density, material velocity and internal energy, even though chemical equilibrium is not achieved.

To account for losses within the reaction zone, source terms are added to the conservation equations of the ZND model. The lateral losses in finite-sized charges can be modeled with a source term in the mass conservation equation expressed either in terms of the radial gradient of the radial velocity [30] or in terms of a cross-sectional area change. Detonations with a mass loss term have a velocity less than the one-dimensional CJ detonation and have a curved shock front. In addition, reactions do not reach equilibrium as they encounter the sonic plane. When the charge diameter becomes small enough, the momentum losses may cause a sufficiently large shock velocity deficit that results in the detonation no longer being able to propagate. Therefore, the ZND model with a mass loss term makes it possible to quantify Khariton’s criterion.

Hence, detonations may be observable in the laboratory in gasless mixtures of reactive powders only if the product volumetric expansion is sufficient and the charge is large compared to the reaction zone length. This study examined some common reactive mixtures to determine if their detonation Hugoniot satisfies the requirements of the CJ theory. Then a simple ZND model including lateral expansion losses was developed to calculate the reaction zone structure for the mixtures that satisfy the CJ requirement in order to consider the competing roles of reaction rate and charge size.

Method

Thermodynamic Equilibrium Considerations / CJ Theory

The first criterion considered is whether the tangency solution of the CJ theory can be obtained. This requires that the detonation Hugoniot lie above the initial state in the *P*-*v* plane and be convex.[2] Ideally, the detonation Hugoniot should be obtained from detailed thermodynamic equilibrium calculations that use a realistic equation of state and take into account the dependence of heat capacities on pressure (and temperature), as well as correct predictions of the existing phases at any given pressure, temperature, and concentration. However, for the purpose of this work, two simple approaches were used to estimate whether the detonation Hugoniot is above the initial state.

The first approach is based on the fact that if the detonation Hugoniot lies above the initial state on a *P*-*v* plane, then at atmospheric pressure a point on this Hugoniot should have a greater specific volume (i.e., lower density) than the initial state in the reactants. In other words, if the product density resulting from constant pressure combustion is less than reactant density, then it may be possible to find a shock velocity that satisfies the CJ condition in this mixture. The chemical composition of the products and the adiabatic flame temperature for constant pressure combustion was calculated for different mixture compositions using the thermodynamic equilibrium code THERMO [31]. The product density at the adiabatic flame temperature was estimated using the linear coefficient of thermal expansion (CTE) of the product at that temperature (note that for the calculations, all materials were assumed to be isotropic, so that the volumetric expansion coefficient was taken as three times the linear expansion coefficient). Most solid products of interest presented in the results section have linear CTE's in the range 7-12 x 10^{-6} K^{-1} at room temperature, but in order to account for the temperature dependence of the thermal expansion coefficient [32] and for possible solid-liquid phase changes, higher values in the range 11-23 x 10^{-6} K^{-1} were used

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[2] Another thermodynamic requirement comes from the ZND theory: the reactant Hugoniot and the detonation Hugoniot must not intersect at a pressure lower than that at the CJ, or tangency, point. This requirement may not be met when the reactant Hugoniot is very steep in the *P*-*v* plane, or when either of the reactant or detonation Hugoniot contains discontinuities that result from phase changes at certain pressures and temperatures. For the mixtures of interest in this study, phase changes along the Hugoniots were neglected and the reactant Hugoniots were generally less steep than the estimated detonation Hugoniot, so that this ZND requirement did not need to be considered further.

(see Fig. 2). Furthermore, the use of a larger CTE may reduce the chances that some mixture compositions are rejected prematurely. For NiAl + 0.52 Ni products, the CTE value for NiAl (16×10^{-6} K^{-1}) was used since it is greater than the ambient temperature value for Ni (13×10^{-6} K^{-1}), similarly for the NiAl + 0.54 Al products, where the CTE value for Al at ambient conditions (23×10^{-6} K^{-1}) was used for the mixture since it is higher than the value for NiAl. The second approach consisted of estimating the actual detonation Hugoniot using the method of Bennett and Horie [22] and comparing its relative position to that of the initial state on the P-v plane. The detonation Hugoniot in this method was estimated by starting with the Hugoniot of the product material and then shifted it vertically on a P-v diagram to account for the increase in thermal energy caused by the chemical reactions. The internal energy change from the initial state to a final state on the detonation Hugoniot was expressed via two equivalent thermodynamic paths (see Fig. 1)

$$e - e_o = \left(e_{opr} - e_o\right) + \left(e_{pr} - e_{opr}\right) + \left(e - e_{pr}\right) \qquad (1)$$

The path on the left hand side is the actual reactive shock transition from the initial state (subscript o), which follows the Rankine-Hugoniot relation

$$e - e_o = \frac{P}{2}\left(v_o - v\right) \quad (2)$$

The other path consists of a conversion from reactant to product at atmospheric pressure and temperature (e_{opr}-e_o is the heat of reaction at atmospheric pressure, or the heat that is extracted from the reaction to keep the products at atmospheric temperature), followed by a shock in the product material (e_{pr}-e_{opr}) and a constant volume heating of the shocked product material (e-e_{pr}). The last step effectively accounts for the addition of the chemical heat release. The shock in the product material relating its initial atmospheric condition (subscripts opr) to its shocked state (subscripts pr, noting that $v_{pr}=v$) follows the Rankine-Hugoniot relation

$$e_{pr} - e_{opr} = \frac{P_{pr}}{2}\left(v_{opr} - v\right) \quad (3)$$

And finally, the constant volume compression can be calculated with

$$e - e_{pr} = \left(\frac{de}{dP}\right)_{v,pr}\left(P - P_{pr}\right) (4)$$

With the known shock Hugoniot of the product material (relating P_{pr} to v), the initial densities in the reactant (v_o) and in the product material at atmospheric conditions (v_{opr}), the heat of reaction at atmospheric pressure (e_{opr}-e_o), and the derivative $(de/dP)_{v,pr}$, the detonation Hugoniot for can be obtained in the P-v plane.

The method of Bennett and Horie requires shock Hugoniot data for the product material, which was not always available. For the compounds whose Hugoniot data did not exist, a substitute material with similar density and sound speed was used instead. Density and Young's modulus were obtained for NiAl and titanium-silicon compounds from [33] and [34], respectively. Note that sound speed was obtained using density and Young's modulus, assuming a Poisson ratio in the range 0.2-0.3 (e.g., see [35]). The Hugoniot of ZnS was used instead of that of MnS, similarly for NiO, TiB_2, and Fe_2SiO_4 that were used as substitutes for NiAl, TiSi, and Ti_5Si_3, respectively. The method of Bennett and Horie also requires the enthalpy of formation of the products. For titanium and silicon mixtures, the enthalpies of formation were obtained from [36]. The enthalpy of formation of ZnS and MnS was obtained from [37], that of NiAl and Ni_3Al from [38-39], and that of TiC and TiB_2 from [40]. The value of the derivative $(de/dP)_{v,pr} = (v/\Gamma)_{pr}$ was approximated as $(v/\Gamma)_{pr} = (v_o/\Gamma_o)_{pr}$, with $\Gamma_0 = 2S - 1$, where S is the slope of the linear shock Hugoniot of the product material in the shock velocity – material velocity (U-u) plane.

Reaction Zone Model using ZND Theory

Governing Equations

The modeling approach used was similar to that of [30, 41]. The quasi-one-dimensional governing conservation equations were derived for a control volume attached to the steady reaction zone, with the space coordinate, x, being zero at the shock and increasing downstream of it. Hydrodynamic conditions (i.e., no stiffness effects) were assumed since the pressures of interest (> 10 GPa) were typically greater than the elastic limits of the materials.[3] The governing equations were therefore

$$\frac{d\rho u}{dx} = -\frac{\rho u}{A}\frac{dA}{dx}$$

$$\rho u \frac{du}{dx} + \frac{dP}{dx} = 0 \qquad (5)$$

$$\frac{de}{dx} + P\frac{dv}{dx} = 0$$

The resulting continuity equation contains a mass loss term that represents the lateral expansion losses averaged over the entire charge diameter. The boundary condition at x=0 is the von Neumann (vN) state immediately downstream of the inert shock, which is obtained using the Rankine-Hugoniot equations for the given shock velocity in the reactants. The other boundary condition is that derivatives of the velocity and thermodynamic variables must be finite (i.e., flow variables must be continuous) at the sonic plane where u=c, c being the local frozen sound speed, i.e., the speed of a sound wave across which no chemical reactions occur. This boundary condition is known as the generalized CJ criterion.

Equation of State

Often, reaction zones of explosives are modeled using the polytropic equation of state

$$e = \frac{Pv}{\gamma - 1} - \lambda Q \qquad (6)$$

where the value of γ is often approximated as 3 and has the same value for products and reactants. In the case of gasless reactants and products, the polytropic equation of state cannot match both the detonation and reactant

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[3] The longitudinal stress in solids under uniaxial strain compression (i.e., one-dimensional compression) is approximately equal to the sum of hydrostatic pressure and 2/3 of the yield stress [42-43]. If the yield stress (on the order of 0.5 GPa or less for most metals) is much less than the pressure, then its effect on the longitudinal stress can be neglected.

Hugoniots using a single value of γ. Instead of using different values of γ for the reactants and products, a Mie-Gruneisen equation of state was used

$$e = e_{ref}(v) + \left(\frac{de}{dP}\right)_{v,ref}\left(P - P_{ref}(v)\right) - \lambda Q \quad (7)$$

with $\left(de/dP\right)_{v,ref}$ =constant. The reference curve was assumed to be a Hugoniot curve whose initial density (ρ_o) is that of the reactants and whose shock velocity — material velocity (U-u) relationship is linear ($U = C_o + Su$). The values for C_o and S were first calculated as the average of the values corresponding to the Hugoniots of the reactant and product material[4]. The Hugoniot of the reactant mixture was obtained by combining the Hugoniot of each component [44] according to the method recommended by [45]. The value of the derivative $\left(de/dP\right)_{v,ref} = \left(v/\Gamma\right)_{ref}$ was approximated as $\left(v/\Gamma\right)_{ref} = \left(v_o/\Gamma_o\right)_{ref}$, with $\Gamma_0 = 2S - 1$. The value of Q was then adjusted until this equation of state could match the reactant Hugoniot (for λ=0) and the detonation Hugoniot calculated using the method of Bennett and Horie (for λ=1), particularly near the vN state and near the sonic plane (tangency point), since these are the states between which the integration of the governing equations is carried out using this equation of state. All other intermediate states occurring in the reaction zone should be well described by the equation of state if it can properly describe the states corresponding to the boundary conditions. The reactant Hugoniot and detonation Hugoniot of Mn+S are compared to the corresponding Hugoniots calculated with the equation of state (EOS) from eq. 7, with the values shown in Table 1.

Note that the detonation Hugoniot is essentially the product material Hugoniot shifted upward on the P-v plane. If we were attempting to match both the Hugoniot of the product material and the detonation Hugoniot using the equation of state from eq. 7, the initial density, C_o, S, and v_o/Γ_o to be used would be those of the product material. In this case, for Q=0, the calculated detonation Hugoniot would match the Hugoniot of the product material, and as Q is increased the detonation Hugoniot should be shifted upward on the P-v plane. The value of Q to be used in the equation of state (eq. 7) to match the detonation Hugoniot would be

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[4] The Hugoniot of the product material was obtained as described in the previous section.

very close to the amount of heat released in forming this product, i.e. $Q \approx e_{opr}\text{-}e_o$. However, since the equation of state (eq. 7) is used to match the reactant Hugoniot when λ=0 rather than the Hugoniot of the product material in the ZND model, the value of Q required in the equation of state may be slightly more or less than the amount of heat evolved in forming the product, depending on the relative positions of the reactant Hugoniot and Hugoniot of the product material on the P-v plane. Finally, the model was used on non-porous mixtures only, so that compaction effects did not need to be incorporated into the equation of state.

In the solution of the governing equations, it is convenient to make use of the frozen sound speed which can be obtained from the equation of state by making use of the following thermodynamic relation

$$\left(\frac{c}{v}\right)^2 = \frac{P + \left(\partial e/\partial v\right)_{P,\lambda}}{\left(\partial e/\partial P\right)_{v,\lambda}} \qquad (8)$$

Combining the conservation equations, the equation of state, and the definition of sound speed, the following equation can be derived

$$\frac{du}{dx} = \frac{\frac{uc^2}{A}\frac{dA}{dx} - uvQ\left(\frac{\Gamma_o}{v_o}\right)\frac{d\lambda}{dx}}{u^2 - c^2} \qquad (9)$$

The numerator of this expression must vanish when u=c in order to satisfy the generalized CJ criterion. This is the boundary condition used at the sonic plane. The other boundary condition for the reaction zone was the vN state, computed by applying the Rankine-Hugoniot relations in the inert reactants for the assumed detonation velocity, D. The differential equations describing the reaction zone were then solved using a fourth-order Runge-Kutta scheme by inserting a reaction rate law (for $d\lambda/dx$) and an area divergence expression (dA/dx) into the du/dx equation, coupled with the continuity and momentum equations. The governing equations were solved by iteration using various values of the charge radius (which is accounted for in the dA/dx expression, to be derived below) until the numerator of the du/dx equation became zero at the same position as the denominator.

Area Divergence

The area divergence source term in the continuity equation is often modeled in terms of the shock wave curvature following the pioneering work of Wood and Kirkwood [30]. The reaction zone solution obtained can then be related to the charge diameter using empirical relations between wave curvature and charge diameter [41, 46-48]. Since detonation has not been observed in gasless reactive powder mixtures, the dependence of wave curvature on charge diameter cannot be obtained empirically. Therefore, a model for the area divergence source term must be constructed which does not depend on prior knowledge about the diameter effect on the detonation front curvature.

Another method that has been proposed is based on the assumption that the area divergence within the reaction zone is the same as that immediately after the sonic plane [49-50]. Since the flow downstream of the sonic plane is supersonic relative to the steady detonation, the expanding flow can be described by a Prandtl-Meyer expansion. This approach is not easy to implement if the reaction products are not described by a polytropic equation of state. Furthermore, this approach is not strictly correct since the Prandtl-Meyer solution applies to planar flows, not cylindrical flows, and since the flow is considered to be supersonic when in fact the flow in the reaction zone is subsonic (one of the consequences of this assumption is that the extent of the lateral expansion is underestimated since pressure at the sonic plane is less than inside the reaction zone).

Alternatively, Fujiwara and Tsuge [51] assumed that the deflection of the confinement material surrounding the reaction zone of an explosive could be described by the Newton hypersonic flow model (explosive was confined in air in their study). This model led to a relation between pressure and confinement flow deflection at the edge of the charge. In this approach, the area change or wall deflection could vary with the pressure in the reaction zone. Applying the Newton hypersonic flow model to solid confinement materials, which can have a sound speed comparable to the detonation velocity, is inappropriate and thus was not used here.

Finally, Dabora [52] treated the initial confinement motion as a one-dimensional shock tube (Riemann) problem in the radial direction. This approach is based on the fact that due to the high pressure in the unreacted material immediately downstream of the shock, the confinement interface is driven to move outward in the radial direction. This is analogous to a one-dimensional shock tube problem. The initial radial velocity of each material is zero, the initial pressure of the confinement is atmospheric, and the initial pressure of the explosive is given by the vN state; mechanical equilibrium is achieved via a shock wave in the confinement and an expansion wave in the unreacted explosive material resulting in motion of the interface. In unconfined cases, the surface of the explosive is treated as a free surface, where pressure is always constant (and near zero), the free surface velocity in this case is obtained as that corresponding to expansion of the explosive to zero pressure. This approach, where a two-dimensional, steady flow is treated as a one-dimensional unsteady flow occurring in a planar "slice" passing through the flowfield, is strictly only valid under the assumptions of hypersonic small disturbance theory (i.e., high Mach numbers and small deflection angles [53]) and cannot formally be applied in the subsonic flow of the reaction zone. However, this approach may predict the interface deflection angle well enough regardless, since Dabora showed that his predictions of confinement/explosive interface motion agreed well with his experimental results. Similar good agreement with this model for experiments with yielding confinement was obtained by Murray and Lee [54-55]. This approach was therefore adopted in the current work to estimate the interface deflection angle. Since the expansion isentrope of the unreacted explosive was not known, and since for condensed materials the Hugoniot curve and isentrope are very close, the isentrope for the reactants was assumed to be identical to the principal Hugoniot of the reactants. Furthremore, if one assumes that the radial velocity of the explosive-confinement interface, ω, is constant in the reaction zone, then dA/dx is also constant within the reaction zone. The resulting area divergence is

$$\frac{1}{A}\frac{dA}{dx} = \frac{2}{R_o}\frac{\omega}{D} \qquad (10)$$

where R_o is the charge radius and ω is the radial velocity of the confinement interface obtained from the solution of the Riemann problem.

Reaction rate

A reasonable model for the reaction rate should be constructed from knowledge of the reaction mechanism. Reaction rate models used for high explosives are typically one of the following types

$$\frac{d\lambda}{dt} = (1-\lambda)^m \frac{a}{\tau} e^{-E_a/RT} \qquad (11)$$

(see for instance [30, 41, 46, 56-62])

$$\frac{d\lambda}{dt} = (1-\lambda)^m \frac{a}{\tau} P^n \qquad (12)$$

(see for instance [41, 47, 48, 63-70]) where a is a frequency factor, τ is a characteristic reaction time, E_a is the activation energy, R is the ideal gas constant, T is temperature, P is pressure, and m and n are exponents. Models of the first type assume that reactions occur as a result of molecular collisions and are strongly temperature sensitive. Models of the second type are based on the fact that reactions in high explosives occur as a result of the deflagrative growth of hot spots initiated by the shock at locations of density discontinuities. The number of hot spots is often dependent on shock strength (i.e., shock pressure) and deflagration velocities in high explosives are strongly pressure dependent, hence the power law pressure dependence of the type P^n in the reaction rate. The constants in the reaction rate models are obtained either as a fit of experimental detonation data, or in rare cases via studies of the kinetics of explosive decomposition reactions.

Despite extensive study of detonation in conventional explosives, the fact that different forms of the reaction rate, using a wide variety of empirically derived parameters, have been used with mixed success in modeling detonation clearly suggests that, for the present study of heterogeneous mixtures that produce little or no gaseous products, the appropriate form of the reaction rate will be a significant unknown. Indeed, since no detonation has ever been observed in this class of heterogeneous mixture, and since very little rate data has been obtained under conditions of high pressure and temperature resulting from shock loading, it becomes even more difficult to generate an empirical fit for the heterogeneous mixtures under study here. The experimental results of Jetté et al. [71] have shown that the delays between shock arrival and onset of bulk temperature increase due to reactions in shocked samples of reactive powders scaled with burning velocities measured at room conditions. Their findings have also led them to suggest that the initiation mechanism was analogous to that in high explosives; namely that the shock wave ignites hot spots at locations of density discontinuities and reactions grow outward via deflagrating fronts. Since bulk temperatures were found to increase many milliseconds after the shock passage[5], and since the time at which bulk temperature began to increase was not very dependent on shock pressure, Jetté et al. concluded that the reaction rate should not be strongly pressure dependent under shock loading conditions.

Furthermore, it is known that burning velocities do not increase with pressure in gasless reactive powder mixtures. Indeed, the burning velocities in many gasless compositions, such as metal+carbon, metal+boron, Zr+Si, $Al+Cr_2O_3$, and $Al+Fe_2O_3+Al_2O_3$, are independent of ambient pressure [72-75]. In Ti+2B and 2Ta+C, burning velocity is independent of ambient pressure for pressures above approximately 30 atm [76-77]. Similarly, in mixtures of Al, Mg, and Ti with Fe_2O_3, as well as mixtures of $Zr+BaO_2$, $Mg+MoO_3$, $Zn+PbO_2$, $Zr+V_2O_5$, $Al+NH_4ClO_4$, and $6Mg+2B_2O_3+C$, burning velocity is either constant at ambient pressure greater than a few 10's of atm or decreasing slightly with an increasing pressure [78-81]. These compositions are in the same class of thermites and self-propagating high-temperature synthesis (SHS) systems as the compositions evaluated in this paper for their detonability, and thus are expected to behave in a qualitatively similar fashion.

Based on the above considerations, shock-initiated reactions in gasless reactive powder mixtures appear to take place as follows: 1) a small fraction of the material is ignited by the shock through distributed hot spots and 2) reaction spreads via burning fronts whose propagation speed is independent (or mostly independent) of pressure. Therefore, a reaction rate model proposed by Hill et al. [82] for high explosives, based on the idea that the reaction rate was dominated by the growth of burning hot spots, should be suitable for modeling gasless reactive powder mixtures. The model of Hill et al. has the form

$$\frac{d\lambda}{dt} = a\,S_b\lambda^{2/3}(1-\lambda)^{2/3} \qquad (13)$$

where λ is the reaction progress variable, or the product mass fraction, S_b is the burning velocity of the reactive material (in mm/s), and a is a rate parameter (units of mm^{-1}). This model can be applied to describe the behavior of reactive

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[5] Note that pressure equilibrated to ambient conditions in a few tens of microseconds in their experiments, well before the time at which bulk temperature increases were observed.

gasless powders, in which a and S_b can be treated as constants (i.e., they are not functions of the shock pressure nor of the local thermodynamic state of the material). Using this simplification, the rate equation can be integrated from the start to the end of the reaction, yielding,

$$a S_b \tau = \int_{0^+}^{1^-} \frac{d\lambda}{\lambda^{2/3}(1-\lambda)^{2/3}} \approx 5.3 \approx 5 \quad (14)$$

where τ is the combustion time. If we assume that τ is approximately the same as the delay time for the appearance of bulk exothermicity measured in [71] using thermocouples and photomultipliers, then the combustion time is related to the burning velocity. The delay time data presented in [71] can be related to the room condition burning velocity via this simple expression

$$\tau = \frac{\Delta}{S_b} \qquad (15)$$

which means that the time required for reactions to reach completion (in seconds) is Δ/S_b (for S_b expressed in mm/s, they obtained $\Delta = 4$ mm) Combining the last two equations gives

$$a \approx \frac{5}{4} \quad (16)$$

An eventual improvement to the model would be to account for the possible slight temperature (and pressure) dependence of burning velocity. In particular, the burning velocity in shocked samples could be different from that in the starting mixture (i.e., the materials in which the burning fronts are propagating have been brought to a higher temperature and density by the shock and they have been mechanically deformed and mixed), but this is accounted for in the correlation to Jetté et al.'s data. Another factor that the correlation accounts for is the average spacing between the hot spots ignited by the shock wave. With those empirical parameters, the current model essentially assumes that the shock produces ignition centers with an average spacing of $\Delta = 4$ mm, from which reaction propagates at a fixed burning velocity.

Results – Thermodynamic Considerations

A summary of the estimated product density resulting from constant pressure combustion compared to the respective reactant density for many gasless mixtures of interest is shown in Fig. 3. The presented mixtures were chosen for their high exothermicity, low production of gas, and because experimental measurements of their shock initiation properties have been reported in the literature. On the bottom axis, the predominant product composition and the adiabatic flame temperature predicted by the thermodynamic equilibrium program are shown, along with the magnitude[6] of the enthalpy of formation of the product for comparison purposes. The linear coefficient of thermal expansion (CTE) used is also shown in the figure. The density for the reactants and products were calculated assuming that no gases (i.e., no porosity) were present. Gases were absent in the products for most mixtures, except the Mn+S mixture (4.65 wt% gas) and Zn+S mixture (31 wt% gas, consisting mainly of gaseous Zn and gaseous S).

The data from Fig. 3 clearly shows that at room temperature, the solid product density is greater than that of the reactants for all compositions considered, except for ZnTe (this particular characteristic of ZnTe was first pointed out in [4]). If the product is brought to the flame temperature, however, the product density estimated using the assumed values for the coefficients of thermal expansion is less than that of the reactants for a few mixtures: 3Ni+Al, Mn+S, Zn+S, and Zn+Te. Those are therefore the mixtures with the greatest potential for detonation. The other mixtures would likely not allow the CJ criterion to be satisfied.

The detonability of mixtures like those in Fig. 3 can also be assessed thermodynamically by comparing the relative locations of the initial state and the detonation Hugoniot computed using the method of Bennett and Horie on the *P-v* plane. Figure 4 presents results for the highly exothermic Ti+2B and Mn+S mixtures, as well as those of the titanium-silicon mixtures, which have large product densities and a low heat release, and two nickel-aluminum mixtures having a different product-to-reactant density ratio. The calculated specific volume of the products resulting from a constant pressure combustion (that was shown in Fig. 3) is also shown in the plots of Fig. 4. Finally, the shock Hugoniots of the product material having room pressure and temperature as their initial state are also shown for reference.

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[6] By convention, enthalpy of formation for an exothermic process is negative, but since all mixtures considered in this work are exothermic, absolute values are presented.

Discussion – Thermodynamic Considerations

The results shown in Figure 3 illustrate that considering product density alone or adiabatic flame temperature (or heat release) alone is not sufficient, the two must be taken into account simultaneously (that is, the height of the dark black column as well as the "stretching" or "thermal expansion" of that column via the heat release, as represented by the light gray column). For instance, Ti+2B, Ti+C, and 5Ti+3Si have large adiabatic flame temperatures (the absolute value of the enthalpies of formation of the first two are very high), but their product density is so much greater than the reactant density, as illustrated by the very short black column in those cases, that the amount of thermal expansion undergone by the product cannot compensate for it. On the other hand, the products of 3Ni+Al and Ti+Ni have relatively low density at room temperature (i.e. long black columns) but the adiabatic flame temperature of these mixtures is low and leads to only a slight decrease in product density (difference between gray and black columns is small). On the other hand the Zn+S mixture which has a relatively low enthalpy of formation and a low adiabatic flame temperature appears to be good a candidate nevertheless due to its low product density. The mixtures most likely to detonate however should be Mn+S and Zn+Te, since ZnTe is the only one whose products are less dense than its reactants at room temperature and since Mn+S has a promising combination of high exothermicity and low product density.

The detonation Hugoniots in Fig. 4 are similar to the Hugoniots of the product materials, but shifted upward due to the effect of heat release. The magnitude of the shift is usually greater in mixtures that have a greater adiabatic flame temperature for constant pressure combustion and/or whose products have a large magnitude of enthalpy of formation. Hence, the location and slope of the Hugoniot of the product material as well as the exothermicity of the reaction must be considered simultaneously since both have an influence on the location of the detonation Hugoniot.

In Fig. 4b and Fig. 4f, corresponding to mixtures of Mn+S and 1.52 Ni+Al, respectively, the product density at room conditions calculated for a constant pressure combustion process is to the left of the detonation Hugoniot curve while it lies to the right for the other mixtures of Fig. 4. The lack of agreement between the predicted product states obtained via the two different methods can be explained by the numerous assumptions made in obtaining both the product density from constant pressure combustion and the detonation Hugoniot. Since neither method is more rigorous than the other, it is advisable to consider both approaches in order to assess the detonability of a mixture.

The CJ tangency criterion cannot be satisfied for the Ni+Al, 1.52Ni+Al, Ti+2B, Ti+Si, and 5Ti+3Si mixtures, since the detonation Hugoniot lies to the left the initial state in the reactants in Fig. 4. These conclusions are in accordance with those made based on the constant pressure combustion predictions shown in Fig. 3 and Fig. 4. Also in accordance with the results of Fig. 3 is the fact that for the Mn+S mixture, the CJ criterion can be satisfied (see Fig. 4b). For this mixture, a tangent to the detonation Hugoniot passing through the non-porous reactant initial state (giving a detonation velocity of 5.90 km/s), a CJ point (at 30 GPa), and a vN point (at 50 GPa) can be obtained, as shown in Fig. 4b. The predicted vN and CJ pressures for this mixture are also well above the minimum pressure necessary for its initiation [71, 83], which means that based on a CJ analysis, self-sustained detonations in this mixture are possible.

In order to account for the effect of initial porosity, the detonation Hugoniot for the Mn+S case was also calculated for reactants of different densities. The results of this calculation show that large variations in initial density do not cause very large changes in the location of the detonation Hugoniot (Fig. 5). However, it is clear that for lower initial densities, a straight line tangent to the detonation Hugoniot passing through the initial state would be less steep, resulting in lower shock velocity and lower pressures.[7] Therefore, from purely thermodynamic considerations (i.e., neglecting the details of how reactions are initiated and how fast they proceed to equilibrium), detonations are more likely to be realized using non-porous samples. In spite of this, the slow reaction rates in reactive powder mixtures, either porous or non-porous, may lead to very long reaction zones, and therefore detonations may be observable only in very large charges.

Results – Reaction Zone Model

Based on the above results deriving from thermodynamic considerations, mixtures with the greatest potential to detonate were non-porous Mn+S, Zn+S, Zn+Te, and

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[7] Recall that for reactive shocks, the initial state does not lie on the detonation Hugoniot.

3Ni+Al. Little experimental work has been performed on Zn+Te, particularly when it comes to shock initiation. Hence, the data necessary to model the reaction zone of a hypothetical detonation in Zn+Te is lacking. The 3Ni+Al mixture is only barely detonable according to Fig. 3, even with its large CTE of $23x10^{-6}$ K^{-1}. Finally, due to its greater heat release, the Mn+S mixture should have greater potential than Zn+S (if we neglect the production of gases in the reaction), since both have similar products. Therefore the Mn+S mixture was used to demonstrate the applicability of the ZND-based reaction zone model to predict the reaction zone length and the dependence of detonation velocity on charge diameter. The burning velocity used for non-porous Mn+S was 4 mm/s [84-85].

The predicted dependence of the detonation velocity with charge diameter for non-porous Mn+S is presented in Fig. 6 for two different confinement types. At a charge radius on the order of 1000 m, the detonation propagates at half the maximum (i.e., CJ) value in unconfined casing and approximately 60% of the maximum value when confined in steel. The lower limit for the detonation propagation velocity was set at the sound speed in the unshocked reactants, since at this speed there is no longer significant compression of the material by the wave front, i.e., the compression wave is no longer a shock. For a sound speed approximately equal to C_o in Table 1, supersonic detonation velocities do not exist for shock velocities below 44% of the CJ value, as shown in Fig. 6. According to the model, a detonation propagating at 44% of the maximum velocity could be achieved in a steel-confined charge with a 30 m radius or an unconfined charge with a 140 m radius.

Discussion – Reaction Zone Model

The trend of Fig. 6 is monotonic so that there appears to be no point where the slope of the curve becomes infinite, which would correspond to a minimum, or critical, charge radius. This lack of a turning point is typically obtained when reaction zones are modeled with reaction rates that do not depend strongly on the thermodynamic state. It was shown by [64-66] that reaction rate models with a power law pressure dependence of the type P^n produce a critical turning point in the detonation velocity – charger diameter curve (i.e., a critical charge diameter) only for a value of n greater than or equal to two. For smaller values of n, there is no critical turning point, hence no critical diameter. It may also be pointed out that

Sharpe [62] obtained similar results with exponential reaction rate models of the type $e^{E/RT}$: for high activation energy, E, a critical turning point existed, while for low activation energy, no turning point existed. When the reaction rate is strongly sensitive to the thermodynamic state, it is very sensitive to the effect of lateral expansions, which means that reactions can be quenched. This implies that a small decrease in diameter can lead to a sudden drop in reaction rate and an immediate failure of the detonation. On the other hand, when the reaction rate is weakly dependent on the thermodynamic state, a decrease in charge diameter leads to a small decrease of the reaction rate. In this case, reactions do not quench but less energy is available to support the shock so that the detonation velocity decreases.
Due to the negligible pressure dependence of the burning velocity of gasless reactive powder mixtures, it should be expected that their behavior would resemble that of explosives whose pressure dependence is on the order of $n < 1$. Explosives of this type also typically contain separate fuels and oxidizers, such as those based on ammonium nitrate (AN) or ammonium perchlorate (AP) mixed with a fuel and/or aluminum powder. Much of what is understood about AN- and AP-based explosives may be applicable to gasless reactive powder mixtures (see, for example [46, 48, 67- 69, 86]). Due to the fact that mixing of the components is required for reactions to take place in these explosives, reaction zones are larger than in molecular explosives. These explosives also typically have significantly curved fronts.

Since reaction time was assumed to be independent of the thermodynamic state in our model, the burning time is constant (given by eq. 15) and reaction zone length should depend linearly on the velocity of the flow immediately downstream of the shock (thus the reaction zone length should be approximately equal to the reaction time multiplied by the vN flow velocity at the beginning of the reaction zone). From the shock velocities and shock Hugoniots calculated using the values in Table 1, the material velocities range from 2.70 to 3.40 km/s in Mn+S as shock velocities range from 50% to 85% of the CJ velocity. For a burning time given by eq. 15 as 1 s for Mn+S, reaction zone lengths should be on the order of 2700-3400 m in Mn+S. This is indeed similar to the model predictions of 1900-3100 m for both steel confined and for unconfined, for the same range of shock velocities. Moreover, for systems with a constant burning time, Khariton's principle could be approximately quantified as follows: burning time < charge radius / sound speed.

This definition states that the burning time should be less than the time it takes for the leading lateral expansion wave to reach the central axis of the charge. If a sound speed on the order of 3 km/s in shocked Mn+S is assumed, the minimum charge radius should be on the order of 3000 m. This is on the same order as the reaction zone length, and according to Fig. 6, it is the radius for which a detonation propagating at approximately 60-70% of D_{CJ} would be observed. Therefore, a simple criterion from Khariton's principle can be used to give an order of magnitude estimate of the minimum charge radius for explosives whose burning time is independent of the thermodynamic state.

Since the ZND reaction zone model depends only on the burning time, every order of magnitude increase in burning velocity leads to a decrease in reaction zone length of the same order (and a decrease in the charge diameter of the same order for a given detonation velocity). Therefore, a self-sustained detonation may be produced in a charge with a diameter of less than 1 m in Mn+S if the burning velocity of this mixture can be increased to approximately 400 mm/s. It is known that burning velocity in reactive powder mixtures can be increased, in some cases, by up to an order of magnitude via mechanical activation using a ball-milling machine. For instance, the burning velocity of 50% TMD Ni+Al powder is on the order of 23 mm/s[8], whereas for the same powder if it is first mechanically processed in a ball-mill, the burning velocity increases to 44 mm/s [71], and this burning velocity can be further increased to 205 mm/s when the ball-milled powder is densified to nearly 100% TMD [85]. It is also known that burning rates can be increased via other types of nanoscale mixing approaches [88]. However, there appears to be a limit to the increase in burning velocity that can be achieved via a reduction in the mixing scales. Weihs et al. [89] showed that reaction occurring on the interface between the two components results in a greater fraction of the mixture being effectively inert product as the scale of the mixing is reduced. Not only does this intermixing layer represent a barrier to mass diffusion, it decreases the reactive mass, and thus the adiabatic flame temperature. Therefore, burning velocity decreased when the size of the intermixing layer

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[8] Note that Hardt and Holsinger [84] obtained values in the range 35-51 mm/s in Ni+Al mixtures made of powders of similar size or slightly smaller size, but pre-heated to 425-500K.

became similar to that of the non-reacted materials. It is therefore unlikely that burning velocity increases by two orders of magnitude or more could be achieved via pre-mixing alone.

Finally, the product mass fraction at the sonic plane predicted by the reaction zone model for Mn+S is displayed in Fig. 7. As expected, when the detonation velocity is lower (as when the charge diameter is smaller), the reaction is less complete at the sonic plane than when the detonation is greater. However, this dependence is not very strong, and the product mass fraction at the sonic plane is very close to one in all cases. Therefore the detonation velocity deficit obtained in small-diameter charges results more from momentum losses than to incomplete reactions. In addition, the extent of the reaction did not depend markedly on the confinement material. This is likely due in large part to the fact that the reaction rate law had no dependence on the thermodynamic state. Therefore, the charge radius had an effect on the flow, but not on the reaction rate. The extent of reactions that took place before the sonic plane is therefore essentially dependent only on how fast the flow reached sonic velocity.

Conclusion

A comprehensive, yet simple, methodology to assess the detonability of heterogeneous powder mixtures that react exothermically without significant gas production was presented. The two conditions that must be considered in the assessment of gasless detonation in reactive powder mixtures were considered: 1) the expansion of the products relative to the reactant density, and 2) the length of the reaction zone relative to the size of the detonating charge (or the reaction time relative to the pressure relaxation time resulting from the finite charge dimensions). The first condition is necessary for a shock wave to be supported by the reactions taking place in the reaction zone, while the second condition is necessary to ensure that the energy released by the reactions is used to support the shock instead of accelerating the reacted products in the transverse direction.

Two simple methods were proposed to show that many highly exothermic and/or fast reacting mixtures do not produce sufficient product volumetric expansion to detonate. The mixtures that were found to satisfy the product volumetric expansion requirement typically possessed one or more of the following features: high reaction temperature, products with large volumetric thermal expansion coefficient, and/or products with a low density at room pressure and temperature. Certain mixtures of nickel and aluminum, manganese and sulfur, zinc and sulfur, and zinc and tellurium appeared to permit detonation when initial reactant density is sufficiently large (i.e., porosity sufficiently low) to ensure that the products' expansion can support a shock in the reactants.

A quasi one-dimensional model of the ZND reaction zone was developed to account for the competition between energy release rate and momentum and energy losses due to lateral expansion. Using this model with an empirically derived relation for the reaction rate, the relationship between the speed of a self-sustained supersonic reactive compression and the charge radius was estimated for micrometric powder mixtures of Mn+S. The results were qualitatively similar to those for commercial blasting explosives whose reaction rate is not strongly dependent on the thermodynamic state, in that the shock velocity – charge radius was monotonic and contained no critical turning point. The calculated reaction zones were very long so that unless burning velocities at least two orders of magnitude greater than in micrometric powders could be achieved, detonations may not be observable in charge diameters less than one meter in such gasless mixtures.

In closing, it is important to point out that this study focused on the conditions required for the propagation of a steady, self-sustained detonation without regard to the initiation process. It is not sufficient for the conditions for steady propagation to be fulfilled for a detonation to be established. The unsteady initiation process may require conditions that were not considered in this article. For instance, although burning reactions can be initiated with relatively weak shock waves and a suitable charge diameter could be constructed, very strong initiating shocks of long duration in addition to much greater charge diameters may be required to ensure that a steady detonation is able to develop.

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Table 1: Parameters used in ZND reaction zone model of Mn+S

Detonation Velocity, D_{CJ} (km/s)	5.90
Initial Density, ρ_o (g/cc)	3.80
C_o (km/s)	2.59
S	1.47
v_o/Γ_o (cc/g)	0.136
Q (kJ/g)	1.80

Fig. 1 Graphical illustration of the calculation method of Bennett and Horie [22]

Fig. 2 Hugoniot curves obtained via eq. (7), along with reactant Hugoniot curve obtained using the method recommended by Petel and Jetté [45] and detonation Hugoniot curve obtained using the method of Bennett and Horie [22] for Mn-S detonation. The Rayleigh line for the detonation process is also shown (D_{CJ} = 5.90 km/s)

Fig. 3 Comparison of predicted product and reactant material densities for a constant pressure combustion process

Fig. 4 Comparison of predicted location of detonation Hugoniot to initial state on pressure-volume plane

Fig. 5 Initial states and predicted detonation Hugoniots for Mn+S mixtures at various starting densities (given in legend)

Fig. 6 Predicted detonation velocity─charge diameter relations for Mn+S in steel confinement and in no confinement. The sonic limit at which point a shock no longer exists is marked with a full circle

Fig. 7 Predicted detonation velocity vs product mass fraction at sonic plane for Mn+S in steel confinement and in no confinement