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ON THE EXISTENCE OF PATHOLOGICAL DETONATION WAVES

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Pathological detonation waves with velocities greater than Chapman-Jouguet (C-J) have been proposed theoretically but never observed experimentally in gaseous, liquid or solid explosives. Two types of pathological chemical reaction zones have been identified within the Zeldovich – von Neumann – Doring (ZND) model: an exothermic chemical decomposition with a mole decrease during from the von Neumann spike state to the C-J state and an exothermic reaction followed by an endothermic reaction (eigenvalue detonation). The high temperatures reached in detonation reaction zones cause sufficient radial and atom formation to insure overall mole increases in gaseous $H_2 + O_2$ detonations. Aluminized explosives exhibit a slight mole decrease when the solid aluminum particles are oxidized, but this does not negate the large mole increase that occurs during explosive decomposition. Porous solid explosives whose products form with more cold compression energy than that of the solid are an unlikely possibility for pathological detonation. Eigenvalue detonations have been postulated for $H_2 + Cl_2$ gas phase detonations and for plastic bonded solid explosives if endothermic binder decomposition follows exothermic explosive decomposition. Chemical kinetic and physical arguments are presented to eliminate these possible pathological detonations. In the case of $H_2 + Cl_2$, highly vibrationally excited HCl molecules dissociate Cl_2 molecules during the exothermic portion of the reaction zone rather than later in the flow process. In the plastic bonded explosives, the binders are located on the surfaces of explosive particles and thus are exposed to “hot spots” created by the three-dimensional Mach stem shock front. Any remaining binder material rapidly reacts in collisions with the high, vibrationally excited reaction products formed during explosive decomposition. Therefore eigenvalue detonations are extremely unlikely to occur in gaseous, liquid or solid explosives.

INTRODUCTION

The existence of pathological detonation waves with steady state detonation velocities greater than those predicted by the Chapman-Jouguet (C-J) hypothesis has been an intriguing possibility since they were first suggested by von Neumann(1) during the development of the Zeldovich – von Neumann – Doring (ZND) model. Two chemical reaction profiles starting at the unreacted von Neumann spike state and ending with equilibrium products have been proposed to create pathological detonations. One is an exothermic reaction that produces fewer moles of reaction products than originally present in the explosive (1). The second possibility has become known as an “eigenvalue” detonation in which an endothermic reaction follows the main exothermic reaction (2). Another pathological

detonation situation could theoretically occur if the reaction products are formed with more cold compression energy than that of the unreacted explosive (3). Non-equilibrium chemical kinetic and physical arguments are presented in this paper to show that pathological detonation waves are extremely unlikely to occur in real gaseous, liquid and solid explosives. This conclusion agrees with the fact that no experimental detonation velocities higher than the C-J values has ever been obtained.

MOLE DECREMENT REACTIONS

Von Neumann (1) first proposed a non C-J detonation velocity solution in which the Rayleigh line is tangent to the envelop formed by unreacted, partially reacted, and complete reaction Hugoniot curves which cross. Figure 1 shows these Hugoniot

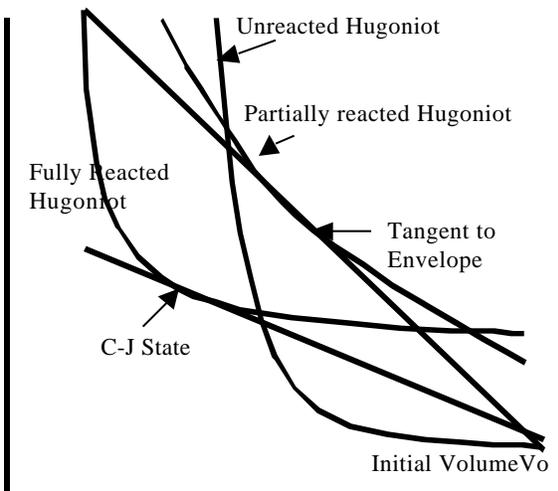


FIGURE 1. Pressure – specific volume curves for the pathological detonation case for an exothermic reaction with a mole decrement

curves plus the C-J and envelop tangent Rayleigh lines for this situation. An exothermic chemical reaction that produces fewer moles of reaction products than present in the original explosive mixture was the first example. A similar set of Hugoniot curves can represent a very porous solid explosive that is shock heated to sufficiently high temperatures that its Hugoniot curve lies to the right of its product Hugoniot curve at high pressures (3).

The gas phase detonation of $2\text{H}_2 + \text{O}_2$ to form two moles of H_2O would produce such a mole decrement, but the high temperatures attained in the detonation wave cause enough OH radicals plus H and O atoms to be formed that the C-J equilibrium state has more moles than the von Neumann spike state (3). The experimentally measured detonation velocities for $2\text{H}_2 + \text{O}_2$ agree closely with the predicted C-J values at all initial temperatures, pressures, and degrees of dilution with various inert gases. All other gaseous, liquid and solid explosives form more product moles than the original explosive molecule or mixture.

An aluminized explosive has a small mole decrement when two aluminum atoms react with three oxygen atoms from H_2O , CO_2 or CO molecules produced by the decomposition of the explosive molecules to form Al_2O_3 . However, each mole of explosive produces several moles of products so that an overall mole increase is ensured.

No higher than C-J detonation velocities have ever been measured for aluminized explosives.

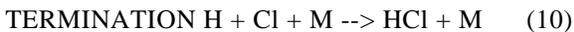
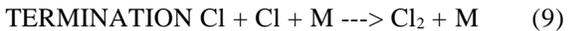
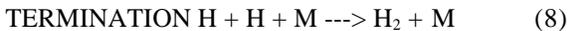
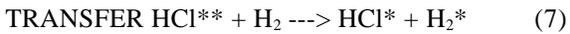
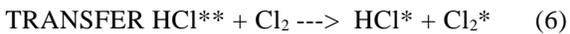
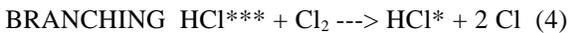
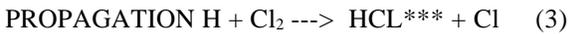
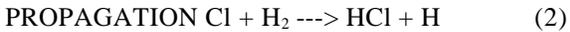
Hugoniot curves similar to those in Fig. 1 can be drawn for a very porous solid explosive whose initial volume V_{00} is much greater than the fully dense explosive specific volume V_0 shown in Fig. 1 (3). The porous unreacted explosive has to be shock heated to high enough temperatures for its Hugoniot to move to the right of the partially and fully reacted product Hugoniot curves. Then a higher than C-J velocity detonation wave could progress through the partially reacted states with a tangent point on the envelop formed by the various Hugoniot curves, as shown in Fig. 1. Porous metals sometimes exhibit this type of Hugoniot curve due to their small heat capacities (4), but the greater heat capacities of large explosive molecules most likely prohibit high enough temperatures for this effect to occur. Once again, no higher than C-J detonation velocities have been observed for porous solid explosives, which obey linear dependencies on the initial density of the solid (5). Therefore it is extremely unlikely that any pathological detonation waves exist for the type of Hugoniot curves shown in Fig. 1.

EIGENVALUE DETONATIONS

The term “eigenvalue detonation” has applied to any set of chemical reactions in which the exothermic reactions occur at faster rates than the endothermic reactions. In such a situation, Rayleigh lines can be drawn tangent to partially reacted Hugoniot curves which have greater enthalpy release than the final equilibrium C-J state. The gaseous explosive mixture of $\text{H}_2 + \text{Cl}_2$ has been suggested as a possible pathological detonation. Guenoche et al. (6) followed the time evolution of the reaction products HCl, H, Cl, H_2 and Cl_2 using reaction rate data obtained in shock tube studies of the various individual reactions. They concluded that the endothermic dissociation of Cl_2 would be slower than the exothermic formation of HCl resulting in an overall endothermic portion of the rear of the reaction zone. Thus a $\text{H}_2 + \text{Cl}_2$ detonation wave could be pathological and exhibit a detonation wave velocity much higher than C-J. However, when the detonation velocities and average pressures of $\text{H}_2 + \text{Cl}_2$ mixtures were measured for various stoichiometries at several initial pressures by Dionne et al. (7), they agreed very closely with C-J

predictions, especially for initial pressures greater than 0.1 atm.

The reason for this disagreement is that Cl atoms are formed at the same time as the HCl molecules through rapid chain branching reactions of Cl₂ molecules with the initially highly vibrational excited HCl molecules. The following reactions must all be considered when discussing H₂ + Cl₂ detonation (3).



where *'s denote increasing vibrational excitation.

Polanyi (8) and many others have shown that the rates of reactions such as (4) and (5) increase by factors of ten with each quanta of vibrational excitation. Since HCl molecules from reaction (3) are formed in the $v=4$ to 8 levels under detonation conditions (3), their collisions with Cl₂ molecules are highly effective in causing dissociation. Additionally, most of the reactions in a three-dimensional gas phase detonation wave occur in the high pressure, high temperature regions behind the mach stem and transverse waves, further increasing the overall rates of reactions (1) to (10). Therefore the overall energy release remains exothermic throughout the reaction zone, and detonation waves in H₂ + Cl₂ mixtures propagate at C-J velocity.

Fickett and Davis (2) discuss an eigenvalue detonation wave solution for two irreversible reactions in which the enthalpy of the first reaction is 100 RTo exothermic and that of the second reaction is 75 RTo endothermic. This combination of reactions has a Rayleigh line tangent to a partially

reacted Hugoniot with an enthalpy of 44.8 RTo, when the first reaction is 75% complete and the second reaction is 40% complete. This Rayleigh line has a higher detonation velocity than the C-J Rayleigh line, which is tangent to the 25RTo Hugoniot curve for complete reaction. This solution is shown in the pressure – specific volume plane in Fig. 2, which is identical to Fig. 5.15 of Fickett and Davis (2). They suggest that this may occur in a plastic bonded explosive when the endothermic decomposition of the binder is sufficiently slower than the exothermic decomposition of the explosive.

This sequence is unlikely for several reasons. First, the binder is located on the outer surfaces of the explosive particles. This is the location of the voids where “hot spots” are formed and where high pressure, high temperature regions are created at the Mach stem interactions of the three-dimensional detonation wave front. Thus the binder layers are subjected to these extreme conditions and begin to react before the explosive particles. Second, the binders used in plastic bonded explosives are not a great deal more thermally stable than the high explosive molecules (9). Thus they react in the same time frame as the explosive molecules when shock heated. Third, once the decomposition of the explosive into highly vibrationally excited reaction product gases begins, the excited gases collide with any remaining binder and rapidly decompose it (10). Fourth, most organic explosive molecules are under-

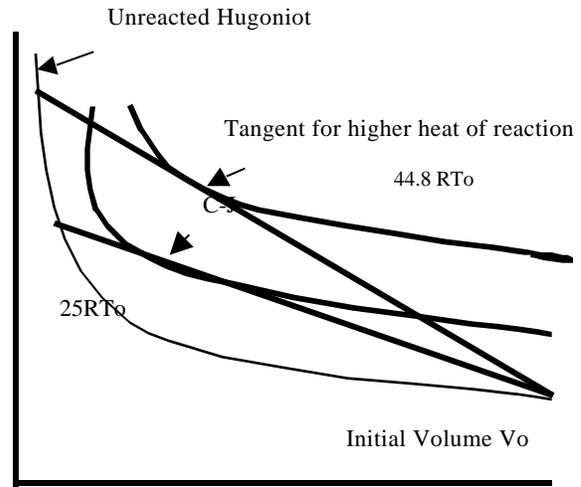


FIGURE 2. Pressure – specific volume states for an Eigenvalue detonation with an exothermic reaction followed by an endothermic reaction oxidized and produce diamond, graphite or

amorphous solid carbon in a relatively slow diffusion controlled process that controls the energy release as the C-J equilibrium state is approached (11). This exothermic solid carbon formation process requires tens to hundreds of nanoseconds as the C-J state is approached, and therefore the binder will have long been fully decomposed and its products equilibrated with the explosive reaction products. The characteristic chemical energy release process for condensed phase explosives of a fast exothermic reaction, which produces vibrationally excited N_2 , H_2O , CO_2 and CO , followed by the much slower exothermic carbon formation process has been measured experimentally in several explosives using embedded gauge and laser interferometric techniques (11,12). Fifth, experimentally no plastic bonded explosives have exhibited higher than C-J detonation velocities. Thus eigenvalue detonation are unlikely to occur for plastic bonded solid explosives.

SUMMARY

The physical and chemical kinetic arguments presented in this paper show that pathological detonations are extremely unlikely to be observed in real gaseous, liquid, and solid explosives. These

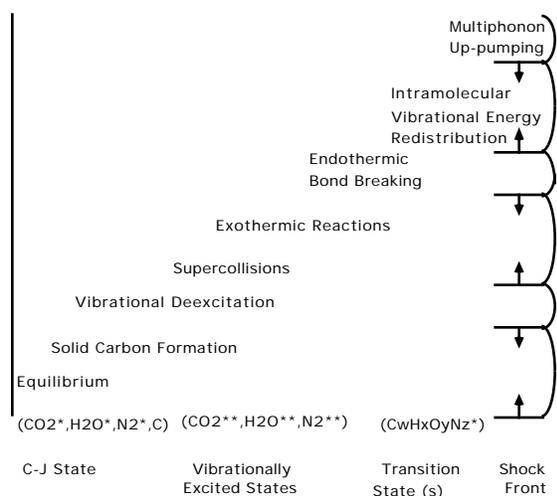


FIGURE 3. The Non-Equilibrium Zeldovich - von Neumann-Doring (NEZND) model of detonation for condensed phase explosives arguments are related to the complex excitation

processes preceding chemical energy release and the equally complex processes that follow formation of highly vibrationally excited reaction products as they approach thermal and chemical equilibrium at the C-J state. Figure 3 shows many of these processes as they have been identified in the Non-Equilibrium ZND (NEZND) model of detonation wave propagation (9). These non-equilibrium processes limit the initial decomposition rates of the explosive molecules, control the rates of the exothermic chain reactions, and provide the chemical energy required to sustain the three-dimensional detonation wave front at a constant C-J velocity.

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