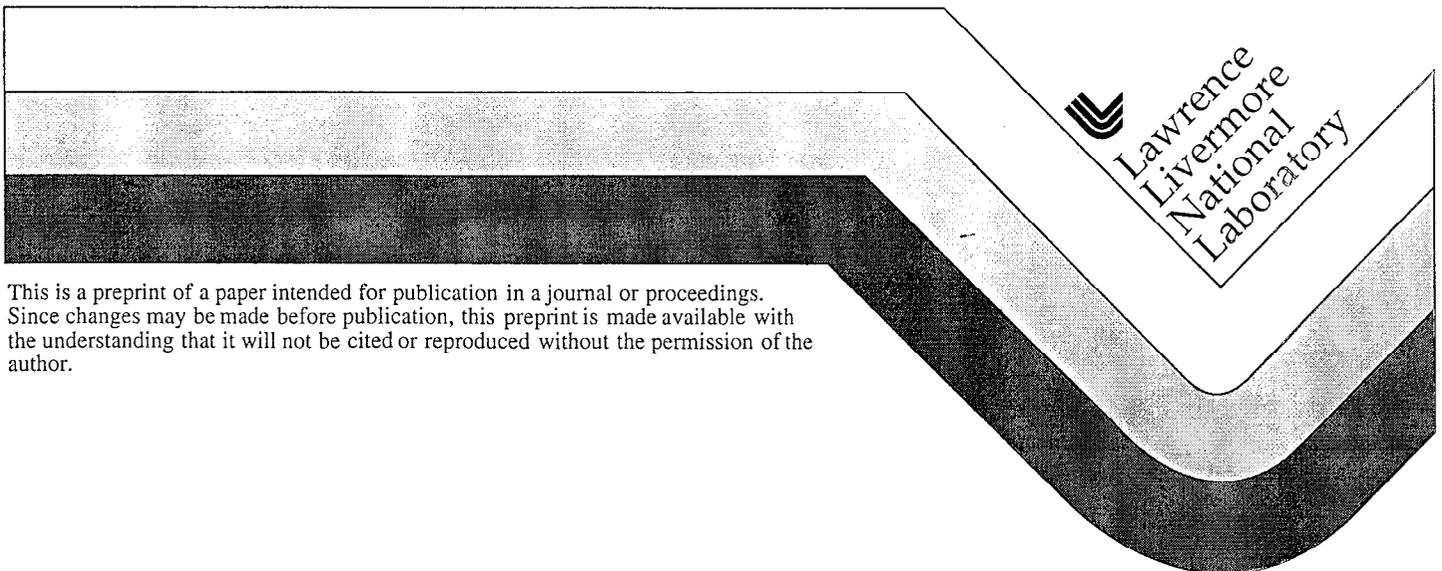


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Kinetic Modeling of Non-Ideal Explosives

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Abstract

We have implemented a Wood-Kirkwood kinetic detonation model based on multi-species equations of state and multiple reaction rate laws. Finite rate laws are used for the slowest chemical reactions, while other reactions are given infinite rates and are kept in constant thermodynamic equilibrium. We model a wide range of ideal and non-ideal composite energetic materials. In addition, we develop an exp-6 equation of state for the product fluids that reproduces a wide range experimental shock Hugoniot and static compression data. For unreacted solids, including solid and liquid Al and Al_2O_3 , we use a Murnaghan form for the equation of state. We find that we can replicate experimental detonation velocities to within a few per cent for a wide range of explosives, while obtaining good agreement with estimated reaction zone lengths. The detonation velocity as a function of charge radius is also correctly reproduced.

INTRODUCTION

The detonation of an energetic material is the result of a complicated interplay between chemistry and hydrodynamics. While the detailed chemical kinetics of detonation in gases have been extensively studied, much less is known regarding chemical kinetic processes governing condensed energetic materials. The primary reason for this is the extreme pressure and temperature immediately behind the detonation wave: pressures of 400 kBar (40 GPa) and temperatures of 4000K are common. The extreme conditions result in very broad spectroscopic features that make the identification of individual chemical species very difficult.

There is a continuing need in the energetic materials field for reliable predictions of detonation velocity and energy delivery. This has traditionally been accomplished through the means of Chapman-Joulet thermodynamic detonation theory. Chapman-Joulet detonation theory assumes that thermodynamic equilibrium of the detonation products is reached instantaneously.

For the purpose of this study we define non-ideal explosives as those with a reaction zone of one mm or more. So-call "non-ideal" explosives are often poorly modeled by Chapman-Joulet the theory. These materials have chemical reaction rates that are slow compared to hydrodynamic time scale 10^{-6} s so that the Chapman-Joulet (CJ) assumption of instantaneous thermodynamic equilibrium breaks down. For example, it is found

experimentally that the detonation velocity of non-ideal explosives varies sharply from the CJ value and depends strongly on the charge radius. We are therefore forced to consider the interaction of chemical kinetics with the detonation wave in order to reach an acceptable representation of detonation in non-ideal explosives. Wood and Kirkwood¹ (WK) proposed a two dimensional steady state kinetic detonation theory that solves many of the limitations of ZND theory. WK considered a cylindrical charge of infinite length. They solved the hydrodynamic Euler equations in the steady state limit along the central streamline of the cylinder. Radial expansion was treated as a source term in the 1-D flow along the streamline.

The WK equations have been extensively analyzed by Erpenbeck² and co-workers. It is found that the detonation velocity depends on the interplay between chemical kinetics and radial expansion. In the limit of no radial expansion, the ZND plane wave result is obtained. When radial expansion is allowed however, the detonation velocity can vary from the C-J prediction. In the limit of strong radial expansion the detonation wave fails; no velocity is found which satisfies the steady-state equations. Bdzil has generalized WK theory to off-axis flow³ and Stewart⁴ and coworkers have studied the effect of kinetic rates on the decrease of detonation velocity with decreasing size and on curvature of the detonation wave.

In the present paper we implement a model of detonation kinetics based on the identification of individual chemical species. The advantage of the present treatment is that the same equations of state and chemical rate laws can be used on a wide range of explosive mixtures. A mixture equation of state based on thermal, mechanical, and partial chemical equilibrium is used. The mixture model is implemented in the Cheetah thermochemical code⁵. Small molecules that are gases at standard conditions are treated with the BKW⁶ real gas equation of state. Solids are treated with a Murnaghan⁷ equation of state. Simple pressure-dependent chemical reaction rates are employed. These rates represent the consumption of the energetic material by the detonation wave. Fast reaction rates (partial chemical equilibrium) are assumed for species other than the initial material.

The Wood-Kirkwood equations are solved numerically to find the steady-state detonation velocity. The radial expansion is derived from measured radii of curvature for the materials studied. We find good agreement with measured detonation velocities using the same set of equations of state and rate laws for each composite. Although our treatment of detonation is by no means exact, the ability to model a wide range of phenomena based on simple equations of state and rate laws is encouraging. We find that the inclusion of detonation kinetics yields a significant improvement in the predicted detonation velocity of materials with long estimated reaction zones. More importantly, we are able to reproduce the dependence of the detonation velocity on charge radius for several materials. For materials with short reaction zones, we recover the results of Chapman-Jouguet thermochemistry.

WOOD-KIRKWOOD DETONATION THEORY

WK theory starts with the hydrodynamic Euler equations coupled to chemical kinetics. The theory treats the detonation along the center of the cylinder. The Euler equations are reduced to their steady state form. The result is a set of ordinary differential equations that describe hydrodynamic variables and chemical concentrations along the center of the cylinder.

The notation is as follows: we use cylindrical coordinates in a frame moving with the shock velocity D . x is the axial coordinate, r is the radial coordinate and u is the axial

particle velocity in the moving frame (equal to $D-U$ in the lab frame). The radial velocity is called ω . Subscripts denote a spatial derivative.

$$\begin{aligned} u_x &= \psi / \eta \\ \rho_x &= -(\rho/u)(u_x + 2\omega_r) \\ E_x + p v_x &= 0 \\ F_x &= R / u \\ \omega_r &= (D - u(t=0)) / R_c \end{aligned} \quad (1)$$

where F is the concentration vector, R is the reaction rate vector and R_c is the radius of curvature. ρ is the density, p is the pressure, E is the specific energy and v is the specific volume. We take the form of these equations from Fickett and Davis⁸ (see Equations 5.28 and 5.37). The expression for ω_r is an approximation that is strictly valid only at the initial jump off of the shock.

We define

$$\eta \equiv 1 - u^2/c^2 \quad (2)$$

to be the sonic parameter, where c is the speed of sound. If the sonic parameter η is greater than zero communication with the shock front is possible. If it is less than zero the region cannot communicate with the shock front. Secondly, we will define the pressure production term

$$\psi \equiv (\partial P / \partial F)_{v,E} \cdot R / \rho c^2 - 2\omega_r \quad (3)$$

Chemical reactions that increase the pressure at constant v, E will increase the value of ψ . Radial expansion, however, decreases the pressure through the ω_r term.

SOLUTION OF THE WK EQUATIONS

The initial conditions for the WK equations are the energy, density, and composition at the start of the shock front. We specify the initial composition to be the same as the unreacted material. The initial energy and density can be determined by specifying the detonation velocity; finding the intersection of the unreacted shock Hugoniot with the Rayleigh line yields the pressure and density at the shock front. This can be done if the shock velocity is specified. From this point on, the system visits a series of (p, v) states of different P with different chemical concentrations. A thermodynamic equilibration at fixed composition then determines the energy at the shock front. Note that the detonation velocity is treated as a specified quantity here.

As the equations are integrated, the shockwave structure is determined for positions behind the shock front. In practice, we use the "Lagrangian time" form of the WK equations, where the time variable is related to position by

$$dx = u dt \quad (4)$$

This choice of variables is most natural for the integration of kinetic laws.

The WK equations support a variety of solutions that have been discussed in great detail by Erpenbeck. Let us consider the behavior of the equations as a function of the specified detonation velocity D . There are three qualitatively different solutions possible. For special detonation velocities, the solutions pass through the sonic plane, defined by $\eta = 0$. Points behind the sonic plane cannot communicate with the shock front. The WK equations are finite when $\eta = 0$ only if ψ also passes through zero. Therefore the sonic solutions are defined by the nonlinear equation

$$\psi(t,D) = \eta(t,D) = 0 \quad (5)$$

It is possible to think of this as the kinetic CJ condition. The next possibility is that η never passes through zero. These solutions are overdriven; that is the pressure increases with distance behind the shock front. These solutions correspond to a rear piston boundary condition that drives the shock front forward. Finally, if $\eta = 0$ when $\psi \neq 0$, the equations become infinite. This means that a steady state flow cannot occur at the specified detonation velocity D .

Of all the solutions generated by the WK equations, only the sonic solutions have the pressure tend to zero as x becomes large. It is these solutions that correspond to steady-state self-propagating flow.

APPLICATION TO COMPOSITE ENERGETIC MATERIALS

The detailed chemistry of composite energetic materials is very complicated. Very many chemical steps are involved in the decomposition of most large energetic material molecules into small simple product molecules. In general the composition reactions are not well characterized, especially at elevated temperatures. The situation is made more complicated by the heterogeneous composite nature of most energetic materials. Void collapse and shear dislocations can lead to so-called "hot spots"- regions of enhanced temperature behind the detonation front. These regions play an essential role in high explosive initiation. They preclude describing the energetic material with a single temperature, and complicate the use of even the simplest Arrhenius chemical kinetic schemes.

Most reactive flow models of high explosive initiation overcome these difficulties through the use of pressure-dependent rates. Pressure-dependent rate laws have been shown to be sufficiently flexible to model a variety of initiation and non-ideal detonation phenomena, while maintaining simplicity. The disadvantage of these rate laws is that they do not explicitly treat the high explosive microstructure or the underlying activated chemical reaction rate laws.

We have inferred effective kinetic rates proportional to P^2 for a variety of ideal and non-ideal explosives and their composites. We find that this choice, while simpler than most reactive flow rate laws for high explosive initiation, is adequate to model steady-state detonation over the range of materials and diameters provided here. It has been noted that the detonation velocity size effect is sensitive to particle size. Many of the samples

considered here are not fully characterized with regard to particle size, so we do not include dependence of kinetic rate laws on particle size.

For the purposes of this study, we model the kinetic processes of the high explosives as being a single decomposition reaction into primary product constituents. The reaction products that we have assumed for the various high explosives, binders and metal reactions are listed in Table 1. However, because we assume that all of the products are in thermochemical equilibrium, the results are independent of the assumed decomposition pathway. This would not be the case if reversible reactions were important.

TABLE 1. EFFECTIVE CHEMICAL REACTIONS CONTROLLED BY KINETICS.

Reactant	Products	R (micro-sec ⁻¹)
al, o ₂	AL ₂ O ₃	0.0075
AP	N ₂ , H ₂ O, O ₂ AND HCL	0.0075
CEF	C ₂ H ₄ , O ₂ , CL AND P	0.01
HMX	CO ₂ , H ₂ AND N ₂	0.2
HTPB	C, CH ₄ AND H ₂ O	0.001
KEL-F	C, CHF ₃ , F ₂ AND CL	0.01
NC-12.2	CO ₂ , H ₂ O AND N ₂	0.01
NM	CO ₂ , N ₂ , H ₂ O AND C	1.0
PARAFFIN	C AND CH ₄	0.01
PETN	CO ₂ , H ₂ O, N ₂ AND C	0.50
RDX	CO ₂ , h ₂ O, n ₂ , o ₂ and c	0.20
TATB	n ₂ , h ₂ O, CO ₂ and c	0.06
TNT	C, CO ₂ , H ₂ O AND N ₂	0.10
VITON	C, CH ₃ F, CH ₄ AND F ₂	0.01

We assume that the kinetic rates are defined by the following equation:

$$d\lambda/dt = (1 - \lambda)RP^2 \quad (6)$$

where P is the pressure, R is the rate constant (see Table 1) and λ represents the amount of unburned reactant normalized to vary between 0 (all unburned) and 1 (all burned). In our kinetics scheme the concentrations of reactants are assumed to be controlled by the kinetic rate, while all of the products are assumed to be in thermochemical equilibrium.

For non-ideal explosives, the effects of equations of state are strongly coupled to the effects of kinetics and hydrodynamics. For the equations of state, the usual process is to fit the covolumes of the product gases to experimental detonation velocities of ideal and non-ideal explosives. For this study we have used a BKW equation of state for product gases with parameters fit only to ideal explosives, which we call BWKC2⁹. A modified Murnaghan EOS was fit to shock Hugoniot data¹⁰ for condensed solids. We also include a solid-liquid phase transition for Al and Al₂O₃.

RESULTS

The explosives mixtures studied here are composed of HMX, NM, RDX, PETN, TATB, TNT and AP, along with a variety of binders. We also model Al combustion in composites. In modeling these composites, we assume that each component material burns at a rate, which is independent of the other components in the composite. We find that this

simple approximation is adequate to describe the detonation velocity of the materials studied here. It should be noted that the approximation may fail for certain materials, most notably binary fuel/oxidizer mixtures, where the presence of one component dramatically accelerates the reaction of the other. Most of the composites contain a single high explosive and a binder. The composites with three or more components include IRX-3A, IRX-4 and PBXN-111. Each rate law was based on calculating the detonation velocity of several materials. The rate laws were adjusted to give the best fit to the experimental detonation velocity and where available the estimated reaction zone. The data for the experimental detonation velocities are taken from Ref. 11.

There are notable deficiencies in the C-J detonation velocity calculations when compared to experiment. In Figure 1 we compare detonation velocities calculated with C-J theory using the BKWC2 parameter set to experimental values. There is good agreement between theory and experiment for the compounds with experimental detonation velocities greater than 8 km/s. These materials are predominantly high explosive with less than 10% binder by weight. The deviation between C-J theory and experiment is quite substantial for experimental detonation velocities less than 8 km/s. These materials are multi-component mixtures containing AP and Al. Generally there is more than 10% of the binder material present by weight.

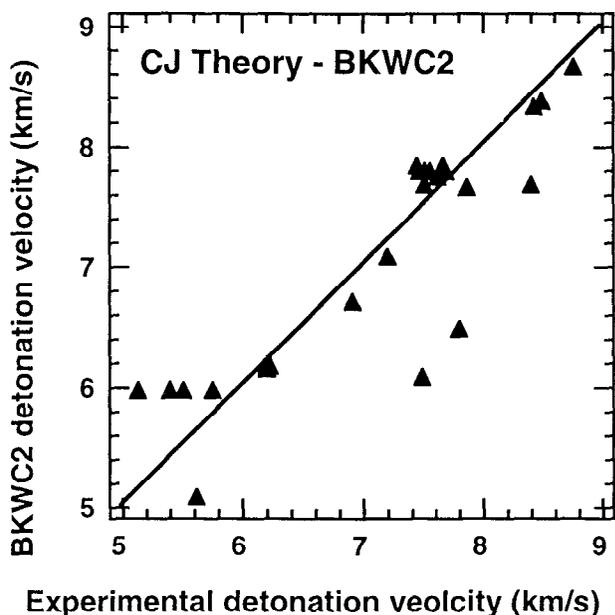


FIGURE 1. DETONATION VELOCITIES (IN KM/S) AS CALCULATED WITH C-J THEORY AND THE BKWC2 EQUATION OF STATE PARAMETER SET.

In Figure 2 we plot detonation velocities obtained with WK detonation theory and the reactions given in Table 1. The kinetic calculations are nearly as accurate at detonation velocities around 5 km/s as they are at 8 km/s. Although the calculations are not exact, all the large deviations from experiment have been eliminated.

Some of the non-ideal explosives that we study have significant amounts of hydroly-terminated poly butiene (HTPB). These non-ideal composites include IRX1, IRX-3A, IRX4, PBXN-110 and PBXN-111. Table 2 gives the compositions of these composites. We find it interesting that the products of this binder are hydrocarbons such as CH_4 and C_2H_6 . For these cases the calculated detonation velocities are sensitive to the equations of state for these hydrocarbons. We have recently developed an improved EOS for hydrocarbons¹², based on an exp-6 potential, which we will use in future studies.

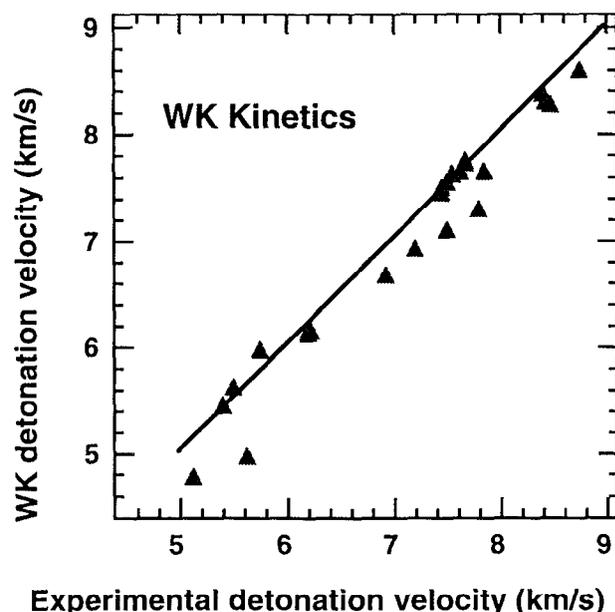


FIGURE 3. DETONATION VELOCITIES (IN KM/S) AS CALCULATED WITH WK THEORY AND THE BKWC2 EQUATION OF STATE PARAMETER SET.

TABLE 2. NON-IDEAL COMPOSITES

Composite	Composition by weight
PBXN-110	HMX, 88%, HTPB, 12%
PBXN-111	RDX, 20%, AP, 43%, AL, 25%, HTPB, 12%
IRX1	HMX, 70.1%, HTPB, 29.9%
IRX-3A	HMX, 69.8%, AL, 10%, HTPB, 20.2%
IRX4	HMX, 30%, AP, 24%, AL, 16%, HTPB, 30%

It is also interesting to calculate the case for which there is data for the detonation velocity and radius of curvature for composites as a function of charge radius. Figure 3 shows our results for PBXN-111. The solid circles are the experimental detonation velocities as a function of radius from Forbes and Lemar¹³, while the open circles are our calculated values. Our calculated values reproduce the experimental values reasonably well, while using generic kinetic rates given in Table 1. The shape of the curve, however, is sensitive to the rates chosen for AP and AL. In addition, for PBXN-111 we find multi-valued solutions⁴ for the detonation velocity. In such a case we take the largest value.

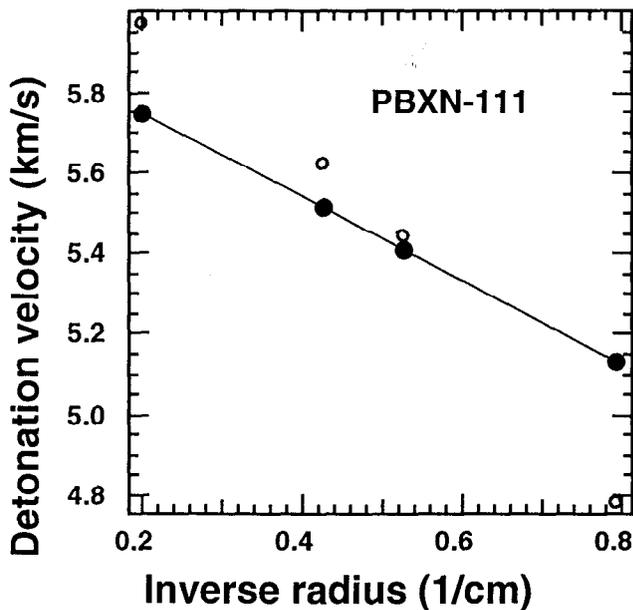


FIGURE 3. WK THEORY PREDICTS THE DETONATION VELOCITY AS A FUNCTION OF SIZE FOR PBXN -111.

Almost half of the composites (8 out of 16) in Figure 1 exhibit significant non-ideal behavior. That is, the experimental detonation velocity is significantly different than the calculated C-J theory detonation velocity. The composites exhibiting significant non-ideal behavior include EDC-35, PBX-9502, PBXN-110, TATB, IRX-1, IRX-3A, PBXN-111 and IRX-4. Seven of these composites contain RDX or HMX, which should have similar kinetic properties. Among these seven composites, there is a correlation between the amount of binder and the per cent deviation of the experimental detonation velocity from that predicted by the C-J theory. The one exception to this correlation is IRX-4, which is a multi-component composite containing 24% AP and 16% Al. We have no explanation for this except to note that a multi-component composite may have complex interactions between the kinetic rates of its constituents.

Kennedy and Jones¹⁴ have previously studied the non-ideal behavior of PBXN-111. Experiments with PBXN-111 have been performed from a charge radius of 50 cm., down to the failure radius which is less than 9.5 cm. Previous estimates of the equilibrium C-J detonation velocity of PBXN-111 by Kennedy and Jones range from 6.75 to 8.00 km/s. Our estimate of the equilibrium C-J detonation velocity of PBXN-111 is 5.97 km/s. A significant difference between our calculations and previous ones, is that with our carbon equation of state we predict all of the carbon is in the gas state at the C-J point, while Kennedy and Jones predict a significant amount of diamond is produced at that state.

We also perform calculations for various mixtures of HMX and Aluminum and compare with the recent data of Gogulya et al.¹⁵, who detonated composites of HMX and Aluminum particles of various sizes. We modeled these experiments with the HMX kinetic rate law in Table 1 and a rate for the Al that depends on particle size, pressure and the detonation product gas density. The results of such a calculation are shown in Figure 4, where we chose a rate law proportional to density of H₂O in the detonation products. This rate law

simulates the general trend of decreasing detonation velocity with increasing the amount of Al in the composite.

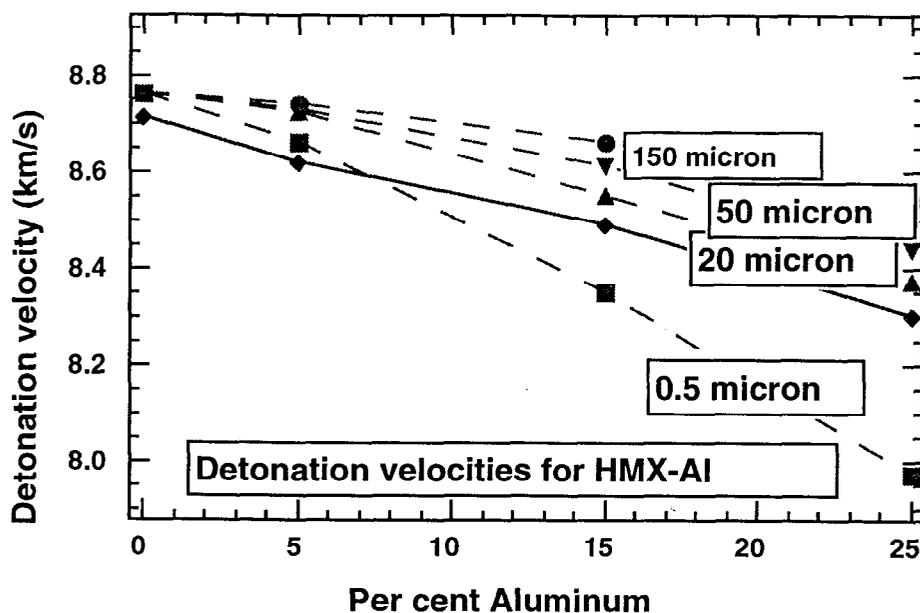


FIGURE 4. DETONATION VELOCITIES FOR HMX/AL COMPOSITES AS A FUNCTION OF AL CONCENTRATION AND PARTICLE SIZE. EXPERIMENTAL VALUES (CONNECTED BY DASHED LINES) FROM REF. 15 ARE COMPARED TO A KINETIC CHEETAH CALCULATION (CONNECTED BY SOLID LINE).

In conclusion we have developed a kinetic model for thermochemical detonations based on Wood-Kirkwood theory and the thermochemical Cheetah code. We find that with a simple model for kinetic processes we are able to model many of the features of non-ideal explosives such as their detonation velocities and their sonic reaction zone widths. In the future, we plan to extent our kinetic modeling study to include temperature and pressure dependent rate laws. In this way we can extend our model to more physically based rate laws and study more complex non-ideal detonation behavior such as shock initiation, hot spot formation and failure processes.

ACKNOWLEDGMENTS

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