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STUDIES OF FAST REACTIONS IN DETONATIONS

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The time-dependent behavior of the flow in reaction zones of the detonating homogeneous explosives nitromethane, liquid TNT, and ideal gases has been investigated using one- and two-dimensional Lagrangian and Eulerian numerical hydrodynamics with Arrhenius chemical reaction. A general model for bulk decomposition of heterogeneous explosives, called Forest Fire, has been developed, which gives the rate of explosive decomposition as a function of local pressure. The model permits description of the process of heterogeneous explosive initiation, propagation, and failure.

1. HOMOGENEOUS DETONATIONS

The hydrodynamic stability of one-dimensional detonations in an ideal gas of constant heat capacity undergoing an exothermic, irreversible, unimolecular reaction with an Arrhenius-law temperature dependence has been studied analytically by Erpenbeck (1). The analysis gives no information about the nature of the time-dependent flow in the case of an unstable solution. Fickett (2) has studied the time-dependent behavior of the flow for finite perturbations (the stability) of the ideal gas reaction zone using a one-dimensional characteristic method. In those cases for which Erpenbeck's linearized analysis has shown the steady-state solution to be unstable to infinitesimal longitudinal perturbations, flows started in a configuration approximating the steady-state solution exhibited nondecaying oscillations; in those cases for which Erpenbeck's analysis showed the steady-state solution to be stable, perturbations were found to decay.

In our monograph (3) we described the results of our studies of the time-dependent behavior of the flow (the stability) of the ideal gas, nitromethane and liquid TNT reaction zones to finite longitudinal and transverse perturbations using finite difference methods to solve the reactive Navier-Stokes equations of fluid dynamics. We also described the time-dependent behavior of the flow of stable overdriven nitromethane detonations formed by pistons of various configurations.

The equation of state for an ideal gas of constant heat capacity undergoing an exothermic, irreversible, unimolecular reaction is as follows. Given I , W , and V , one calculates P and T from

$$P = \{[I + (1 - W)Q](\gamma' - 1)\}/V$$

and

$$T = [I + (1 - W)Q]/C_v$$

$$\gamma' = 1.2 \quad T_c, V_c, P_c = 1 \quad C_v = 5$$

$$I_c = 5 \quad R = 1 \quad U_c = 0$$

The Arrhenius rate law is

$$dW/dt = ZW \exp(-E^*/RT)$$

Erpenbeck predicts that an ideal gas detonation with $f = 2$, $E^* = 50$, and $Q = 50$ will be stable to one-dimensional perturbations but unstable to two-dimensional perturbations, and that with $Q = 0.2$ it will be stable for all perturbations. The results of some of the numerical calculations using one- and two-dimensional Lagrangian and Eulerian hydrodynamics are summarized in Table I. The results are in agreement with the predictions of Erpenbeck and give us confidence in our numerical approach for determining stability of detonation waves. We shall now proceed to determine the stability of nitromethane and liquid TNT detonations to one- and two-dimensional perturbations.

To study the stability of detonations, we wish to use a piston that will establish, as quickly as possible, flow conditions in the fluid which closely approximate the steady-state (time-independent) flow conditions. We refer to such a piston as the steady-state piston.

The stability results for nitromethane and liquid TNT using a reasonable range of values for the kinetic and equation-of-state parameters are summarized in Table II.

The shock front pressure versus time for nitromethane detonations with velocities of 0.6850 and 0.6650 cm/ μ sec is shown in

TABLE I
Summary of ideal gas calculations

| Heat of explosion, Q | Frequency factor, Z^* | Activation energy, E^* | $(D/D_{CJ})^2$ f | D | t_{CJ} | Spike pressure P_{max} | C-J pressure P_{CJ} | Results |
|------------------------|-------------------------|--------------------------|-----------------------|-------|----------|--------------------------|-----------------------|------------------------------|
| 50 | 200 | 50 | 1.0 | 8.013 | 0.800 | 67.5 | 55.0 | Unstable 1-D Unstable 2-D |
| 60 | 82.5 | 50 | 2.0 | 9.64 | 0.800 | 84.0 | 72.0 | Stable 1-D Unstable 2-D |
| 0.2 | 3×10^7 | 50 | 2.0 | 1.873 | 1.325 | 9.20 | 3.19 | Stable 1-D Stable 2-D |

* Z is adjusted so that $H^* = 0.5$ when the time is 1.0.

TABLE II
Summary of nitromethane and liquid TNT calculations

| Activation energy, E^* kcal/mole | Frequency factor, Z (μsec^{-1}) | Grimeson γ | Thickness of reaction zone | Result |
|---------------------------------------|---|-------------------|----------------------------|--|
| Nitromethane | | | | |
| 53.6 | 1×10^{10} | 0.68 | 2000 A | stable at 6750 m/sec unstable at 6650 |
| 53.6 | 4×10^{10} | 1.70 | 1600 A | stable at 6750 unstable at 6650 |
| 40 | 1.27×10^{11} | 0.68 | 77,000 A | stable at 6400 (C-J) |
| 40 | 1.27×10^{11} | 1.70 | 69,000 A | stable at 6650 unstable at 6550 |
| 30 | 2.37×10^{11} | 1.70 | 705,000 A | stable at 6400 (C-J) |
| Liquid TNT | | | | |
| 41.1 | 2×10^{10} | 1.66 | 1.1×10^4 cm | stable at 6000 unstable at 6500 |
| 30 | 3.14×10^{11} | 1.66 | 7.3×10^4 cm | stable at 6400 (C-J) |

* Experimental value.

[†] Z adjusted to give an explosion time of 1.4 μsec at 1180°K (85 kbar) to agree with shock initiation experimental data.

[‡] Z adjusted to give an explosion time of 0.7 μsec at 1227°K (125 kbar) to agree with shock initiation experimental data.

Fig. 1 using the SIN and 2DE codes (3). Figure 2 shows the 0.6650/ μ sec unstable case where the initial perturbation grows and reaches a steady amplitude by the fourth cycle.

Two dimensional perturbations in C-J nitromethane and liquid TNT detonations do not grow, and the two-dimensionally perturbed flow decays to one-dimensionally perturbed flow. Nitromethane with E^* 's of 40 and 53.6 at C-J velocity and with an E^* of 53.6 at 0.7130 cm/ μ sec was calculated using the 2DL and 2DE codes (3). In all cases the two-dimensional perturbation did not grow and the stability was identical with that observed for one-dimensional perturbations. The two-dimensionally perturbed calculations are shown in Ref. 3 in detail.

The amount of overdrive necessary to stabilize the nitromethane and liquid TNT detonation decreases with decreasing activation energy and is independent of the frequency factor. The partially reacted Hugonions are very sensitive to the equation of state used for the mixture of undecomposed explosive and detonation products. We have used a γ of 1.70 in addition to a γ of 0.68 in Table II to illustrate the magnitude of this effect.

We now proceed to determine the time-dependent behavior of the flow of stable overdriven nitromethane detonations formed by a constant velocity piston.

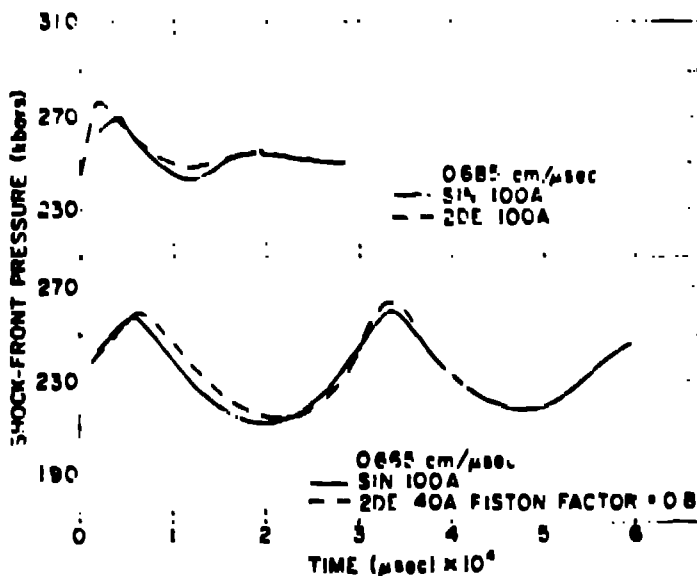


Fig. 1. The shock-front pressure vs time for nitromethane with various amounts of overdrive, for various numerical methods. $E^* = 53.6$, $Z = 4 \times 10^8$, and $\gamma = 0.68$. The mesh size is given for each method, and the detonation velocity is given in cm/ μ sec.

As shown in Table II, nitromethane with an activation energy of 40 kcal/mole and a γ of 0.68 was found to be stable at C-J detonation velocity. With a stable detonation, we can study how the reaction zone is formed by constant-velocity pistons that initially shock the unreacted nitromethane to less than the C-J pressure.

The pressures at various positions of the flow as a function of time are shown in Fig. 3 for a 0.21 cm/ μ sec constant-velocity piston. The calculations with a resolved

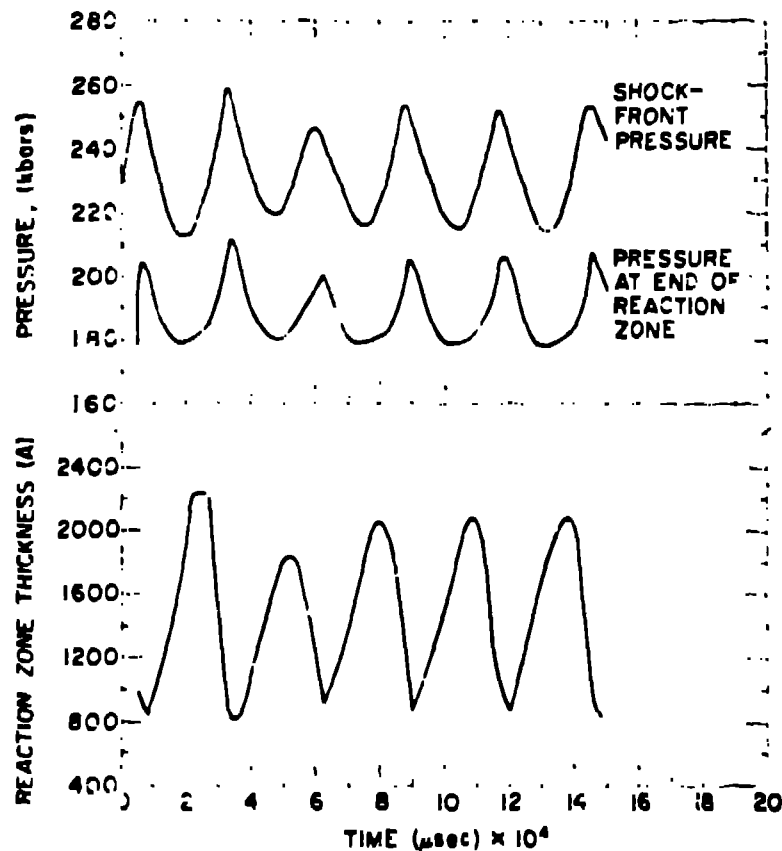


Fig. 2. The shock-front pressure, the pressure at the end of the reaction zone and the reaction zone thickness of a nitromethane reaction zone with a detonation velocity of 0.665 cm/sec, $\gamma = 0.68$, $P^* = 53.6$, $Z = 4 \times 10^5$, 100 A mesh.

reaction zone show details of the process of shock initiation of nitromethane. The basic features are identical to those of the flow computed with an unresolved reaction zone (3). The shocked nitromethane first completely decomposes at the piston and achieves a detonation with a peak pressure that builds up toward the C-J pressure of the high density shocked nitromethane. The detonation wave overtakes the shock wave and the pressure at the end of the reaction zone decays toward the piston pressure.

11. HETEROGENEOUS DETONATIONS

Heterogeneous explosives, such as PBX-9404 or Composition B, show a different behavior than homogeneous explosives when propagating along confining surfaces. A heterogeneous explosive can turn sharp corners and propagate outward, and depending upon its sensitivity, it may show either very little or much curvature when propagating along a metal surface. The mechanism of initiation for

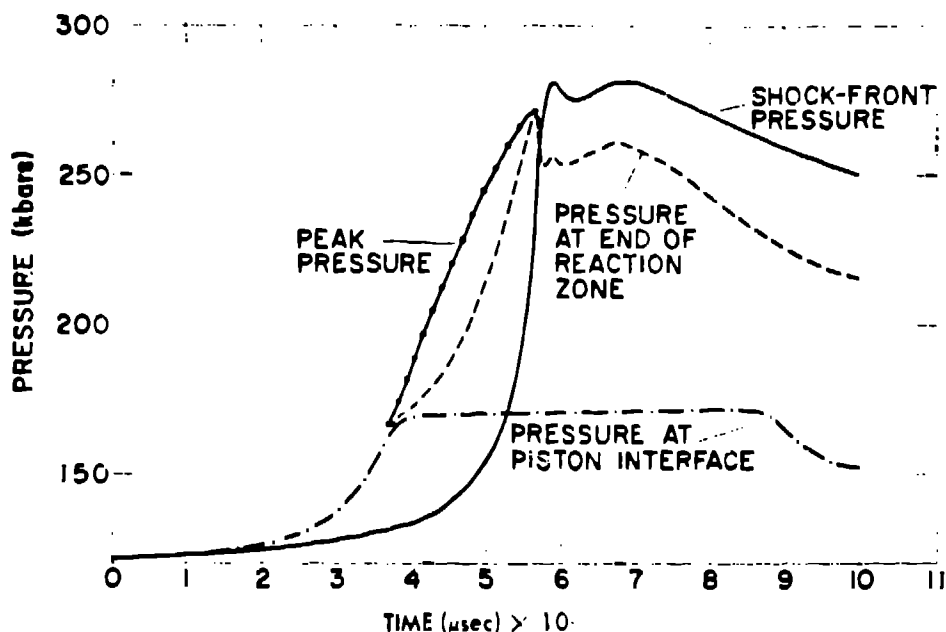


Fig. 3. The shock initiation of nitromethane by a 0.21 cm/ μ sec constant-velocity piston. $E^* = 40$, $Z = 1.27 \times 10^6$, $\gamma = 0.68$, 4000 A mesh; the reaction zone is resolved.

heterogeneous explosives is different than the Arrhenius kinetic model found adequate for homogeneous explosives. Heterogeneous explosives are initiated and may propagate by the process of shock interaction with density discontinuities such as voids. These interactions result in hot regions that decompose and give increasing pressures that cause more and hotter decomposing regions. Some heterogeneous explosives may require hot spots even for the propagation of the detonation wave.

We developed Forest Fire to model the bulk decomposition of a heterogeneous explosive. Forest Fire, described in Ref. 3, may be used to reproduce the explosive behavior in many one- and two-dimensional situations where data are available. Forest Fire gives the rate of explosive decomposition as a function of local pressure, or any other state variable, in the explosive.

The experiments of interest are those that enable direct solution of the time behavior of the shock-pressure wave as the shock builds to detonation. Such information forms a data line in space for the fluid flow equations. With some simple assumptions the flow equations can be solved in the neighborhood of the data line, and consequently, the reaction rate consistent with the time behavior of the shock-pressure wave can be solved.

Some experiments that give direct information about the shock-pressure front are

- A. Distance to detonation as a function of initial shock pressure

$$\ln(\text{run}) = \alpha_1 + \alpha_2 \ln(P - P_0) ,$$

where run = distance to detonation,

α_1 , α_2 , and P are constants, P_0 is usually 0, and P = pressure.

This relation is called the "Pop plot" and is shown in Fig. 4.

- B. Shock velocity as a function of particle velocity

$$U_s = C + S U_p ,$$

where U_s = shock velocity, U_p = particle velocity, and C and S are constants from fits to experimental data.

These relations, together with the shock jump relations, define the state space line for the shock front.

- C. If pressure as a function of time is reported at various mass points, these data can be used to estimate pressure gradients behind the shock and a time-pressure history at a single point.

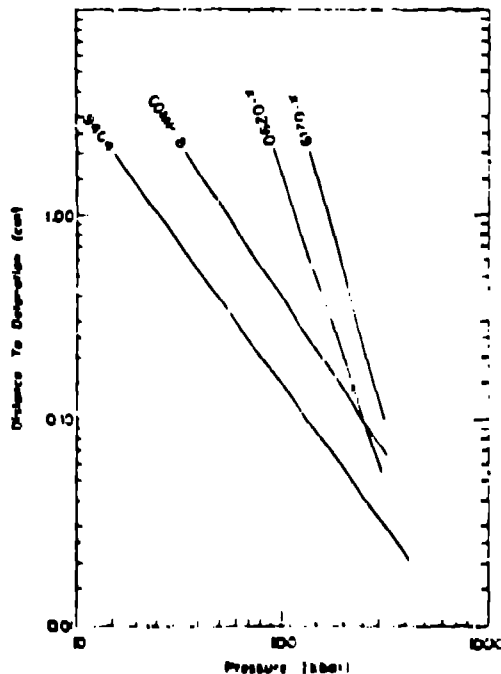


Fig. 4. Pop plots for X-0219, X-0290, Composition B, and PBX-9404.

The single-curve buildup principle (3) is the assumption that a reactive shock wave grows to detonation along a unique line in distance, time, and state space. Experiments have often shown this relation to be plausible to the accuracy of the experiments. Applying the single-curve buildup principle to Pop plots gives the interpretation that the Pop plots are direct descriptions of the shock front.

Fig. 5 shows the decomposition rate calculated, using the Forest Fire model, as a function of pressure for several explosives.

Dick (3) performed a radiographic study of a detonation wave proceeding up a block of a very insensitive TATB-based

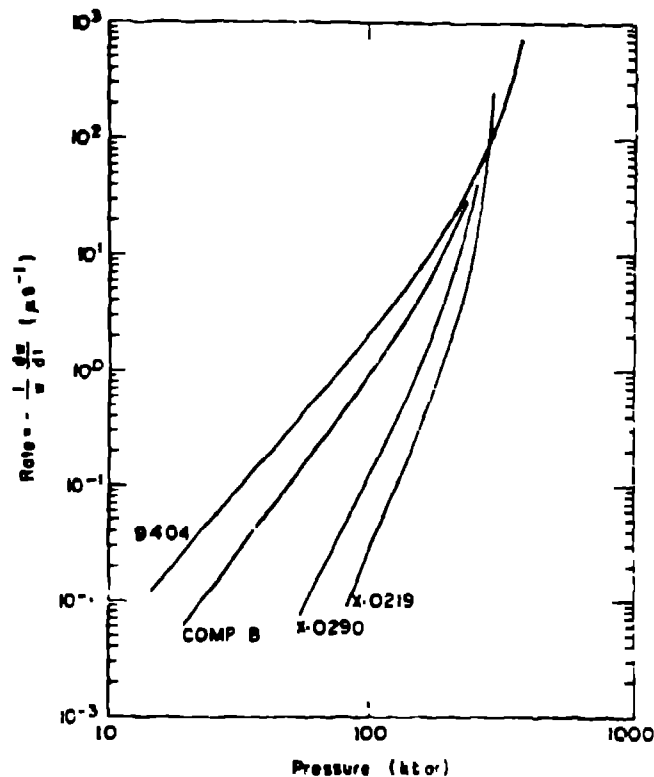


Fig. 5. Forest Fire rate vs pressure.

explosive, X-0219, and its failure to propagate completely around a corner. Dick's experimental profiles and the calculated profiles using the Forest Fire model are shown in Fig. 6. The amount of explosive that remains undecomposed after passage of the shock wave depends primarily upon the curvature of the detonation wave before it turns the corner. If the wave is sufficiently curved, the detonation proceeds like a diverging detonation wave and little or no explosive remains undecomposed. If the wave is flat, or nearly so, when it arrives at the corner, then much more partially decomposed explosive will remain after shock passage.

Calculations were performed using the Forest Fire burn in 2DL (3) for 0.7- and 1.3-cm-radius cylinders of X-0219 confined by Plexiglas and for half-thickness slabs of 1.3 and 2.6 cm. The thinner charges developed greater curvature and the 0.7-cm-radius cylinder failed to propagate. Calculations were also performed using the Forest Fire burn in the 2DE code for 0.65- and 1.3-cm-radius cylinders of X-0219 confined by air. The 0.65-cm-radius cylinder failed to propagate as shown in Fig. 7. The experimentally determined failure radius is 0.75 cm. Similar calculations were performed for PBX-9404, Composition B, and X-0290. Results are compared with experimental failure radius in Table III. These results suggest that the dominant feature of failure in heterogeneous explosives is the same hot spot decomposition reaction that determines the shock initiation behavior.

III. CONCLUSIONS

The time-dependent behavior of the flow in the reaction zones of ideal gases, nitromethane, and liquid TNT have been investigated using one- and two-dimensional Lagrangian and Eulerian numerical hydrodynamics.

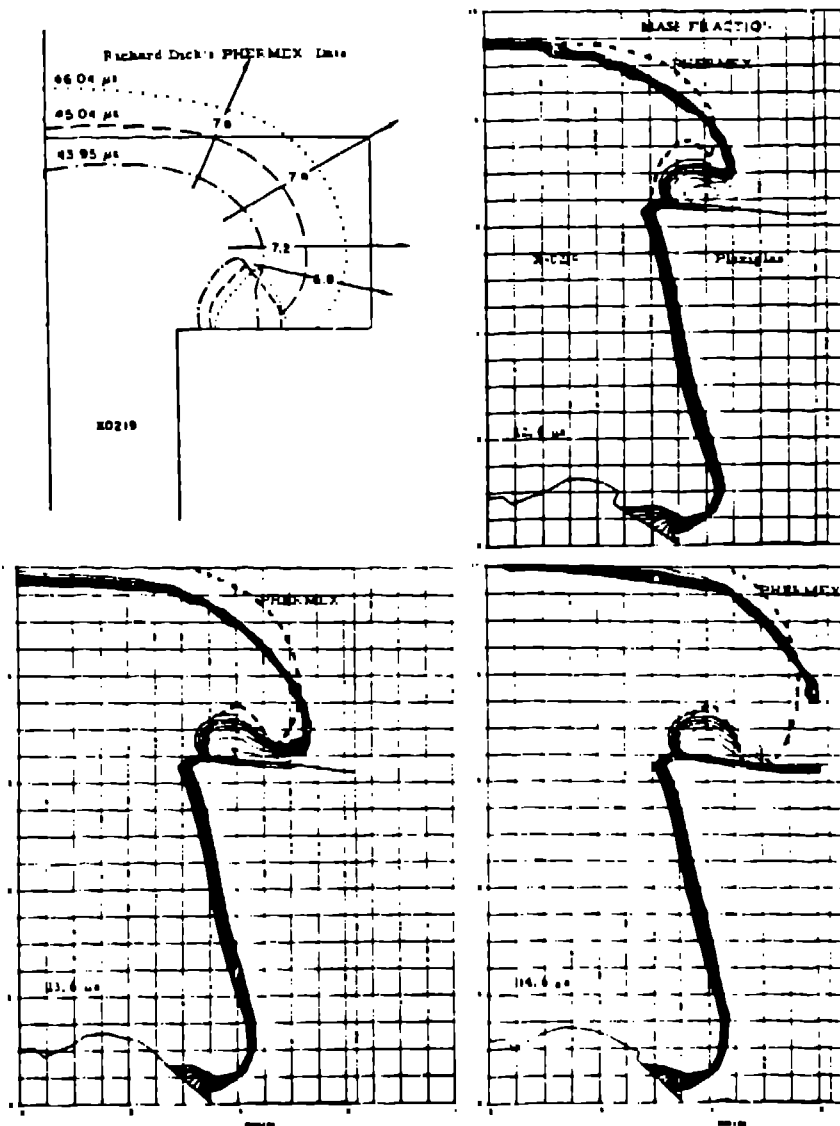


Fig. 6. Radiographic and calculated 2DL profiles of a detonation wave propagating around a corner of X-0219. The corner was filled with air in the experiment and with Plexiglas in the calculations.

In those cases for which Erpenbeck's analysis showed the steady-state solution of ideal gas detonations to be unstable to infinitesimal longitudinal and transverse perturbations, flows started in a configuration approximating the steady-state solutions exhibited a bounded instability; in those cases for which Erpenbeck's analysis showed the steady-state solution to be stable, perturbations were found to decay. The two-dimensional ideal gas instability has not been numerically studied for a sufficient time to determine its final amplitude and period.

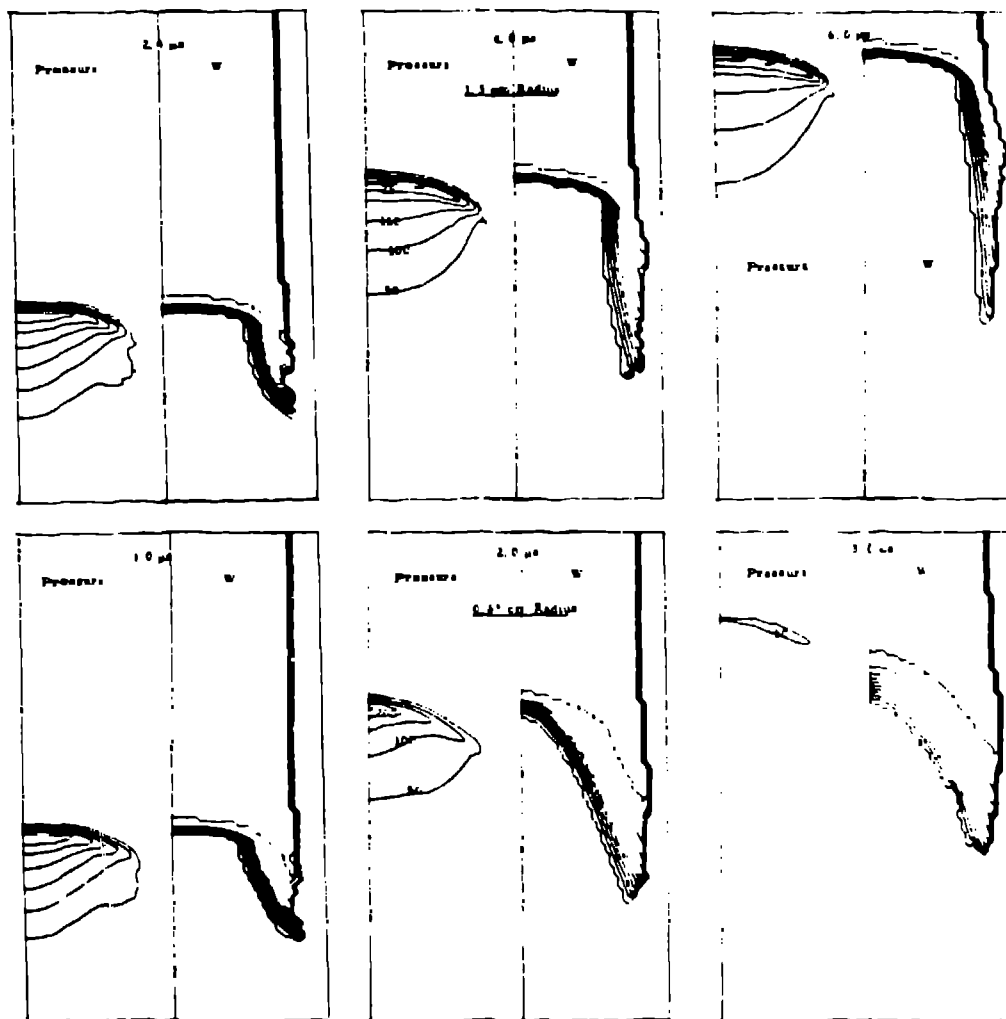


Fig. 7. Pressure and mass fraction profiles for a 0.65- and a 1.3-cm-radius cylinder of X-0219 calculated using the 2DE code with the Forest Fire burn model.

The nitromethane and liquid TNT detonations exhibited the same stability to transverse and longitudinal perturbations as to longitudinal perturbations alone.

The details of the structure of the reaction zone are strongly dependent on the properties of the equation of state for the mixture of undecomposed explosive and detonation products. The amount of overdrive necessary to obtain a steady detonation and the period and magnitude of the oscillation of an unstable detonation are strongly dependent on the activation energy and are independent of the frequency factor.

TABLE III
Experimental and calculated failure radii

| Explosive | Experimental failure radius (cm) | Calculated results |
|-----------|----------------------------------|-------------------------------|
| X-0219 | 0.75 ± 0.05 | 1.3 propagated 0.7 failed |
| X-0290 | 0.45 ± 0.05 | 0.5 propagated 0.3 failed |
| Comp B | 0.214 ± 0.03 | 0.3 propagated 0.2 failed |
| PBX-9404 | 0.06 ± 0.01 | 0.1 propagated 0.05 failed |

For significant ranges of values for the activation energy and for the amount of overdrive, the time dependent, one- or two-dimensional model of detonation exhibits unstable pulsating detonation. If the explosive is sufficiently overdriven the detonation becomes stable. Stable overdriven detonations are formed by a constant velocity or stepped-velocity piston only after the detonation travels many

reaction zone lengths. If the velocity of the piston is abruptly decreased to a sufficiently low value, sufficiently soon after its initial motion, the detonation fails. A constant-velocity piston results in initiation, from shock heating of the bulk explosive, of an overdriven detonation that slowly decays just as in the shock initiation of homogeneous explosives.

Since the details of the chemical kinetics are crucial to the stability behavior, one probably cannot expect real detonations to closely reproduce the time-dependent behavior of the theoretical model with simple Arrhenius kinetics.

Real detonations of condensed explosives can exhibit unstable periodic behavior. The steady-state Chapman-Jouguet theory of the detonation process will not properly describe the behavior of real detonations that exhibit such unstable periodic behavior.

Detonation initiation and propagation of heterogeneous explosives cannot be described adequately using Arrhenius kinetics. The Forest Fire model can describe the decomposition that occurs from hot spots formed by shock interactions with density discontinuities in heterogeneous explosives and can also describe the passage of heterogeneous detonation waves around corners and along surfaces. Failure or propagation of a heterogeneous detonation wave depends upon the interrelated effects of the wave curvature and the shock sensitivity of the explosive. Some of the basic differences have been described between homogeneous and heterogeneous explosive propagation and failure. The differences are a result of the different nature of the fast reactions in homogeneous and heterogeneous explosives.

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