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University of California

**A Study of the One-dimensional,
Time-dependent Reaction Zone
of Nitromethane and Liquid TNT**

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**A Study of the One-dimensional,
Time-dependent Reaction Zone
of Nitromethane and Liquid TNT**

by

Charles L. Mader

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ABSTRACT

The time-dependent reaction zones of nitromethane and liquid TNT have been investigated using one-dimensional numerical hydrodynamics with Arrhenius chemical reaction and accurate equations of state. The formation of an overdriven stable detonation in nitromethane by various types of pistons has been investigated. A piston whose velocity decreases abruptly to a lower value produces an initially short reaction zone which lengthens and decreases in pressure, when the second and lower velocity occurs, until the rate of release of chemical energy exceeds that necessary to sustain the wave. If the stepped-velocity piston has a sufficiently small lower step, failure of the detonation occurs in the time and space scale of interest. If the detonation is not sufficiently overdriven, the solution of the equations is nonsteady and periodic, oscillating about the steady-state (time-independent) solution.

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I. INTRODUCTION

The hydrodynamic stability of one-dimensional detonations in an ideal gas of constant heat capacity undergoing an exothermic, irreversible, unimolecular reaction that obeys an Arrhenius rate law has been studied by Erpenbeck^{1,2}.

Fickett and Wood³ have used the method of characteristics to obtain numerical solutions of the hydrodynamic equations for Erpenbeck's model. They treated shocks as jump discontinuities. In those cases for which Erpenbeck's linearized analysis has shown the steady-state (time-independent) solution to be unstable to infinitesimal longitudinal perturbations, flows started in a configuration approximating the steady-state solution 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. These results prompted us to undertake a similar numerical study of nitromethane and liquid TNT. An understanding of the reaction zone would also be a necessary first step before we could numerically reproduce such phenomena as detonation failure caused by side rarefactions traveling inside the reaction zone.

II. COMPUTATIONAL METHOD

The objective of the computation was to obtain a complete solution to the Navier-Stokes equations of fluid dynamics for a reactive material, using the best available equations of state. The partial differential equations were written in Lagrangian finite-difference form appropriate to plane, one-dimensional motion. Sufficient viscosity was used to smear the shocks over at least three finite-difference meshes if the mesh was too large for realistic values for the viscosity. Use of the Navier-Stokes equation in the numerical treatment of the detonations, avoiding the difficulty of treating a shock discontinuity, gave results for the ideal gas model essentially identical with results obtained using the

Fickett and Wood method of characteristics with sharp shocks and no viscosity. The results do not depend strongly upon viscosity.

Up to 2500 mesh points were used in the calculations. The number of mesh points in a reaction zone depends upon the initial size of the mesh, the thickness of the reaction zone, and the amount the mesh is compressed. For example, a 620-A reaction zone in nitromethane has 120 mesh points whose initial thickness was 10 A.

Appendix A contains a more detailed description of the hydrodynamic equations.

The equation of state used to describe the fluid is the HCM equation of state for condensed explosive, detonation products, and any mixture of condensed explosive and detonation products. The details of the structure of the reaction zone are strongly dependent upon 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 not as dependent upon the equation of state details but are very dependent on the activation energy.

The equation of state is described in more detail in Appendix B.

III. THE NITROMETHANE REACTION ZONE

A. Piston Velocity of 0.3 cm/ μ sec

The formation of an overdriven detonation in nitromethane by a 0.3-cm/ μ sec constant-velocity piston was computed using a 5-A mesh and realistic values for the viscosity. The shock thickness was 15 A, the steady-state spike pressure or shock-front pressure was 272 kbar, the pressure at the end of the reaction zone was 242 kbar, the detonation velocity was 0.7130 cm/ μ sec, and the reaction zone was 620-A thick (defined as the distance from mass fraction of 0.999 to 0.01). These values were determined using the steady-state piston described in Section D.

The formation of the reaction zone in the pressure-volume plane is shown in Figure 1, and in the pressure-distance plane in Figure 2. The steady-state reaction zone profiles of pressure, temperature, and mass fraction are shown in Figure 3. The shock-front pressure and reaction zone thickness are shown as a function of time in Figure 4. The formation of an approximately stable reaction zone profile requires many (~ 10) reaction zone lengths.

A steady reaction zone is achieved when the rate of release of chemical energy at all points in the zone is just sufficient to sustain the wave.

The constant velocity piston initially produces a long reaction zone. As a result of the release of chemical energy, the pressure increases and the reaction zone length decreases until a more steady profile is obtained. The pressure overshoots the stable pressure profile in regions of the reaction zone during the process of forming a steady profile.

B. Stepped-Velocity Pistons

The formation of an overdriven detonation by a piston whose initial velocity of 0.4 cm/ μ sec is decreased to 0.3 cm/ μ sec when complete decomposition occurs at the piston/nitromethane interface was computed using a 5-A mesh and realistic values of the viscosity. The initial reaction zone was about 100-A thick, and the shock-front pressure was 360 kbar. The steady-state reaction zone thickness for a 0.3-cm/ μ sec piston is 620 A, and the shock-front pressure is 272 kbar as described in Section A. The formation of the reaction zone in the pressure-volume plane is shown in Figure 5. The shock-front pressure and reaction zone thickness are shown as a function of time in Figure 4 for the 0.3-cm/ μ sec, constant-velocity piston, and for the 0.4/0.3-cm/ μ sec, stepped-velocity piston. The 0.4/0.3 stepped-velocity piston results in a reaction zone thickness of 100 A at 3×10^{-6} μ sec which increases to a maximum of 920 A at 4.25×10^{-5} μ sec and then decreases to 610 A

by 7×10^{-5} μsec . The 0.4/0.3 stepped-velocity piston produces an initial shock-front pressure of 365 kbar, which decreases to 248 kbar by 1.5×10^{-5} μsec and remains almost constant for the next 10^{-5} μsec ; during this time the reaction zone thickness increases from 300 to 600 Å. Once the reaction zone thickness is larger than the steady-state thickness, the shock-front pressure begins to increase toward the steady-state shock-front pressure.

Figure 6 shows the shock-front pressure and reaction zone thickness for the 0.4/0.3- and 0.4/0.05-cm/ μsec pistons. The 0.4/0.05-cm/ μsec piston produces a detonation that fails to propagate in the time scale of interest.

A decreasing-step piston produces an initially short reaction zone that cannot support the overdriven wave when the second, lower, step occurs. The reaction zone lengthens, and the pressure decreases until the release of chemical energy exceeds that necessary to sustain the wave. If the piston has a small enough lower step, the release of chemical energy cannot exceed that necessary to sustain the wave in the time scale of interest, and failure occurs. If the piston has a large enough lower step, the release of chemical energy occurs at a greater rate than that necessary to sustain the wave, the shock-wave pressure increases, and the reaction zone length decreases until a more steady profile is obtained. Oscillations of decreasing magnitude about the steady-state solution occur for periods of many reaction zone lengths.

C. Sawtooth Pistons

The formation of an overdriven steady detonation by a "sawtooth" piston whose velocity decreases to a minimum constant value was computed using a 10-Å mesh.

If one had an ideally programmed piston, a steady-state reaction zone could be achieved as soon as the end of the reaction zone was reached at the piston. However, a piston that is programmed either too slow or too fast produces a stable reaction zone in about the same

distance or time as the more violent step pistons, even though the deviations of the reaction zone length and pressure profile from the steady-state values may be considerably smaller. This is a result of the process of attempting to balance the release of chemical energy at all points in the zone so that it is just sufficient to sustain the wave. The shock-front pressure and reaction zone thickness as a function of time for various sawtooth pistons are shown in Figure 7. The sawtooth-piston particle velocity decreases with increasing time at the rate of $A\delta t$, where A is a constant and δt is the product of the cycle number and the time increment in μsec . The time increment was set equal to $1/5$ the mesh size in cm. The $2.5 \times 10^3 \delta t$ piston is closest to the ideal or steady-state piston. The shock-front pressure and reaction zone thickness are within 1% of the steady-state values after $12 \times 10^{-5} \mu\text{sec}$. The velocity of the $4 \times 10^3 \delta t$ piston decreases too fast, and the shock pressure cannot be maintained from behind, so it drops below the steady-state value, producing a reaction zone that is initially thicker than the steady-state value. The velocity of the $1.5 \times 10^3 \delta t$ piston does not decrease fast enough, so the shock pressure increases and produces a reaction zone that is initially thinner than the steady-state value.

D. The Steady-State Piston

To study the stability of detonations, we wish to use a piston that is as close to the steady-state piston as possible so that the deviations from the steady state will be as small as the mesh used will permit. To accomplish this for any desired detonation velocity, we initially set the piston velocity equal to that particle velocity of the undecomposed condensed explosive that corresponds to the detonation (shock) velocity. The piston compresses and heats the explosive next to it, and a certain amount of reaction occurs. The intersection of the Rayleigh line with the corresponding Hugoniot is used to determine the proper piston velocity for the next time step. The piston velocity

computed in this manner approximates the steady-state piston. A detailed description of the method used to compute the steady-state piston is presented in Appendix A.

The approximate steady-state profiles computed in the above manner for nitromethane at the BKW C-J state are shown in Figure 8 for a Grüneisen γ of 1.7 and 0.68. The partially reacted Hugoniot is 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 the γ of 0.68 used previously to illustrate the magnitude of this effect.

For a γ of 0.68 the reaction zone thickness is 2460 Å, while for a γ of 1.70 the thickness is 1620 Å. The temperature profile for a γ of 0.68 has a maximum at about 900 Å, while the highest temperature for a γ of 1.70 is at the end of the reaction zone.

The shock front pressure as a function of time for nitromethane with a γ of 0.68 and a mesh size of 100 Å is shown in Figure 9 for various amounts of overdrive. For a detonation velocity of 0.6850 cm/ μ sec, the initial perturbation introduced by the large mesh quickly decays. For a detonation velocity of 0.6650 cm/ μ sec, the initial perturbation grows and reaches a steady amplitude by the fourth cycle, as shown in Figure 10. Using a smaller mesh size reduces the magnitude of the initial perturbation for a detonation velocity of 0.6850 cm/ μ sec and reduces the deviation from the steady-state solution thereafter, as shown in Figure 11. The magnitude of the initial perturbation is proportional to the mesh size. Using a 25-Å mesh size for a detonation velocity of 0.6650 cm/ μ sec reduces the magnitude of the initial perturbation, and by the second cycle it has grown to an amplitude that closely resembles the steady amplitude reached by the fourth cycle for the 100-Å case shown in Figure 10.

The shock-front pressure as a function of time for nitromethane with a γ of 1.7 and a mesh size of 100 Å is shown in Figure 12. As for the $\gamma = 0.68$ case, the 0.6850-cm/ μ sec velocity is stable and the

0.6750-cm/ μ sec case is unstable. The pressure at the end of the reaction zone is not perturbed as much on the first cycle for the $\gamma = 1.70$ case, where the temperature maximum is at the end of the reaction zone, as it is for the $\gamma = 0.68$ case, where the temperature maximum is inside the reaction zone.

The period from peak to peak for the C-J cases is about 1×10^{-3} μ sec, as estimated from the overdriven cases.

The amount of overdrive necessary to stabilize the nitromethane detonation decreases with decreasing activation energy and is independent of the frequency factor. If one assumes an activation energy of 40 kcal/mole instead of the "experimental" value of 53.6, the nitromethane detonation for a γ of 0.68 is stable at the C-J velocity of 0.6460 cm/ μ sec. The nitromethane detonation for a γ of 1.7 and an activation energy of 40 kcal/mole is unstable at 0.6550 cm/ μ sec and stable at 0.6650 cm/ μ sec.

IV. THE LIQUID TNT REACTION ZONE

As described in the author's studies^{4,5} of the shock initiation of liquid TNT, it is necessary to adjust the heat capacity or the reaction kinetics to obtain the experimental induction time for initiation by a 125-kbar shock. In this study we chose to adjust the frequency factor, primarily because the pressure-distance profiles obtained by adjusting the heat capacity are almost square and result in very sharp gradients that are difficult to resolve numerically.

The approximate steady-state profiles for liquid TNT at the BKW C-J state are shown in Figure 13 for a γ of 1.66 and a γ of 1.0. The reaction zone thickness is about 1×10^{-3} cm for both γ 's. The temperature profile for $\gamma = 1.0$ has a maximum at about 2.5×10^{-4} cm, while the maximum temperature for γ of 1.66 is at the end of the reaction zone.

The shock-front pressure and the pressure at the end of the reaction zone as a function of time for the steady-state piston arc shown in Figure 14 for $\gamma = 1.0$ and in Figure 15 for $\gamma = 1.66$. In both cases the 0.6600-cm/ μ sec case is stable and the 0.6500-cm/ μ sec case is unstable.

For the C-J cases, the period from peak to peak is about 6×10^{-2} μsec .

The amount of overdrive necessary to stabilize the liquid TNT detonation decreases with decreasing activation energy. If one assumes an activation energy of 30 kcal/mole instead of the "experimental" value of 41.1 kcal/mole, the liquid TNT detonation for a γ of 1.66 is stable at the C-J velocity of 0.6406 cm/ μsec .

V. THE IDEAL GAS

As described in the Introduction, Erpenbeck's^{1,2} linearized analysis of the detonation equations for ideal gases predicts that certain cases will be unstable to infinitesimal longitudinal perturbations. Fickett and Wood³ have used the method of characteristics with sharp shocks to describe the time dependent flow and found agreement with the results of Erpenbeck's analysis.

Our use of the Navier-Stokes equation could yield results strongly dependent on viscosity. We have studied the formation of unstable, periodic reaction zones over an order of magnitude in mesh size and viscosity and concluded that the stability results are essentially independent of viscosity. To further check this conclusion, we performed calculations for the Erpenbeck and Fickett ideal gas detonation model. As shown in Appendix C and Figure 16, both stable and unstable detonations resulted. The results are in excellent agreement with the nonviscous linearized analysis of Erpenbeck and the sharp-shock solutions of Fickett and Wood. For example, for the unstable case of $E^* = 50$, $\gamma = 1.2$, $Q = 50$, and $f = 1.6$, with sufficient viscosity to smear the shock front over 10 cells, we obtained the same period and final amplitude as Fickett and Wood had obtained with no viscosity.

We conclude that our numerical solutions of the nonlinear equations of detonation are satisfactory and that the results are not strongly dependent upon viscosity.

VI. EXPERIMENTAL EVIDENCE

We have described the reaction zones one obtains by solving the one-dimensional hydrodynamic equations with Arrhenius kinetics and as realistic equations of state as we have available. The partially reacted Hugoniot, and therefore the steady-state profiles, are very sensitive to the parameters and to the details of the equation of state used for the mixture of undecomposed explosive and detonation products. The amount of overdrive necessary to stabilize a detonation decreases with decreasing activation energy. The space and time scale is so small that the approximation of treating a discrete particle field as a continuum introduces large uncertainties into experimental values used in the equation of state and kinetics.

It is impossible to know how closely these idealized one-dimensional reaction zones resemble real three-dimensional reaction zones without a detailed experimental description for comparison. Unfortunately, the time and space scale of interest is not readily accessible experimentally, and only a very limited amount of experimental evidence is available. We shall describe and attempt to interpret the experimental evidence.

The reaction zone conductivity measurements of Hayes⁶ are the most extensive reaction zone evidence available; however, the interpretation of the results is not obvious. Since the carbon content correlates well with the second conductivity peak, it is reasonable to suppose that this peak is a result of carbon precipitation and that the first peak is the end of the reaction zone. If the experimental data are interpreted in such a manner, the reaction zone thickness of nitromethane is less than 1×10^{-4} cm, that of liquid TNT is 1×10^{-3} cm, and that of Composition B (60/40 RDX/TNT) is 1×10^{-2} cm.

Craig, from his free-surface velocity measurements with very thin metal plates, estimates that the reaction zone thickness of liquid TNT is about 1×10^{-2} cm, that of Composition B is about 1.4×10^{-2} cm, and that of nitromethane is less than 2×10^{-3} cm^{7,8}. It is not at all obvious why the two techniques give similar thicknesses for Composition B

and quite different thicknesses for liquid TNT.

The failure of the steady-state C-J detonation theory for many explosives has been demonstrated by Davis, Craig, and Ramsay⁹, and the existence of an unstable periodic detonation is a possible explanation for the failure of the theory. The very slow buildup to C-J pressure in slab geometry and the failure of scaling as observed by Craig⁷ could result, at least in part, from a periodic detonation wave. It is conceivable that the dark waves observed in nitromethane may be a result of a periodic detonation wave. Any other explanation of the above observations that permits one to have detonations occurring off the Rayleigh line appears equally valid at the present state of understanding.

One may conclude that, while the experimental evidence does not conflict with the results of our study of the idealized one-dimensional reaction zone, neither does it support it. We must await more conclusive experimental evidence and in the meantime extend the theoretical investigations to two-dimensional reaction zones.

VII. CONCLUSIONS

The time-dependent reaction zones of nitromethane and liquid TNT have been investigated using one-dimensional, numerical, reactive, viscous, hydrodynamic equations with accurate equations of state.

The time-dependent, one-dimensional model of detonation for nitromethane and liquid TNT exhibits unstable pulsating detonation until the explosives are sufficiently overdriven, and then the detonations become stable. The formation of a stable overdriven detonation by a constant-velocity or stepped-velocity piston requires that the detonation travel many reaction zone lengths. For sufficiently small lower-step pistons, failure of the detonation occurs in the time scale of interest. A constant-velocity piston results in initiation from mean shock heating of an overdriven detonation that slowly decays just as in the shock initiation of homogeneous explosives. The amount of overdrive necessary to obtain a stable detonation depends primarily upon the activation energy.

APPENDIX A

THE HYDRODYNAMIC EQUATIONS

The Lagrangian conservation equations in one dimension for slabs, cylinders, and spheres are:

$$\frac{\partial U}{\partial t} = -R^{\alpha-1} \frac{\partial P}{\partial M} \quad \text{Conservation of momentum}$$

$$V = R^{\alpha-1} \frac{\partial R}{\partial M} \quad \text{Conservation of mass}$$

$$\frac{\partial E}{\partial t} = \frac{-\partial P U R^{\alpha-1}}{\partial M} \quad \text{Conservation of energy}$$

where $E = I + 0.5U^2$; and

$$\frac{\partial R}{\partial t} = U$$

$$dM = \rho_0 r^{\alpha-1} dr = \rho R^{\alpha-1} dR$$

where dM is element of mass per unit of solid angle ($\alpha = 2$ or 3) or of surface ($\alpha = 1$). Here, P is the sum of the viscous pressure and the equation of state pressure. The nomenclature is given at the end of this Appendix.

The Arrhenius rate law is

$$\frac{\partial W}{\partial t} = + ZW e^{-E^*/R_g T} .$$

The hydrodynamic equations were solved using the SIN difference equations described in references 5 and 10.

The difference form of the viscosity equation

$$q = (-4/3)(\mu)(\rho) \frac{\partial U}{\partial M}$$

is

$$q_j^{n+1} = 1.3333 \frac{\mu}{v_j^{n+1}} \frac{\left(u_{j-1/2}^{n+1/2} - u_{j+1/2}^{n+1/2} \right)}{M_j} .$$

μ has the experimental value of 20 millipoises or 2×10^{-8} mbar- μ sec and produces a shock thickness of approximately 15 Å for a nitromethane detonation.

The steady-state piston was computed by iteration for a given detonation velocity by using the amount of reaction that has occurred in a cell near the piston to determine the proper particle velocity of the piston as outlined below.

1. Given a W , assume a V .
2. Calculate I from $I - I_0 = 0.5 (\rho_0)^2 (D)^2 (V_0 - V)^2$.
3. With V , I , and W , compute P from HQM equation of state.
4. Find P_r from $P_r = (\rho_0)^2 (D)^2 (V_0 - V)$, the Rayleigh Line.
5. Iterate on V until $P_r - P$ is less than 1×10^{-5} .
6. Calculate $U = \sqrt{(P - P_0) (V_0 - V)}$ and assign it to the piston velocity.
7. Advance the time step, permitting reaction. With the new W find the new piston velocity starting with step 1.

This method of computing the steady-state piston was first used by W. Fickett³.

NOMENCLATURE

D	detonation velocity
E	total energy in mb-cc/gm
E*	activation energy
I	internal energy in mb-cc/gm
j	net point of the Lagrangian net
M	mass
n	time cycle
P	pressure in megabars
q	viscous pressure
R	Eulerian radius
r	Lagrangian radius
R _g	gas constant
T	temperature in °K
t	time
U	particle velocity in cm/μsec
V	specific volume in cc/gm
W	mass fraction of undecomposed explosive
Z	frequency factor
α	= 1 for slabs; = 2 for cylinders; = 3 for spheres
ρ	= 1/V

Subscript

o	initial state
---	---------------

APPENDIX B

THE EQUATION OF STATE

The Fickett and Wood¹¹ beta equation of state was chosen as the form for the equation of state of the detonation products off the C-J isentrope. The pressure, volume, temperature, and energy values along the C-J isentrope were computed using the BKW equation of state^{12,13,14} as recently calibrated by Mader¹⁵. The Grüneisen equation of state was chosen as the equation of state of the undetonated explosive off the experimental Hugoniot. Pressures and volumes on the Hugoniot are available from experimental data. Temperatures on the Hugoniot were calculated using the technique of Walsh and Christian¹⁶. The equation of state for mixtures of condensed explosive and detonation products was computed assuming pressure and temperature equilibrium.

THE HOM EQUATION OF STATE

Knowing I, V, W calculate P, T

1. Condensed component ($W = 1$, then $I = I_s$, $V = V_s$)

For volumes smaller than V_o the experimental Hugoniot data are expressed as a linear fit of the shock and particle velocities. The temperatures are computed using the technique of Walsh and Christian^{10,16}.

$$(a)^{(1)} \quad U_s = C + S U_p$$

$$P_H = \frac{C^2 (V_o - V_s)}{[V_o - S(V_o - V_s)]^2}$$

$$(b) \quad \ln T_H = F_s + G_s \ln V_s + H_s (\ln V_s)^2 + I_s (\ln V_s)^3 + J_s (\ln V_s)^4$$

$$(c) \quad I_H = \frac{1}{2} P_H (V_o - V_s)$$

(1) Designation of equations is that of reference 10.

$$(d) \quad P_s = \frac{\gamma_s}{V_s} (I_s - I_H) + P_H \quad \text{where} \quad \gamma_s = V \left(\frac{\partial P}{\partial I} \right)_V$$

$$(e) \quad T_s = T_H + \frac{(I_s - I_H) (23,890)}{C_V}$$

2. Gas component (detonation products, for example) ($W = 0$, then $I = I_g$, $V = V_g$)

The pressure, volume, temperature, and energy values of the detonation products along the C-J isentrope are computed using the BKW equation of state^{14,15} and are fitted by the method of least squares to equations (g) through (i).

$$(g) \quad \ln P_i = A + B \ln V_g + C (\ln V_g)^2 + D (\ln V_g)^3 + E (\ln V_g)^4$$

$$(h) \quad \ln I_i = K + L \ln P_i + M (\ln P_i)^2 + N (\ln P_i)^3 + O (\ln P_i)^4$$

$I_i = I_i - Z$ (where Z is a constant used to change the standard state so as to be consistent with the condensed explosive standard state)

$$(i) \quad \ln T_i = Q + R \ln V_g + S (\ln V_g)^2 + T (\ln V_g)^3 + U (\ln V_g)^4$$

$$(j) \quad -\frac{1}{\beta} = R + 2S \ln V_g + 3T (\ln V_g)^2 + 4U (\ln V_g)^3$$

$$(k) \quad P_g = \left(\frac{1}{\beta V_i} \right) (I_g - I_i) + P_i \quad \text{where} \quad \beta = \frac{1}{V} \left(\frac{\partial I}{\partial P} \right)_V$$

$$(l) \quad T_g = T_i + \frac{(I_g - I_i) (23,890)}{C_V'}$$

3. Mixture of condensed explosive and detonation products

$$(n) \quad V = W V_s + (1 - W) V_g$$

$$(o) \quad I = W I_s + (1 - W) I_g$$

$$(p) \quad P = P_g = P_s$$

$$(q) \quad T = T_g = T_s$$

The equation of state and rate parameters for nitromethane and liquid TNT are given in Table I and in Figures 17 through 24.

THE NOMENCLATURE

C, S coefficients to a linear fit of U_s and U_p
 C_V heat capacity of condensed component in cal/gm/deg
 C_V' heat capacity of gaseous component in cal/gm/deg
 I total internal energy in mb-cc/gm
 P pressure in megabars
 T temperature in °K
 U_p particle velocity
 U_s shock velocity
 V total volume in cc/gm
 V_0 initial volume of condensed component in cc/gm
 W mass fraction of undecomposed explosive

Subscripts

g gaseous component
 H Hugoniot
 i isentrope
 s condensed component

TABLE I. EQUATION OF STATE AND RATE PARAMETERS

	<u>Nitromethane</u>		<u>Liquid TNT</u>	
<u>Condensed</u>				
C	+ 1.647	- 001	+ 2.0	- 001
S	+ 1.637	+ 000	+ 1.65	+ 000
T_s	+ 5.41170789261	+ 000	+ 4.23681503433	+ 000
G_s	- 2.72959322666	+ 000	- 8.59732701624	+ 000
H_s	- 3.21986013188	+ 000	- 1.60609786333	+ 001
I_s	- 3.90757138698	+ 000	- 1.37639638610	+ 001
J_s	+ 2.39028184133	+ 000	- 2.05713430231	+ 000
C_v	+ 4.14	- 001	+ 3.83	- 001
α	+ 3.0	- 004	+ 2.3153	- 004
V_o	+ 8.86524823	- 001	+ 6.91085	- 001
$\gamma_s(1)$	+ 0.6805	+ 000	+ 1.66	+ 000
$\gamma_s(2)$	+ 1.70	+ 000	+ 1.00	+ 000
T_o	+ 3.0	+ 002	+ 3.581	+ 002
<u>Gas</u>				
A	- 3.11585072896	+ 000	- 3.55947543414	+ 000
B	- 2.35968123302	+ 000	- 2.41906238253	+ 000
C	+ 2.10663268988	- 001	+ 2.13148095464	- 001
D	+ 3.80357006508	- 003	+ 5.42681375493	- 002
E	- 3.53454737231	- 003	- 1.68309952849	- 002
K	- 1.39936678316	+ 000	- 1.47916342276	+ 000
L	+ 4.79350272379	- 001	+ 5.14388037177	- 001

TABLE I - continued

M	+ 6.06707773429	- 002	+ 9.02702839234	- 002
N	+ 4.10672785525	- 003	+ 8.50384728393	- 003
O	+ 1.13326560531	- 004	+ 3.21650937265	- 004
Q	+ 7.79645302519	+ 000	+ 7.68605532614	+ 000
R	- 5.33007196907	- 001	- 4.70441838903	- 001
S	+ 7.09019736856	- 002	+ 9.90648501306	- 002
T	+ 2.06149976021	- 002	+ 5.24087425648	- 003
U	- 5.66139653675	- 003	- 4.02187883702	- 003
C _v	+ 5.56	- 001	+ 5.0	- 001
Z	+ 1.0	- 001	+ 1.0	- 001

Reaction

E*	+ 5.36	+ 004	+ 4.11	+ 004
Z	+ 4.0	+ 008	+ 2.0	+ 006

BKW CJ Parameters

P _{CJ}	+ 1.30	- 001	+ 1.57	- 001
D _{CJ}	+ 6.463	- 001	+ 6.406	- 001
T _{CJ}	+ 3.120	+ 003	+ 3.126	+ 003

APPENDIX C

THE IDEAL GAS MODEL

The equation of state for an ideal gas of constant heat capacity undergoing an exothermic, irreversible, unimolecular reaction is, given I, W, and V

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

$$T = \frac{[I + (1 - W) Q]}{C_v} .$$

The PIC form of the viscosity¹⁰ was used with $K = 1.0$.

The values of the parameters were

$$\gamma = 1.2$$

$$Q = 50$$

$$C_v = 5$$

$$R = 1$$

$$T_o, V_o, P_o = 1$$

$$I_o = 5$$

$$D_{CJ} = 6.809$$

$$U_o = 0$$

The results of the calculations are summarized below.

E*	50	50	10	10
Z ⁽¹⁾	206	82.5	207	3
f	1.6	2.0	1.6	1.0
Δx ⁽²⁾	0.35	0.385	0.35	0.272
Δt	0.0035	0.00385	0.0035	0.00272
D	8.613	9.63	8.613	6.809
Result	Unstable	Stable	Stable	Stable
P _{W=1}	67.5	84.0	67.5	42.2
P _{W=0}	55.0	72.0	55.0	21.5

(1) Z is adjusted so as to have $W = 0.5$ when the time is 1.0.

(2) Δx is adjusted so as to have about 25 space zones for $W = 1.0$ to $W = 0.5$.

NOMENCLATURE

C_v	heat capacity
D	detonation velocity
E^*	activation energy
f	degree of overdrive = $(D/D_{CJ})^2$
I	internal energy
P	pressure
Q	heat of explosion
R	gas constant
T	temperature
U	particle velocity
V	volume
W	mass fraction of undecomposed explosive
Z	frequency factor
Δx	mesh width
Δt	time increment
γ	C_p/C_v

Subscripts

o	initial state
p	constant pressure
v	constant volume

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Fig. 1. Pressure-volume profiles for formation of reaction zone of overdriven detonation in nitromethane with 0.3-cm/ μsec constant-velocity piston.

Fig. 2. Pressure-distance profiles of reaction zone of overdriven detonation in nitromethane with 0.3-cm/ μ sec constant-velocity piston.

Fig. 3. Steady-state reaction zone profiles of nitromethane overdriven with 0.3-cm/ μ sec constant-velocity piston and with a detonation velocity of 0.7130 cm/ μ sec.

Fig. 4. Shock-front pressure and reaction zone thickness as a function of time for nitromethane with a $0.4/0.3\text{-cm}/\mu\text{sec}$ stepped-velocity piston and a $0.3\text{-cm}/\mu\text{sec}$ constant-velocity piston.

Fig. 5. Pressure-volume profiles for formation of the reaction zone of an overdriven detonation in nitromethane with 0.4-cm/ μ sec piston velocity until complete decomposition occurs at the piston, at which point the piston velocity is set equal to 0.3 cm/ μ sec.

Fig. 6. Shock-front pressure and reaction zone thickness as a function of time for nitromethane with a 0.4/0.3-cm/ μsec stepped-velocity piston which forms a steady-state detonation and a 0.4/0.05-cm/ μsec stepped-velocity piston which forms a failing wave.

Fig. 7. Shock-front pressure and reaction zone thickness as a function of time for nitromethane with various sawtooth pistons that form steady-state detonations. U_p is piston particle velocity, and $\delta t = n(\Delta t)$ where Δt is time increment and n is cycle number.

Fig. 8. Approximate steady-state profiles for nitromethane at C-J detonation velocity of 0.6460 cm/ μ sec.

Fig. 9. Shock-front pressure vs time for various detonation velocities (shown in meters per second) using steady-state piston for nitromethane with $\gamma = 0.68$ and a 100-A mesh.

Fig. 10. Reaction zone of nitromethane using steady-state piston with a detonation velocity of $0.6650 \text{ cm}/\mu\text{sec}$, $\gamma = 0.68$, and 100-Å mesh.

Fig. 11. Effect of mesh size using steady-state piston for nitro-methane with $\gamma = 0.68$; $\mu = 4 \times 10^{-7}$ for 100-Å and 1×10^{-7} for 25-Å mesh.

Fig. 12. Shock-front pressure and pressure at end of reaction zone vs time for various detonation velocities (shown in meters per second) using steady-state piston for nitromethane with $\gamma = 1.7$ and a 100-A mesh.

Fig. 13. Approximate steady-state profiles for liquid TNT at C-J detonation velocity of $0.6406 \text{ cm}/\mu\text{sec}$.

Fig. 14. Shock-front pressure and pressure at end of reaction zone vs time for various detonation velocities (shown in meters per second) using steady-state piston for liquid TNT with $\gamma = 1.0$ and a 500C-A mesh.

Fig. 15. Shock-front pressure and pressure at end of reaction zone vs time for various detonation velocities (shown in meters per second) using steady-state piston for liquid TNT with $\gamma = 1.66$ and a 5000-A mesh.

Fig. 16. Shock-front pressure and pressure at end of reaction zone vs. time for various values of $f = D^2/D_{CJ}^2$ using steady-state piston for an ideal gas with $E^* = 50$, $\gamma = 1.2$, and $Q = 50$.

Fig. 17. Nitromethane Hugoniots and Rayleigh line.

Fig. 18. Nitromethane pressure-volume Hugoniot. Pressure is in mbars and volume in cc/gm.

Fig. 19. Nitromethane temperature-volume Hugoniot. Temperature is in °K and volume in cc/gm.

Fig. 20. Nitromethane pressure-particle velocity Hugoniot. Pressure is in mbars and volume in cc/gm.

Fig. 21. Liquid TNT Hugoniots and Rayleigh line.

Fig. 22. Liquid TNT pressure-volume Hugoniot. Pressure is in mbars and volume in cc/gm.

Fig. 23. Liquid TNT temperature-volume Hugoniot. Temperature is in °K and volume in cc/gm.

Fig. 24. Liquid TNT pressure-particle velocity Hugoniot. Pressure is in mbars and the volume in cc/gm.