The Ignition Temperature of Solid Explosives Exposed to a Fire

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THE IGNITION TEMPERATURE OF SOLID EXPLOSIVES
EXPOSED TO A FIRE

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INTRODUCTION

When a system containing solid explosive is engulfed in a fire it receives a heat flux that causes the temperature of the system to rise monotonically. The temperature rise can often be approximated by a linear rise for extended periods of time. When some portion of the explosive, usually near the surface, reaches its ignition temperature it will begin to burn. If the explosive is unconfined, or can breach its confinement at low pressure, it will burn, not explode. Typically the burn front will propagate through a slab or shell at speeds on the order of a centimeter a minute. If the explosive is confined, the gas resulting from its burning will generate pressures high enough to rupture the confinement, but the peak pressure will generally be only a fraction of the pressure from a true detonation.

When a system is not engulfed in the fire, but is close enough to be heated slowly by the fire, the behavior will be different. If the explosive is heated slowly it will have a nearly uniform temperature and ignition will occur inside the explosive. This almost always causes an explosion, even when the explosive as a whole is unconfined. The reason for this behavior is not well understood but slow heating of an explosive generally results in a more violent explosion than fast heating.

These two situations are recognized by fast and slow cookoff tests used with munitions. Many munitions pass the fast cookoff test with heating rates around 2 K/min. Slow cookoff tests with heating rates around 4 K/hr generally result in an explosion. (The equations in this paper assume absolute temperatures in Kelvins, equal to Celsius + 273.16.)

Mathematical models predicting the time to explosion are usually based on the assumption that the explosive has a uniform initial temperature and that the outer surface is suddenly raised to some temperature and held there. The earliest such models were those of Semenov\(^1\) and Frank-Kamenetskii\(^2\). Many numerical calculations use the same boundary conditions, as exemplified by the work of Zinn and Mader\(^3\). These models predict a critical temperature for explosion. Below the critical temperature heat loss exceeds the heat generated by chemical reactions everywhere in the explosive and no explosion occurs.

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Above the critical temperature heat generation exceeds heat loss *somewhere* in the explosive. The chemical heat generation increases roughly exponentially with temperature while heat loss by conduction increases only linearly with temperature. The result is a thermal runaway that is usually associated with ignition of the explosive.

This paper analyzes a different boundary condition, a linear temporal increase of the surface temperature. The results are similar to the constant boundary temperature except that at higher heating rates the ignition temperature is higher than the critical temperature, defined above. The only other relevant calculation that we could find for this boundary condition was the work of Boddington. He and his coworkers did an asymptotic analysis for a linearly increasing temperature on the boundary, assuming a single Arrhenius rate coefficient. This paper considers more realistic, multi-step, reaction schemes representing some real explosives. We used the multi-step reaction schemes of McGuire and Tarver for HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) and TATB (2,4,6-trinitro-1,3,5-benzentriamine). These schemes require numerical solutions. We also did calculations for a single Arrhenius rate coefficient, to compare with earlier work. The calculated ignition temperatures fit a relatively simple curve and a mathematical model explains features of the curve fit.

**BASIC THEORY OF THERMAL RUNAWAY**

The governing partial differential equation considers heat conduction and chemical generation of heat

\[ \rho C \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left( \lambda \frac{\partial T}{\partial x} \right) + \frac{dQ_{\text{chem}}}{dt} \]  

(1)

where \( r \) is the density, \( C \) the heat capacity per unit mass, \( \lambda \) the thermal conductivity of the explosive and \( \frac{dQ_{\text{chem}}}{dt} \) is the heat release rate due to the chemical reaction.

When the chemical heat release rate is negligible, solutions of the transient heat conduction problem can be obtained. The general solution for slab geometries is of the form \( \exp(-x^2/4\alpha t) \), where the thermal diffusivity, \( \alpha \) equals \( \lambda / \rho C \). The exact form of the solution is determined by the boundary conditions, but the temperature approaches steady state with a time constant no less than \( x^2/4\alpha \). Values of \( \alpha \) from Table I give time constants on the order of 100 seconds at a depth of 1 cm. The time constant is quadratic in \( x \) so the time constant will be on the order of 400 seconds at a depth of 2 cm and 10,000 seconds at a depth of 10 cm. The behavior of cylindrical or spherical explosive systems is qualitatively similar.

If we use Arrhenius kinetics for the chemical heat release term in Eq. 1 we get

\[ \rho C \frac{\partial T}{\partial t} = \lambda \gamma^2 T + \rho \Delta H, Z[A] e^{-T_o/T} \]  

(2)
where $\Delta H_r$ is the heat of reaction per unit mass, $[A]$ is the mass fraction of reactant and $\lambda$ is assumed to be independent of temperature. (I have used the activation temperature, $T_a$, in place of the traditional activation energy, $E_a$, equal to $RT_a$, to emphasize the dimensionless nature of the exponent.)

At low temperatures the chemical heat production rate is low so the system approaches a steady state where the left hand side of Eq. 2 vanishes and the conduction term cancels the chemical heat release everywhere in the explosive. At high temperatures the highly non-linear chemical heat release term completely overwhelms the conduction term. The rising temperature causes yet higher chemical heat release, resulting in thermal runaway. The critical temperature, $T_C$, is the highest boundary temperature for which a steady state can exist. Above this critical temperature the chemical heat release exceeds conduction somewhere in the explosive and $\partial T/\partial t$ becomes positive, increasing in magnitude as the temperature runs away.

If the surface temperature is just slightly above the critical temperature the explosive will have time to reach steady state and ignition will occur near the center of a symmetric system. If the surface temperature is several degrees above the critical temperature, the center will not reach steady state before thermal runaway occurs at some location between the center and the surface. As the surface temperature is raised, thermal runaway occurs progressively closer to the boundary. Examples are found in Zinn and Mader.2

Frank-Kamenetskii2 discusses the critical temperature at length. We give a brief derivation. Let the surface temperature be $T_s$, and $T = T_s + \delta T$, where $\delta T/T_s << 1$. Substituting this in the Eq. 2 and expanding the exponent in a series yields a partial differential equation in $\delta T$.

$$\rho C \frac{\partial (\delta T)}{\partial t} = \lambda \nabla^2 (\delta T) + \rho \Delta H_r Z[A] e^{-T_a/T_s} e^{T_a \delta T/T_s^2}$$

where typical values of $T_a/T_s$ are between 30 and 50. For values of $T_a \delta T/T_s^2 << 1$ this equation has steady state solutions where the time derivative vanishes. If $L$ is some characteristic thickness or radius of the piece of explosive we can make the steady state equation dimensionless by substituting $\xi = x/L$

$$\frac{\partial^2 (\delta T)}{\partial \xi^2} = W(T_s) e^{T_a \delta T/T_s^2}$$

where the dimensionless parameter

$$W(T_s) = (\rho \Delta H_r L^2 / \lambda) Z[A] e^{-T_a/T_s}$$

The left hand side of Eq. 4 is proportional to $\delta T$ and cannot have a magnitude more than a few times $\delta T$. The minimum value of the exponential on the right hand side is 1, so solutions of Eq. 4 exist only for sufficiently small values of $W(T_s)$. Frank-Kamenetskii2 has shown that for slab geometry there are no solutions of Eq. 4 for $W(T_s) > 0.88$. The
value of surface temperature, $T_s$, that yields this value of $W(T_s)$ is the critical temperature, $T_c$. If the explosive is a cylinder, the critical value of $W(T_s)$ is 2.0, and it is 3.32 for a sphere. Critical temperatures exist for more complex chemical reaction mechanisms, provided the reaction rate is a monotone increasing function of the temperature.

The critical temperature is useful for safety studies because the explosive will not ignite below that temperature. However, caution should be used with calculated critical temperatures because the chemistry of explosives is complex and there are instances where actual systems containing explosives have ignited well below the calculated ignition temperature. Therefore system tests are advisable. Critical temperature is of limited use for systems engulfed in a fire. The fire temperature is generally much higher than the critical temperature so the system will eventually reach ignition temperature. In that case we would like to know how long it will take to reach ignition.

**Numerical Solutions for Linearly Increasing Surface Temperature**

Numerical solutions of the one-dimensional version of Eq. 1 were done for a slab with temperature $T_s = T_0 + \beta t$ at the surface $x = 0$ and no heat flow out of the surface at $x = L$. Three reaction schemes were used: a single Arrhenius rate coefficient as in Eq. 2 and multi-step reaction sets for HMX and TATB developed by McGuire and Tarver. The chemical kinetic and thermal parameters are summarized in Table I. Calculations were done using standard finite difference and finite element methods.

**Table 1. Summary of Chemical Kinetic Reaction Schemes**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate</th>
<th>$\Delta H_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arrhenius</td>
<td>$3.5 \times 10^{19} \exp(-30,000/T) [A]$</td>
<td>2000</td>
</tr>
<tr>
<td>HMX</td>
<td>$1.4 \times 10^{21} \exp(-26,300/T) [A]$</td>
<td>300</td>
</tr>
<tr>
<td></td>
<td>$1.9 \times 10^{16} \exp(-22,500/T) [B]$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$1.6 \times 10^{12} \exp(-17,500/T) [C]^2$</td>
<td></td>
</tr>
<tr>
<td>TATB</td>
<td>$6.5 \times 10^{12} \exp(-21,000/T) [A]$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$3.5 \times 10^{19} \exp(-30,000/T) [A][B]$</td>
<td>900</td>
</tr>
<tr>
<td></td>
<td>$1.6 \times 10^{15} \exp(-27,500/T) [B]^2$</td>
<td>950</td>
</tr>
</tbody>
</table>

$[A]$, $[B]$, $[C]$ and $[D]$ are mass fractions. Coefficients in reactions preserve mass fraction, not atoms.

Calculated ignition temperatures are shown in Fig. 1. A few relevant experimental data points are shown for LX-10 (95% HMX) and LX-17 (92.5% TATB). There have been many fast and slow cookoff experiments so one would expect to find a wealth of experimental data for this boundary condition from fast and slow cookoff tests. However, when one examines this data many of the tests are for mixtures of explosives. Even if we have kinetic schemes for the individual components of the explosive it is probable that intermediate products of the two explosives interact, so we cannot simply add two reaction rates. Other cookoff tests are done with insulation between the heated surface of the...
Figure 1. Numerical calculations of ignition temperature as a function of heating rate for a single Arrhenius reaction rate and multi-step models for HMX and TATB. Experimental results for LX-10 (95% HMX) and LX-17 (92.5% TATB) are also shown.

munition and the explosive, so it does not match our chosen boundary condition. As a result there is surprisingly little good experimental data to compare with our numerical calculations.

A FUNCTION TO FIT THE NUMERICAL DATA

Along with the results of numerical calculations, Fig. 1 shows curve fits of the form

$$T_{ign} = \frac{T_1}{1 - b \ln \beta}$$  \hspace{1cm} (5)

where the surface temperature is rising $\beta$ K/sec. Different values of the fitting parameters, $T_1$ and $b$, are used for each kinetics model. The form of Eq. 5 was initially obtained by guessing the appropriate functional form and rejecting those that didn't fit well.

The form of Eq. 5 has a physical basis. With a linearly increasing surface temperature the steady state temperature distribution within the explosive is no longer uniform. Instead it is a parabola$^7$.

$$T_u = T_s - \frac{\beta L^2}{2\alpha} \left( \frac{2x/L - x^2/L^2}{\delta T} \right)$$  \hspace{1cm} (6)

Let $T = T_u + \delta T$, where $\delta T$ is the small contribution to the total temperature due to the chemical reaction. Substituting this into Eq. 2 and expanding the exponential gives an equation analogous to Eq. 4.
\[
\frac{\partial^2 (\delta T)}{\partial T_s^2} = W(T_s) e^{-T_s \beta l^2 \left( \frac{x - \gamma x^2}{\alpha T_s^2} \right)} e^{T_s \delta T / T_s^2}
\]  

At very low heating rates this has a critical temperature very close to that of Eq. 4. At higher heating rates the exponential term in the middle is less than 1 so the critical value of \( W(T_s) \) must be greater than that from Eq. 4 and ignition will generally occur near the surface. Note that \( \delta T \) is also a function of \( x \) so Eq. 5 must be integrated to determine the functional form of \( \delta T \). This has been done using several approximations, yielding an equation for the critical temperature with \( \eta = T_a / T_s^2 \) and \( p = \eta L^2 / \alpha \)

\[
T_{\text{ign}} = T_a \left( \frac{T_a}{\eta L^2 Z \Delta H_r e^1}{\ln \left[ \frac{\eta L^2 \Delta H_r e^1}{p^2 \alpha C} \right]} \ln \left[ \frac{\beta^2}{1 - (1 + p \beta / L) e^{-p \beta}} \right] \right)
\]  

This is similar in form to Eq. 5, though more complicated. It differs from Eq. 5 by asymptotically approaching the classical Frank-Kamenetskii critical temperature as it should. The time to explosion is a trivial calculation, \( t_{\text{ign}} = T_{\text{ign}} / \beta \). However, one should use these calculated ignition temperatures with caution unless they have been checked by actual tests of the system being considered. The chemistry of explosives is complicated and anomalously low ignition temperatures are not infrequent in real systems.

REFERENCES
