A Theoretical Method to Compare Relative Bulk Thermal Sensitivities of Several Common High Explosives

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The author dedicates this paper to the memory of *Charles Lavern Mader*, his friend and mentor for more than 55 years.

Abstract: Simultaneous numerical solutions of the second and first order partial differential equations describing the first order decomposition of seven explosives are presented. The solutions were used to compare the critical rates of heat production per unit mass of each material. The lower such a rate is the more sensitive is the explosive. The relative sensitivities of Tetryl, PETN, RDX, TNT, HMX and TATB are as might have been predicted. However, PBX9404 shows apparently enhanced thermal sensitivity compared with these six explosives. This provides a warning that some modern low vulnerability composite explosives based partly on propellant ingredients might constitute enhanced thermal threats.

Keywords: Theoretical · Simultaneous · Partial differential equations · Thermal initiation · Critical conditions · Thermal power density

1 Introduction

Lee [1] developed a simple method for determining the relative sensitivity of bare explosives to detonation by projectile impact. The criterion is the critical level of power per unit mass transmitted to the explosive by the impact of the projectile. The concept of critical power in relation to the bulk thermal explosion of self-heating materials when exposed suddenly to uniform heating in a hot bath was first cited by Semenov [2]. He identified criticality as the borderline between explosion or ignition and no event. Explosion was deemed to occur when the rate of heat production in the reactant exceeded the rate of heat loss. He assumed that the temperature was uniform within the reactant and that during self-heating there existed a discontinuity in temperature at the surface of the reactant. The rate of heat production, i.e. generation of power within the reactant is given by the usual Arrhenius equation multiplied by the heat of decomposition:

$$Q(dc/dt) = (dQ_1/dt) = -QcA\exp(-E/RT) \qquad (1)$$

where Q (J/mol) is the exothermicity of the reaction, c (mol/m³) its concentration, t (s) time, A (s⁻¹), the pre-Arrhenius Factor, E (J/mol), the Activation Energy, R, the Gas Constant (J/K⁻¹mol⁻¹) and T (K) the temperature. The rate of heat loss from the reactant surface is described by a linear relationship, approximating to the 5/4th Power Law

$$dQ_2/dt = \chi A(T_s - T_o)/V \qquad (2)$$

where χ (J/m².K.s) is a surface heat transfer coefficient, V (m³) volume and A (m²) area. dQ_1/dt and dQ_2/dt have units of *Watts/unit volume.* The subscripts $_{amb, s}$ and $_0$ refer to ambient, reactant surface and hot bath conditions.

Semenov's concept was superseded by that of Frank-Kamenetskii [3] whose theory incorporated a distributed, rather than a uniform temperature in the reactant, based on its finite thermal conductivity and a zero-order decomposition reaction. The latter implies the existence of subcritical steady states, leading to a criticality criterion based on conditions which are just sufficient to cause a steady state not to exist. Later Thomas [4] and Gray and Harper [5] showed that Semenov's theory applied perfectly well to a well-stirred fluid reactant, or to one with infinitely large thermal conductivity, or in a perfectly thermally insulated environment, i.e. where χ was zero; Frank-Kamenetskii's concept implied $\chi \to \infty$. As is often the case, reality is somewhere between two apparently incompatible theories.

In 1967 the basic characteristics of Thermal Explosion Theory were reviewed by Gray and Lee [6], but no reference was made to the balance between power generation of the decomposing reactant and rate of heat loss when analytical solutions to the heat conduction-based theory were discussed for the infinite slab or cylinder. No analytical solution was then available for the sphere. Frank-Kamenestskii's critical criterion

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$$\delta_{crit} = (QEr^2 c_0 A exp(-E/RT_0)/\lambda RT_0{}^2)$$

embodies the equality of heat production $Qc_0 A exp(-E/RT_0)$ and heat loss $\delta_{crit} \lambda RT_0{}^2/Er^2$.

A few relatively simple numerical solutions were made by others using the limited computing power available then, but only for zero-order decomposition reactions. Zinn and Mader [7] carried out some numerical calculations to support their experimental work involving the dropping of 1 inch diameter spheres of explosives into liquid Wood's Metal in 1960. In 1981 Merzhanov and Abramov [8] reviewed thermal explosion theory with computation of the self heating of explosives showing time-dependent temperature profiles where Bi (the Biot Number) is very small, i.e. the Semenov case and Bi is very large, i.e. the Frank-Kamenetskii case. However, no data on the variation of the critical criterion, δ_{crit}, or power density were reported.

It is now generally accepted that most explosives decompose thermally according to first-order reaction kinetics and criticality is associated with the identification of conditions leading to a sudden increase in the temperature at the centre of the reacting mass. The concept of distributed temperature in the reactant requires that, instead of simply comparing an exponential with a linear process in order to identify a critical condition, a pair of non-linear partial differential equations linking temperature and reactant concentration at all points in the reacting mass has to be solved simultaneously.

2 Aims of the Study

The aims of this study were to devise a solution to the simultaneous second and first-order partial differential equations describing thermal explosion of a reactant undergoing a first-order self-heating reaction in a spherical environment at a uniform temperature. Although these equations do not describe the processes exactly, deviations are regarded as relatively minor. The solutions to these equations were then to be used to provide data to determine whether explosion could be ascribed to the generation of power by the decomposing explosive just in excess of some critical value. This concept is analogous to the one in which critical power dissipation within an explosive resulting from the impact of flat-fronted cylindrical projectiles was used by Lee [1] to compare numerically the shock sensitivities of explosives and also provide an alternative theory to that of Walker and Wasley [9]. The analogous criterion for criticality in thermal explosion theory is likely to be critical power generation at the hottest (central) point through self-heating in the reactant and heat conduction from the environment in which it is immersed. The similarity between this and the shock case is that the theory deals with what is happening within the reactant rather than relying on phenomenological observations.

3 Experimental Procedure

The approximate dimensional second-order partial differential heat balance equation for thermal explosion in spherical symmetry is

$$C_p\rho(\partial T/\partial t) = \lambda\{\partial^2 T/\partial x^2 + (2/x)\ \partial T/\partial x\} - Q(\partial c/\partial t) \quad (3)$$

Reactant decomposition with first order chemical kinetics is described by the first-order partial differential equation

$$\partial c/\partial t = -cA exp(-E/RT) \quad (4)$$

where C_p (J/kg.K) is specific heat capacity, ρ (kg/m^3) is density, λ (J/mKs) is thermal conductivity and x (m) distance. The heat flow (power) balance in equations (3) and (4) is in terms of W/m^3. Already the middle term of equation (3) is an approximation, as is the assumption that parameters λ and C_p are constant and independent of temperature and reactant concentration. Solutions require two boundary conditions and an initial condition.

Initial Condition: $c = c_{0-}$ and $T = T_{amb}$ for $0 \leq x \leq r$ where x and r (m) are, respectively, distance from the centre and radius of the sphere and T_{amb} is the uniform initial ambient temperature (K) at all points in the spherical reactant before it is immersed in the hot bath.

Boundary Conditions: At the centre of the spherical reactant; temperature and composition symmetry are maintained, i.e. $\partial T/\partial x = 0$ and $\partial c/\partial x = 0$ when $x = 0$.

At the outer surface of the spherical reactant; $x = r$,

$$\lambda(\ \partial T/\partial x) = -\chi(T_s - T_0) \quad (5)$$

Following Frank-Kamenetskii [9] the second and first order partial differential equations (3) and (4) may be transformed into dimensionless form using

$$\theta = E(T - T_0)/RT_0{}^2,\ z = x/r \text{ and } \gamma = c/c_0$$

These transformations enable the generation of solutions which are consistent extensions of Frank-Kamenetskii's earlier work relating to steady state (zero order) reaction kinetics in infinite, slab, cylinder and spherical geometries. In this case of first order reaction, a dimensionless time variable, $\tau = (\lambda t/C_p\rho r^2)$, and parameter, $B = QE/C_p.MW.RT_0{}^2)$, are required, where the molecular weight of the reactant, $MW = \rho/c_0$. The dimensionless equations to be solved are

$$\partial\theta/\partial\tau = \partial^2\theta/\partial z^2 + (2/z)(\partial\theta/\partial z) + \delta\ \gamma exp[\theta/(1 + \varepsilon\theta)] \quad (6)$$

and

$$(\partial\gamma/\partial\tau) = -\gamma(\delta/B)exp[\theta/(1 + \varepsilon\theta)] \quad (7)$$

where $\delta = (QEr^2\rho.Aexp(-E/RT_0)/\lambda RT_0^2 MW)$, $E/RT_0 - E/RT = \theta/(1+\varepsilon\theta)$ and $\varepsilon = RT_0/E$. δ is in the same form as Frank-Kamenetskii's [3] critical criterion with c_0 replaced by ρ_0/MW.

The Initial Conditions transform to

$$\gamma = 1 \text{ and } \theta = \theta_{amb} \text{ for } 0 \le z \le 1 \text{ when } \tau = 0 \qquad (8)$$

The Symmetry Boundary Condition transforms to

$$\partial\theta/\partial z = 0 \text{ at } z = 0 \text{ for } \tau \ge 0 \qquad (9)$$

The Surface Boundary Condition transforms to

$$\partial\theta/\partial z = -(\chi r/\lambda)\theta_s = -Bi\theta_s \qquad (10)$$

where $Bi = 10^8$ is a Biot Number, consistent with the earlier assumption of $\chi \to \infty$.

The partial differential equations (6) and (7) now include a density based concentration. The equation is parabolic and a preferred method of solution of such equations is via the Crank and Nicholson [10] procedure. This incorporates conversion of a central finite-difference scheme into a tri-diagonal matrix. Normally, stability would be assured provided that $(\lambda\partial\tau/C_p\rho\partial z^2)$ does not exceed a relatively small number, which is easily achieved by choice of time and distance step sizes. However, the presence of the exponential in equations (6) and (7) renders them highly non-linear and the standard Crank-Nicholson technique may lead to instability. This is avoided by a technique recommended by Murphy [11] incorporating a skewed calculation point between time steps. Adjacent time steps are designated by subscripts j and $j+1$ and position by subscript i. Instead of centring the calculation of temperature at a time midway between two time steps, say at $(\theta_{i,j} + \theta_{i,j+1})$ 0.5, the point of calculation is skewed by using a factor other than 0.5, α, between 0.6 and 0.25 with complement q. In this analysis $\alpha = 0.6$ and $q = 0.4$ applies to the unknown values of θ and γ at time step $j+1$ and j, respectively. The finite difference time step is $d\tau = p$ and the distance step is $h = 0.01z$.

The finite difference form of equation (6) is written as a tri-diagonal matrix for $i = 2$ to $imax-1$.

$$(SW_i - S)\,\theta_{i-1,j+1} + (2S+1)\,\theta_{i,j+1} - (S+SW_i)\,\theta_{i+1,j+1} = $$
$$-(SMW_i - SM)\,\theta_{i-1,j} - (2SM-1)\,\theta_{i,j} + \qquad (11)$$
$$(SM + SMW_i)\,\theta_{i+1,j} + p.\,\delta.\,\gamma_{i,j}\,exp[\theta_{i,j}/(1+\varepsilon\,\theta_{i,j})]$$

where $\alpha p/h^2 = S$, $qp/h^2 = SM$, $\alpha p/W_i h^2 = SW_i$ and $qp/W_i h^2 = SMW_i$.

The boundary conditions at the centre and the surface were determined by appropriate substitution into equation (11) of the skewed central finite difference forms of equations (9) and (10). The symmetry concept enables $\theta_{-1,j+1}$ and $\theta_{-1,j}$ to be equated to $\theta_{+1,j+1}$ and $\theta_{+1,j}$, respectively, so the central boundary condition can be written as

$$(2S+1)\,\theta_{1,j+1} - 2S\,\theta_{2,j+1} = (1-2SM)\,\theta_{1,j} + $$
$$2SM\,\theta_{2,j} + p.\,\delta.\,\gamma_{1,j}\,exp[\theta_{1,j}/(1+\varepsilon\,\theta_{1,j})] \qquad (12)$$

and the surface boundary condition becomes

$$-2S\,\theta_{imax-1,j+1} + [(2S+1) + 2hBi\,(S + SW_{imax})]$$
$$\theta_{imax,j+1} = 2SM\,\theta_{imax-1,j} + [(1-2SM) - $$
$$2hBi(SM + SMW_{imax})]\theta_{imax,j} + \qquad (13)$$
$$p.\,\delta.\,\gamma_{imax,j}\,exp[\theta_{imax,j}/(1+\varepsilon\,\theta_{imax,j})]$$

where $imax = 101$ denotes the position of the surface of the sphere.

It was not possible to use the skewed time step procedure to follow the changes in $\gamma_{i,j}$ over time in the tri-diagonal matrix calculations. Equations (11), (12) and (13) use values of γ at the previous time-step, designated by j. Provided that time steps are small and, at 10^{-5} in this case they are, overall errors are negligibly small.

The skewed time step was used in the version of equation (7) solved simultaneously with the second order partial differential equation

$$(1/\gamma)(\partial\gamma/\partial\tau) = -(\delta/B)exp[\theta/(1+\varepsilon\theta)]$$

Integrating between τ and $\partial\tau$

$$ln(\gamma_{i,j+1}/\gamma_{i,j}) = -(\delta/B)p.exp[(\alpha\theta_{i,j+1} + q\theta_{i,j})/$$
$$(1+\varepsilon\{\alpha\theta_{i,j+1} + q\theta_{i,j}\})]$$

Setting $av_i = \alpha\theta_{i,j+1} + q\theta_{i,j}$ and $avg_i = (\delta/B)p.exp[av_i/(1+av_i)]$

The equation for the calculation of the concentration at time step $j+1$ is given by

$$\gamma_{i,j+1} = \gamma_{i,j}\,.exp[-avg_i] \qquad (14)$$

Three types of experiment were performed. In the first, physicochemical and thermochemical data for each explosive shown in Table 1 were entered and the parameters $T_{amb} = 298.13$ and $Bi = 10^8$ were imposed. Based on this, the initial dimensionless temperature (θ_{amb}) is negative, the dimensionless hot bath temperature (θ_0) is zero and positive temperatures arising from self heating are generally less than about 4–5 prior to ignition or explosion of the reactant.

When the cgs system of units was used, results showing δ_{crit} of the order of 3.5 to 3.9 were obtained; its value for zero order reactions is 3.32 [3]. The value of Bi implies surface boundary transparency to heat flow. An initial value of δ was selected and the code run until a maximum temperature was calculated at the centre of the reactant. If this temperature was found to exceed $+5$, explosion was deemed to have occurred. The code notes whether explosion or non-explosion occurs and resets the value of δ. If no explosion has occurred

Table 1. Thermochemical data for explosives studied in cgs and SI formats.

Explosive cgs units SI units	Density (ρ) g/cm^3 kg/m^3	Molecular Weight (MW) g/mole g/mol	Heat of eaction (Q) cal/mole J/mol	Activation Energy (E) cal/mole J/mol	Arrhenius Factor (A) S^{-1}	Heat Capacity (C$_p$) cal/g °C J/kgK	Thermal Cond. (λ) cal/cm °C s J/m K s
PETN	1.72 1.72×10^3	316.15	9.485×10^4 3.969×10^5	4.7×10^4 1.966×10^5	6.3×10^{19}	0.239 $1.\times10^3$	6.9×10^{-4} 2.887
Tetryl	1.71 1.71×10^3	287.15	1.436×10^5 6.008×10^5	3.84×10^4 1.607×10^5	2.51×10^{15}	0.213 8.912×10^2	6.83×10^{-4} 2.858
HMX	1.89 1.89×10^3	296.17	1.481×10^5 6.197×10^5	5.27×10^4 2.205×10^5	4.3×10^{12}	0.231 9.665×10^2	1.0×10^{-3} 4.184
RDX	1.712 1.712×10^3	222.13	1.11×10^5 4.644×10^5	4.71×10^4 1.971×10^5	2.02×10^{18}	0.232 9.707×10^2	2.53×10^{-4} 1.059
TNT	1.65 1.65×10^3	227.13	6.81×10^4 2.849×10^5	3.44×10^4 1.439×10^5	2.51×10^{11}	0.254 1.063×10^3	6.22×10^{-4} 2.602×10^{-1}
TATB	1.86 1.86×10^3	258.18	1.549×10^5 6.627×10^5	5.99×10^4 2.506×10^5	3.18×10^{19}	0.215 8.996×10^2	1.3×10^{-3} 5.189
PBX9404	1.84 1.84×10^3	288	1.472×10^5 5.95×10^5	3.13×10^4 1.31×10^5	5×10^{19}	0.324 1.356×10^3	9.2×10^{-4} 3.849×10^{-1}

δ is increased and vice versa. A further aspect of the code is that should explosion or non-explosion recur in two successive runs, the value of δ is increased or reduced according to a formula involving a factor. If the events recorded are not the same, then the factor by which a new value of δ is calculated is reduced. This process of straddling continues until a suitably precise value of δ leading to a non-explosive event is recorded. Originally, other data, including peak centre temperature of the reactant, maximum time to explosion (number of time steps), radius of the just subcritical sphere and dimensionless concentration were recorded, but some of these were later found to be redundant or misleading.

In the second code the approximate critical value of δ was used to display curves of dimensionless temperature and dimensionless reactant concentration as functions of time. The critical value, $\delta_{crit,}$ was straddled much more closely by use of double or quadruple precision calculations in Absoft20 Fortran.

The third code presented $\partial\theta/\partial\tau$, $\partial\gamma/\partial\tau$, γ_1 (concentration at the centre of the reactant), r (radius of reactant), τ, (dimensionless time), number of time steps, the dimensional time, t, when θ_1, i.e. the centre temperature, is close to 0 and the dimensional time step.

4 Results

Several hundred thousand solutions of the tri-diagonal matrices composed of equations (11) to (14) simultaneously subject to boundary and initial conditions (8), (9) and (10) were required for the determination of the dimensionless temperature and concentration history for each value of δ in the first code. More than fifty separate sets of these solutions were generated automatically to reach a value of δ within either $\pm10^{-7}$ in single precision, $\pm10^{-14}$ in double precision or $\pm10^{-25}$ in quadruple precision. This process

takes about two to three minutes using Absoft20 Fortran on an iMac 10.15.3 Catalina 64 bit OS, with a 4GHz Intel Core I7 processor and 32GB 1867 MHz DDR3. In early runs the critical value of δ was approached to a precision of 10^{-7}. Such is the sensitivity of the temperature near criticality as a function of δ that the second code was written which started with the earlier 'critical' value of δ and which enabled criticality to be approached closer by manually selecting values of δ in double and quadruple precision. This second code generates curves of dimensionless centre temperature as functions of dimensionless time as shown in Figure 1 where two pairs of explosion and non-explosion graphs are shown.

The situation shown in Figure 1 posed a problem. The two curves to the left were obtained using δ_{crit} determined using single precision limited to 7 decimal places and the two to the right were determined using double precision limited to 14 decimal places. The four curves were truncated for clarity at values of $\theta=-2$ during warm-up and $+$
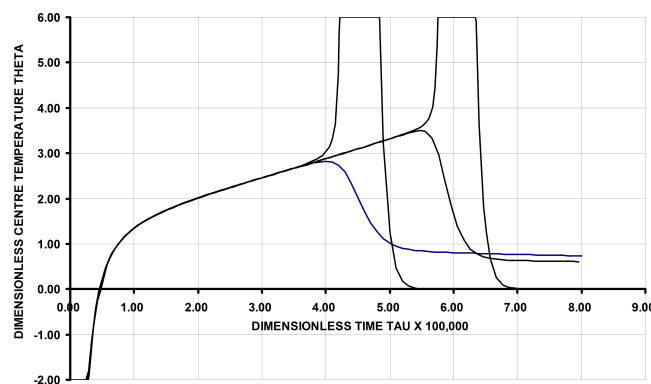
Figure 1. Dimensionless centre temperature v. dimensionless time $\times$ 100,000 in a sphere of RDX dropped into a bath at 440 K.

6 during explosion. A set of data in quadruple precision limited to 25 decimal places showed the same pre-explosion and pre-peak temperature characteristics, but an apparently higher peak non-explosion centre temperature. At the scale in Figure 1 the centre temperature - time profiles of all curves appeared indistinguishable below the separation point when explosion occurred. This is an outcome of the non-physical nature of the 'Critical Condition', since an event occurs or it does not. This, and the evidence that the peak temperature of the reactant prior to explosion is a function of the closeness of the value of δ_{crit} to the hypothetical, but unreachable 'true' value, suggested that the apparent peak temperature at the centre of the reactant close to the event should not be used as a criterion for criticality. Moreover, it meant that a value of δ_{crit} determined to a precision of 6 decimal places appeared to show a similar temperature time profile as one determined using apparently higher precision right up to the point where explosion started. The peak temperature reached in each run on each material studied coincided with the appearance of an inflection point in the associated concentration – time curve, as expected.

While all curves of temperature versus time are indistinguishable in the scale of the curves in Figure 1 up to the bath temperature θ_0, on closer examination small differences were observed in rates of reaction in curves of non-explosions and explosions for δ very close to δ_{crit}. These minute differences in the rates of reaction distinguish explosion from non explosion when $\theta = 0$ and are the bases for the crucial determination of what constitutes the criterion separating explosion from non explosion. This is hardly surprising, since δ_{crit} is based on the balance of heat production and loss at the bath temperature θ_0.

The dimensionless temperatures and concentrations and their slopes with respect to time were recorded across θ_0 in the third code. The dimensionless rate of concentration change, $d\gamma/d\tau$, can be used to determine the dimensional rate of reaction at θ_0 using the definitions of γ and τ following equations *(6)* and *(7)* for each explosive studied. The expression for power per unit mass generated at the centre of the reacting sphere is given by

$$(Q\lambda/C_p\rho r_0^2 MW)(d\gamma/d\tau) \tag{15}$$

in *Watts/kg*, if SI units are used, or multiplied by 4.184 x 10³ if cgs units are used: log–log graphs of *log(bath temperature)* v. *log(initiation power)* may be plotted as shown in Figure 2. The relationships are not quite linear. The equations of the curves are shown in Table 2.

The negative sign on the right hand side of equation *(7)* is indicative of the loss of reactant as the decomposition proceeds. At any given temperature the greater the power density required to cause initiation, the less sensitive is the material and vice versa. As the temperature of the bath increases, the contribution to the generation of instability in the reacting mass by the self-heating reaction declines.
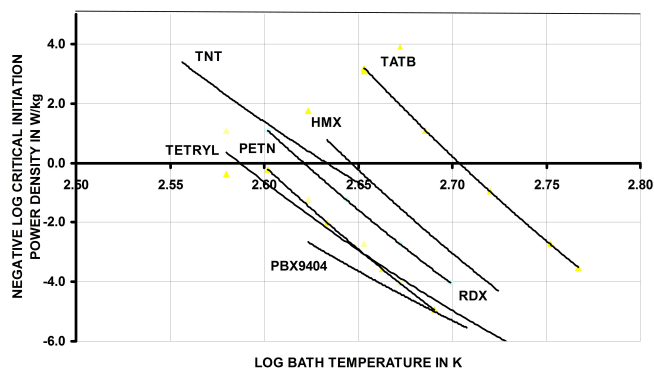
Figure 2. Log bath temperature in K versus negative Log critical initiation power density in W/kg.

Table 2. Equations of the curves in Figure 2. Y denotes negative log of critical initiation power density in W/kg and X log bath temperature in K.

Explosive	Equation of the curve
PBX 9404	$Y = 39.21.X^2 - 243.90.X + 365.21$
TETRYL	$Y = 52.57.X^2 - 321.87.X + 480.88$
PETN	$Y = 61.54.X^2 - 379.21.X + 569.82$
RDX	$Y = 55.16.X^2 - 345.21.X + 525.91$
TNT	$Y = 49.55.X^2 - 301.21.X + 449.59$
HMX	$Y = 64.66.X^2 - 402.66.X + 612.01$
TATB	$Y = 67.84.X^2 - 426.62.X + 657.52$

5 Discussion

The importance of this work and the earlier work of Lee [1] is that it provides a means by which the relative sensitivities of energetic materials to initiation by shock and thermal processes can be compared. Above all it removes from the process of comparison factors other than ones within the reactant and it links shock and thermal initiation via a common principle involving relative tolerance to the rate of deposition or generation of energy within a reacting mass.

The assumption of first order kinetics, while retaining all of the other simplifications to the equations governing heat transfer and criticality in thermal decomposition in spherical symmetry, had little effect on δ_{crit} for the explosives studied here. These are of the order of 3.5 to 3.9, compared with 3.32 for zero order kinetics when cgs units are used. It is important to note that, in line with early studies by Thomas [4], as the Biot Number $Bi \rightarrow 0$, $\delta_{crit} \rightarrow a$ *minimum value*. In fact, δ_{crit} values could not be obtained with values of Bi approaching zero.

Doubtless there are likely to be shortcomings in the data used in this analysis. Most were from Gibbs and Popolato [12]. The possibility that explosives decompose thermally in far more complex a manner than has been assumed here has already been alluded to. However, the principle that an explosive can withstand the generation of heat within it without catastrophic consequences up to a

given level is consistent with earlier work in which a similar conclusion was reached concerning the effects of planar shocks and follows Semenov's original assertion concerning criticality [2]. Figure 2 might be regarded as a set of thermal equivalents to Pop-Plots, although the log-log relationships are not strictly linear.

The data in Table 2 enable direct comparison of the thermal sensitivity of all of these explosives at the same bath temperatures over the whole range of temperatures involved in the determination of the curves and beyond.

These results indicate surprisingly that PBX9404 appears to be the most thermally sensitive of the seven explosives studied here. This is probably due to the presence of nitrocellulose (NC) (3 %) in the composition. It and tris-beta chloroethylphosphate (CEF) (3 %) were added as plasticisers to HMX and diphenylamine (DPA) (0.1 %) as a stabiliser for the nitrocellulose to aid processing and charge preparation. The increase in thermal sensitivity may not have been thought to be a problem, if it were considered or tested for at all. The increase in the thermal hazard compared with HMX is undoubtedly due to the additives mentioned above. Their effect raises the issue of the potential enhanced thermal sensitivity of modern plastic bonded explosives, some with closer resemblance to propellants than PBX9404. The relative thermal insensitivity of HMX compared with RDX is likely to be due to its higher melting point compared with RDX, which occupies a position not unexpected in relation to the other explosives examined in this work. The question is whether modern RDX-based insensitive high explosives exhibit enhanced thermal sensitivity.

TATB, RDX, TNT, TETRYL and PETN all seem to occupy relative positions which might have been predicted. Most explosives were studied at temperatures above their melting points and no account has been taken of the effects of Latent Heat of Fusion on their behaviour. It was assumed that they each were in some notional container with high thermal transmissibility, since the Biot Number used in the calculations was 10^8 in order to maintain coincidence with the surface heat transfer criterion originally postulated by Frank-Kamenetskii [3] for his studies on zero order self-heating criticality.

6 Conclusions

Determination of theoretical values of critical thermal initiation power density in W/kg indicates few surprises in the ranking of the explosives studied here. The exception may be the apparent enhanced potential thermal sensitivity of PBX9404 compared with HMX. While PBX9404 is not now widely used, many new low vulnerability explosives based on RDX and incorporating materials also used in propellants may impart enhanced thermal sensitivity to them. This might constitute an area where weapons vulnerability is compromised.

The encouraging feature of this work lies in the coincidence between prediction and experience in the apparent relative sensitivity of the other six explosives studied. This suggests that the thermochemical decomposition data used in this study, some of which are more than sixty years old, are likely to be adequate to order relative thermal sensitivity of these explosives. It is not clear whether equivalent data are available for more modern explosives, but it is suggested that these data may be required.

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