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REACTIVE THERMAL WAVES IN ENERGETIC MATERIALS

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ABSTRACT

Reactive thermal waves (RTWs) arise in several energetic material applications, including *self-propagating high-temperature synthesis* (SHS), *high explosive cookoff*, and the *detonation of heterogeneous explosives*. In this paper I exmaine *ideal* RTWs, by which I mean that 1) material motion is neglected, 2) the state dependence of reaction is Arrhenius in the temperature, and 3) the reaction rate is modulated by an arbitrary mass-fraction-based reaction progress function. Numerical simulations demonstrate that one's natural intuition, which is based mainly upon experience with inert materials and which leads one to expect diffusion processes to become relatively slow after a short time period, is invalid for high energy, state-sensitive reactive systems. Instead, theory predicts that RTWs can propagate at very high speeds. This result agrees with estimates for detonating heterogeneous explosives, which indicate that RTWs must spread from hot-spot nucleation sites at rates comparable to the detonation speed in order to produce experimentally-observed reaction zone thicknesses. Using dimensionless scaling and further invoking the high activation energy approximation, I obtain an analytic formula for the steady plane RTW speed from numerical calculations. I then compute the RTW speed for real explosives, and discuss aspects of their behavior.

APPLICATIONS

Reactive thermal waves (RTWs) play an important role in many energetic material systems, from self-propagating high-temperature synthesis (SHS) to high explosive (HE) cookoff to the detonation of heterogeneous explosives. The detailed mechanisms of reactive thermal waves depend on the system in question. For SHS, reaction occurs between two powders (e.g., aluminum and iron oxide in the case of the well-known thermite reaction). This problem involves both mass and heat diffusion, and therefore depends on the respective particle sizes and their morphology, as well as the constituent thermal properties[1].

Deflagrating energetic materials exhibit purely conductive burn waves under special circumstances. The classic example is the *strand burner* test, in which a (typically unconfined) stick of energetic material is ignited at one end. A burn front travels down the stick, and the propagation speed is measured as a function of atmospheric pressure. The resulting curve, known as *Vieille's law*, depends on the pressure raised to a power that is typically less than unity. The value of the pressure exponent is an important metric for rocket propellant safety. In this low-pressure regime, the density of combustion product gases is of order 1000 times less than that of the solid reactants. The associated expansion produces a significant amount of reaction product motion, such that even this simple system is far from a purely thermal wave.

For neat-pressed energetic material pellets, and even for materials with binder, there is a tendency for product gases zip ahead through cracks, pores, and flaws in the energetic material. This process has been called *erratic burning*[2]. Because it exploits random flaws in the material, and because it also generates high internal pressures that tend to fracture unconfined pellets, this process (as the name implies) is very non-steady. Rocket propellants are formulated with rubbery binder to specifically avoid this dangerous behavior. We have recently derived a simple model that describes the basic features of flame intrusion into energetic material cracks[3,4].

The cookoff of secondary explosives tends to be violent only if the system is heavily confined. In these situations reaction products have no volume to expand into; therefore, hot product gas is forced into flaws, and may also create its own damage via the formation of burning crack networks[5]. Such systems can develop RTWs of a sort, but they are less well defined than conductive burn waves, in that they necessarily involve convective burning within pre-existing flaws and/or artificially-generated damage features. Hot gases are forced into porous spaces, which ignite exposed surfaces. Once these surfaces are lit they subsequently burn in a conductive manner unless or until additional flaws are accessed. Thus, convective burning increases the global burning rate by increasing the amount of burning surface area. Generally, there is a complex competition between how fast surface area is ignited (which promotes explosion), and how fast confinement is lost (which quenches explosion). I have recently presented a simple model that addresses the basic physical mechanisms by which reaction in cookoff explosions runs away[6].

In a detonating heterogeneous explosive, the post-shocked, pre-burned temperature field is spatially nonuniform. Depending on HE material properties and conditions, there is a often a strong tendency for reaction to start at the hottest regions and to spread out, in the form of RTWs, to consume the surrounding material. In general this heterogeneous reaction mode competes with homogeneous volumetric burning of the explosive. In contrast to the cookoff problem, the detonation shock pressure is evidently high enough to not only homogenize the initially heterogeneous material, but also to convert it to a supercritical fluid. In this situation the density of the reactants is of the same order as that of the reaction products. In the limit that the two densities are equal, reaction propagates as a purely thermal wave, without any bulk fluid motion. That is the case that I shall examine here.

MORE ON REACTIVE THERMAL WAVES IN HETEROGENEOUS DETONATIONS

Despite their importance, RTWs do not appear to have received a great deal of theoretical attention as isolated entities. Y. Partom formulated a numerical model to calculate RTW speeds, for use in his void collapse model for shock initiation[7]. In this paper I study RTWs in isolation, with the goals of examining their structure and determining an analytic function for their propagation speed. Such an expression, with its parameter dependence, would comprise one of several important ingredients needed for the formulation of a physically-based reaction rate law.

Following Partom[7] who followed Boddington[8] (who studied the hot spot criticality problem), I argue that RTW propagation within a detonation reaction zone can be reasonably modeled as a purely thermal problem. Ignoring mass motion simplifies the analysis considerably, and allows one to obtain simple answers at an approximate level. Lest this assumption seem extreme, I have previously noted that virtually all reactive-burn models implicitly make it (though not in a self-consistent manner), in that they implicitly assume that the reactant and product densities are equal in the way that they treat burn topology[9]. Thus, the connection to cookoff (the subject of this session) is that I am treating the detonation reaction zone using a classical cookoff-type description, which, ironically, I have argued is *not* particularly valid for post-ignition cookoff problems.

It is straightforward to estimate that RTWs in heterogeneous detonation reaction zones must propagate at several kilometers per second in order to explain observed behavior. The residence time of a fluid element in a reaction zone of thickness Δ is of order Δ/c, where c is the sound speed at the sonic surface. If reaction proceeds as RTWs from hot-spot nucleation sites, then the time necessary to complete the reaction will depend on the number density of nucleation sites. Nevertheless, it seems sensible that hot spots will occur preferentially at grain boundaries, because that is where most of the deformation, inter-particle interaction, and energy dissipation occur. Assuming this to be the case, the time to complete reaction will be of order the time necessary for a thermal wave to propagate from the edge of large particles to the center. Thus, the reaction time can also be expressed as r/v, where r is the radius of the largest particles and v is the thermal wave speed. Equating the two expressions for the reaction time, we find that $v/c = \mathrm{O}[r/\Delta]$. For heterogenous explosives it is often the case that $r/\Delta = \mathrm{O}[1]$, such that $v = \mathrm{O}[c]$.

Menikoff and Sewell[9] have pointed out that inferred RTW speeds are much faster than can be explained by classical (inert) diffusion, and have suggested that hot spots must therefore propagate by a different mechanism. In this paper I propose that the mechanism is classical diffusion in the presence of a very large and highly state-sensitive heat release. I demonstrate that, under these conditions, the character and rate of conductive heat transfer profoundly changes. Temperature gradients no longer dissipate over time, but are maintained at very high values that lead to a much faster spreading of thermal disturbances.

Imagine the limit in which the RTW thickness approaches zero. In that case the wave is a temperature shock; however, under the present assumptions there is no pressure or density change associated with it. The temperature shock is propagated forward as molecules on the hot side of the surface perturb those on the cold side, thereby initiating prompt reaction and heat release. If the medium were an ideal gas, perturbations would occur via molecular collisions. In the reaction zone of a condensed-phase explosive, in which the density is ~2 g/cc, molecular interaction occurs via close-range intermolecular forces. In either case, the disturbance is propagated forward at acoustic speeds. Specifically, the RTW speed evidently cannot exceed the acoustic speed of burned material.

In summary, I have argued that both the theoretical upper bound of RTW speeds and experimentally-inferred RTW speeds in detonation reaction zones are of order the acoustic speed of burned high-pressure explosive. Let us now examine the mathematical behavior of RTWs to see whether they possess the required temperature-shock-like character.

MODEL PROBLEM

Consider a RTW propagating in a pre-mixed energetic material, in which the density of the reactants is equal to that of the reaction products. We shall consider waves in planar, cylindrical, and spherical geometry. The reactive heat equation is:

$$\frac{\partial T}{\partial t} = \kappa \left(\frac{\partial^2 T}{\partial x^2} + \frac{j}{x} \frac{\partial T}{\partial x} \right) + \frac{q}{c} \frac{\partial \chi}{\partial t}, \tag{1}$$

where T is temperature, t is time, x is distance, κ is thermal diffusivity, χ is product mass fraction, q is specific heat release, c is specific heat capacity (assumed to be constant), and j is an integer index, the value of which is set according to the problem dimensionality (0 = planar, 1 = cylindrical, 2 = spherical).

The last term in Eq. 1 is given by

$$\frac{\partial \chi}{\partial t} = \mathrm{g}[\chi] Z e^{-T^*/T}, \tag{2}$$

where Z is the pre-exponential factor, $T^* = E/R$ is the activation temperature (where E is the activation energy and R is the universal gas constant), and g is the reaction progress function. The most common expression for g is $1 - \chi$, which expresses a first order reaction.

Next we define a non-dimensional temperature ϕ as follows:

$$\phi = \frac{T - T_0}{T_m - T_0}, \tag{3}$$

where T_m is the maximum temperature that the system can attain via self-heating, and T_0 is the temperature of the unreacted material ahead of the wave. The maximum temperature occurs for full reaction under adiabatic conditions. Thus T_m is given by the condition

$$c\,(T_m - T_0) = q. \tag{4}$$

Substituting Eq. 4 into Eq. 3, ϕ becomes

$$\phi = \frac{c\,(T - T_0)}{q}. \tag{5}$$

Using the definition in Eq. 5, T^*/T becomes

$$\frac{T^*}{T} = \frac{1}{\tilde{T}_0 + \tilde{q}\,\phi}. \tag{6}$$

where $\tilde{T}_0 = T_0/T^*$ is the dimensionless initial temperature, and $\tilde{q} = q/(cT^*)$ is the dimensionless heat release.

In this problem the smallest value of T^*/T is order 10. In cases where $T^*/T >> 1$, D. Frank-Kamenetskii (F-K) showed[10] that T^*/T can be approximated by

$$\frac{T^*}{T} \approx \frac{1}{\tilde{T}_0} - \theta. \tag{7}$$

where θ is the F-K temperature defined by

$$\theta = \frac{T^*}{T_0^2}(T - T_0) = \frac{\tilde{q}\,\phi}{\tilde{T}_0^2} \equiv \alpha\,\phi. \tag{8}$$

Unlike criticality applications for which the F-K *high activation energy approximation* (Eq. 7) was first introduced, the purpose for making the approximation in this case is not to simplify the mathematics per se. Based on previous experience, there seems little hope of solving this problem analytically either with or without the high activation energy approximation; moreover, the numerical problem is as easily performed with or without it. Instead, its purpose is to yield as simple a non-dimensional problem as possible by 1) reducing the overall number of parameters from two (namely, $\tilde{T}_0$ and $\tilde{q}$) to a single composite parameter, $\alpha = \tilde{q}/\tilde{T}_0^{\,2}$, and 2) eliminating all parameters from the initial conditions. Doing so will allow us to deduce an analytic expression for the RTW speed; moreover, we shall show that the parameter α usefully characterizes the degree of heterogeneity of reaction behavior.

Next we define a non-dimensional distance $\tilde{x} = x/x_r$, and a non-dimensional time $\tilde{t} = t/t_r$, where the reference values x_r and t_r are yet to be determined. Incorporating these definitions into Eqs. 1 and 2 gives

$$\frac{1}{t_r}\frac{\partial\phi}{\partial\tilde{t}} = \frac{\kappa}{x_r^2}\left(\frac{\partial^2\phi}{\partial\tilde{x}^2} + \frac{j}{\tilde{x}}\frac{\partial\phi}{\partial\tilde{x}}\right) + \frac{1}{t_r}\frac{\partial\chi}{\partial\tilde{t}} \tag{9}$$

and

$$\frac{1}{t_r}\frac{\partial\chi}{\partial\tilde{t}} = Z\mathrm{g}[\chi]\mathrm{e}^{-1/\tilde{T}_0}\mathrm{e}^{\alpha\,\phi}, \tag{10}$$

where Eq. 8 has been substituted into Eq. 10. Examination of Eq. 10 shows that all free parameters except α are eliminated by defining

$$t_r = \frac{\mathrm{e}^{1/\tilde{T}_0}}{Z}. \tag{11}$$

Upon inserting Eq. 11 into Eq. 9, all free parameters in Eq. 9 are eliminated by defining

$$x_r = \sqrt{\frac{\kappa}{Z}}\,\mathrm{e}^{1/(2\,\tilde{T}_0)}. \tag{12}$$

Thus, the reference speed $v_r = x_r / t_r$ is given by

$$v_r = \sqrt{\kappa\, Z}\, \mathrm{e}^{-1/(2\,\tilde{T}_0)}. \tag{13}$$

The dimensionless wave speed, $\tilde{V} = V / v_r$ can depend only on α, which is the only parameter in the problem. Thus, the exact dimensional wave speed is

$$V = \tilde{V}[\alpha] \sqrt{\kappa\, Z}\, \mathrm{e}^{-1/(2\,\tilde{T}_0)}, \tag{14}$$

where $\tilde{V}[\alpha]$, which depends on the reaction progress function g, must be determined with the aid of numerical computations.

The speed in Eq. 14 depends on the geometric mean of the fundamental diffusion and reaction rate constants. This mathematical structure underscores the fact that this is a reactive-diffusive wave. If either effect were to go away (i.e., if either κ or Z were to be zero) then the wave speed would likewise be zero. Moreover, the wave speed is exponentially modulated by the upstream temperature. In other words, the speed is very sensitive to how close the upstream material is to spontaneously cooking off. The fact that the reactive thermal wave speed depends on the upstream temperature was previously observed by Partom[7], and the result is not widely known.

The equations to be solved are

$$\frac{\partial \phi}{\partial \tilde{t}} = \frac{\partial^2 \phi}{\partial \tilde{x}^2} + \frac{j}{\tilde{x}}\, \frac{\partial \phi}{\partial \tilde{x}} + \frac{\partial \chi}{\partial \tilde{t}} \tag{15}$$

and

$$\frac{\partial \chi}{\partial \tilde{t}} = \mathrm{g}[\chi] \mathrm{e}^{\alpha\, \phi}. \tag{16}$$

subject to the initial condition

$$\phi[\tilde{x}, 0] = \phi_{00}\, \mathrm{e}^{-(\tilde{x}/\sigma)^2}. \tag{17}$$

Equation 17 represents an idealized hot-spot nucleation site, which, for a detonation wave in a heterogeneous material, is generated by the mechanical work associated with shock compression.

The term "hot spot" has become somewhat of a catchall phrase in the explosives business. I contend that this condition is unfortunate, in that inadequate descriptive terminology may significantly obfuscate the essential physical mechanisms. In this paper, I define a *hot spot* as a local maximum in the post-shocked, pre-burned temperature field. This relatively hot region comprises a potential nucleation site. Each such site is either *subcritical* (meaning that it is insufficient to initiate an RTW) or *supercritical* (meaning that it is sufficient to initiate an RTW). The essential point is that one must clearly distinguish between unreacted hot-spot nucleation sites, and the RTWs that each may or may not initiate. This distinction becomes dramatic in the following section where we examine RTW behavior.

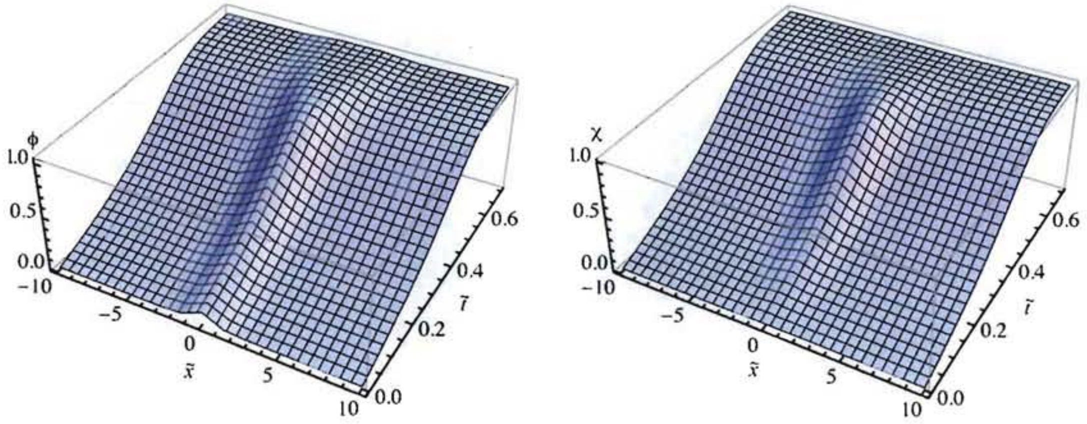
Subcritical hot spots would dissipate without producing a significant amount of reaction, if given that chance. In reality, subcritical hot spots in a detonation reaction zone are consumed by RTWs emanating from supercritical hot spots before that can happen. For supercritical hot spots, the energy released by reaction soon swamps that contained in triggering hot spots. Consequently a RTW soon "forgets" its starting conditions, such that all established RTWs are nominally identical. The criticality question is settled after a brief time; subsequently, the post-shocked, pre-burned explosive is left with a number density η of nominally identical (and ideally, randomly-centered) RTWs. This state of affairs is an underappreciated simplifying feature, with a likely complication being that RTW progress may be nontrivially staggered according to differing explosion times associated with supercritical hot spots of different sizes, peak temperatures, and temperature profiles.

NUMERICAL RESULTS FOR STEADY 1D WAVES

One may seek steady solutions to Eqs. 15 and 16 by attempting to eliminate $\tilde{x}$ and $\tilde{t}$ in favor of a composite variable $\xi = \tilde{x} - \tilde{V}\,\tilde{t}$, where $\tilde{V}$ is the yet-to-be-determined dimensionless propagation speed in Eq. 14. Doing so, one finds that the equations can only be expressed in terms of ξ alone if $j = 0$ (i.e., in the planar case). Consequently, the cylindrical and spherical cases do not possess steady travelling wave solutions. On the other hand, cylindrical and spherical waves become progressively more planar as they grow, and will propagate at essentially the plane wave speed above some radius. It is tempting to assume that all RTWs propagate at the plane wave speed despite any curvature, just as one often assumes that curved detonation shocks travel at the Chapman-Jouguet speed. We shall leave that subject for another time, and concentrate on steady plane waves only.

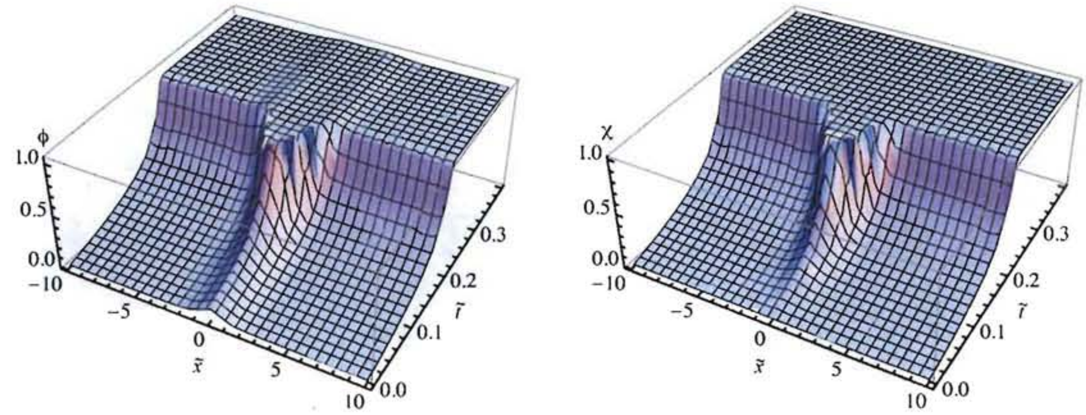
Solutions of Eqs. 15 and 16 for a first order reaction are plotted in Figs. 1-4 for four values of α, each progressive value of which is twice the proceeding one. In Fig. 1 ($\alpha = 3$), reaction is completely homogeneous in character. The hot spot perturbation simply "rides on top of" a homogeneous cookoff response. The behavior of Fig. 2 ($\alpha = 6$) is similar; however, comparing the two figures one can see that a slight amount of reaction occurs due to the hot spot. In Fig. 3 ($\alpha = 12$) the behavior is quite different. There is an induction time, followed by thermal explosion of the hot spot. Upon thermal explosion an RTW is initiated that propagates outward. At the same time, the material that it is propagating into is homogeneously cooking off. The upstream material cooks off completely when the RTW has reached the point $\tilde{x} = 5$. The behavior of Fig. 4 ($\alpha = 24$) is qualitatively like that of Fig. 3. Quantitatively, 1) thermal explosion of the hot spot occurs sooner, 2) homogeneous thermal explosion occurs sooner and more suddenly, 3) the RTW travels faster, and 4) the RTW travels farther (to $\tilde{x} = 8$) prior to homogeneous cookoff.

Presumably these trends continue as α is further increased; however, there are complications in doing so. In Sec. 2 I argued that RTWs would be expected to propagate fast enough to reproduce observed detonation behavior only if their structure is sufficiently shock-wave-like. Figures 3 and 4 demonstrate that this is in fact the case. What is not clear from these figures is that RTW structure becomes increasingly narrow (and hence increasingly difficult to calculate) as α increases. The computations in this study were performed using the *Mathematica* PDE solver, for which the highest value I have been able to calculate is $\alpha = 27$. Presumably, specialized algorithms employing shock-capturing methods could compute higher values. As we shall see in the following section, the current capability is adequate; however, an ability to compute higher values of α would be useful.



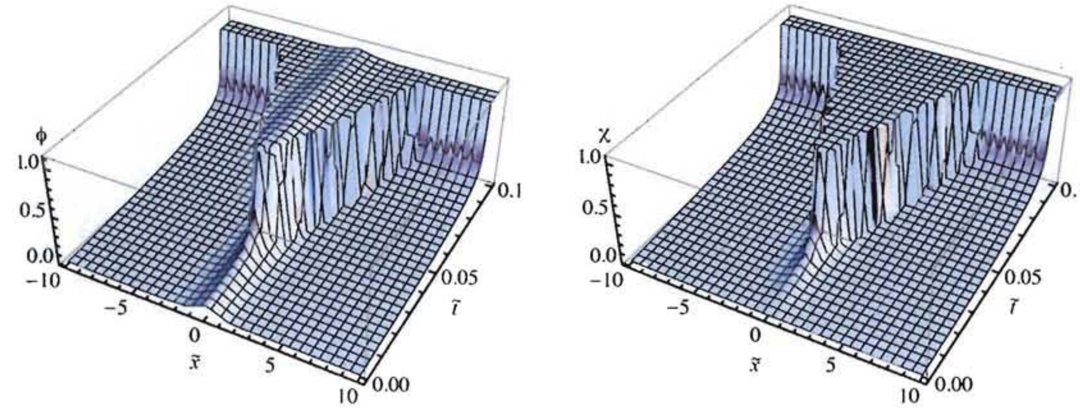
a) Dimensionless Temperature **b) Mass Fraction Reacted**

Figure 1: $\alpha = 3$. Reaction is homogeneous in character. The initial temperature perturbation "rides on top of" the homogeneous cookoff.



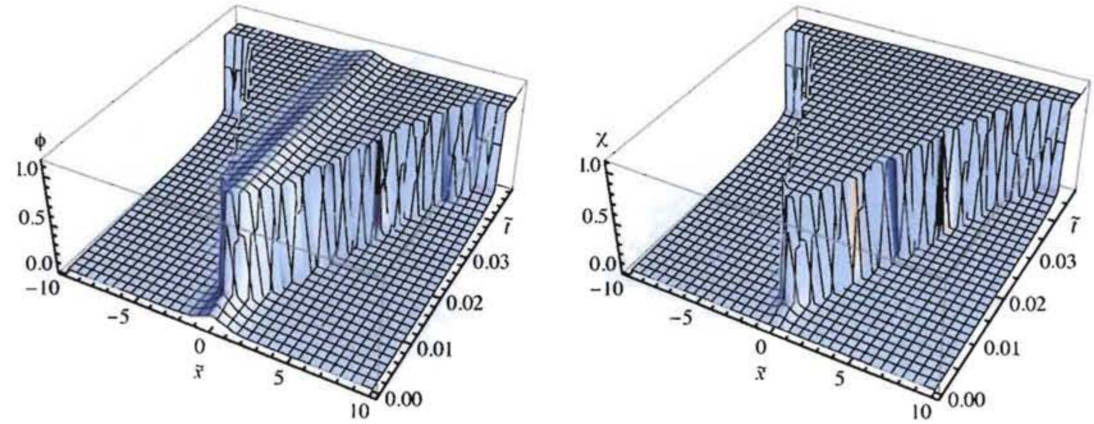
a) Dimensionless Temperature **b) Mass Fraction Reacted**

Figure 2: $\alpha = 6$. Reaction is substantially homogeneous, but transitional. By comparison to Fig. 1, one can see that the initial temperature perturbation contributes a small amount of reaction.



a) Dimensionless Temperature **b) Mass Fraction Reacted**

Figure 3: $a = 12$. Reaction is substantially heterogeneous. An obvious RTW emanates from the hot spot. Eventually, the material ahead of the RTW cooks off.



a) Dimensionless Temperature **b) Mass Fraction Reacted**

Figure 4: $\alpha = 24$. The behavior is qualitatively like, but more heterogeneous than, Fig. 3 (i.e., less reaction occurs ahead of the RTW prior to homogeneous cookoff).

DEDUCTION OF THE 1D STEADY WAVE SPEED

By judicious nondimensionalization together with the high activation energy approximation, we have reduced the problem of finding the RTW speed to the determination of a universal function $\tilde{V}[\alpha]$. It seems doubtful that $\tilde{V}[\alpha]$ can be derived analytically. If it can, solutions could evidently only be attained for sufficiently simple forms of $g[\chi]$—most likely the first order reaction assumed here. Lacking alternatives, I seek to deduce the form of $\tilde{V}[\alpha]$ by numerical calculations. At this point I make the distinction between an analytic *solution* and an analytic *formula*. Provided that we can numerically measure $\tilde{V}[\alpha]$ with good accuracy, we can fit an analytic formula that contains the full parameter dependence, just as if the solution were fully analytic. Such a solution serves the same purpose as a fully analytic solution, with minimal error in the fit region for judiciously chosen fitting forms.

The complication in finding $\tilde{V}[\alpha]$ is that the problem is scaled by the initial temperature, which the calculation assumes is the upstream temperature for all time. However, at the α–values I am able to calculate, the bulk material starts to cook off in the time necessary for the wave to become established and the speed to be measured. Hence, there is a value of α associated with the exponential term in the computation, and a different time-changing value of α associated with the upstream condition. Thus, the behavior that develops differs from that which was assumed at the outset. The rising upstream temperature causes the established wave to accelerate, as shown in Fig. 5.

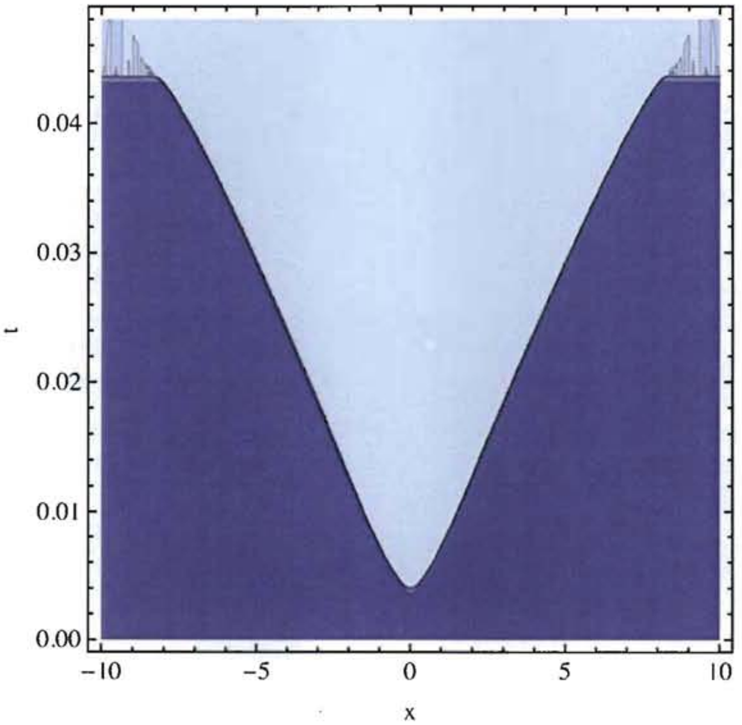


Figure 5: Contour plot for $\alpha = 12$. The established RTW accelerates as it travels into progressively hotter energetic material. This effect complicates the deduction of $f[\alpha]$.

There are a several ways that one could try to get around this problem. Firstly, if one had the capability to compute the RTW problem for a range of sufficiently large α, then the behavior would be sufficiently heterogeneous that, to an excellent approximation, ϕ would remain virtually zero ahead of the wave—over a long enough distance to obtain accurate wave speeds to pair with the calculated values of α. The problem with this method is that the behavior for smaller values of α (those that we are interested in, actually), would have to be extrapolated.

Secondly, one could assume that wave propagation is quasi-steady, and continuously update the valued of α used in the calculation to match the current upstream value. The result would not reflect how a real wave develops in time; however, the local speed $\tilde{V}[\tilde{t}]$, plotted parametrically versus $\alpha[\tilde{t}]$, would trace the desired curve. The known problem with that scheme is that the standard *Mathematica* solver I am using does not support this capability. Specialized algorithms would have to be written.

A third strategy would be to again assume that the wave is quasi-steady, and extrapolate the wave speed at calculable values of α, to its behavior in the large-α limit. This method does in fact work, but only because $\tilde{V}[\alpha]$ turns out to be very simple in form. To implement the extrapolation method, we begin by computing the RTW speed curves for several values of α, as shown in Fig. 6. Each curve has a "U" shape, because the wave speed is infinite at the initiating hot spot, and is also infinite at the point where volumetric thermal explosion occurs. To minimize any nonsteady effects, we pick off the speed at the minimum of each curve, where the acceleration is zero. The locus of these points is illustrated by the dashed curve.

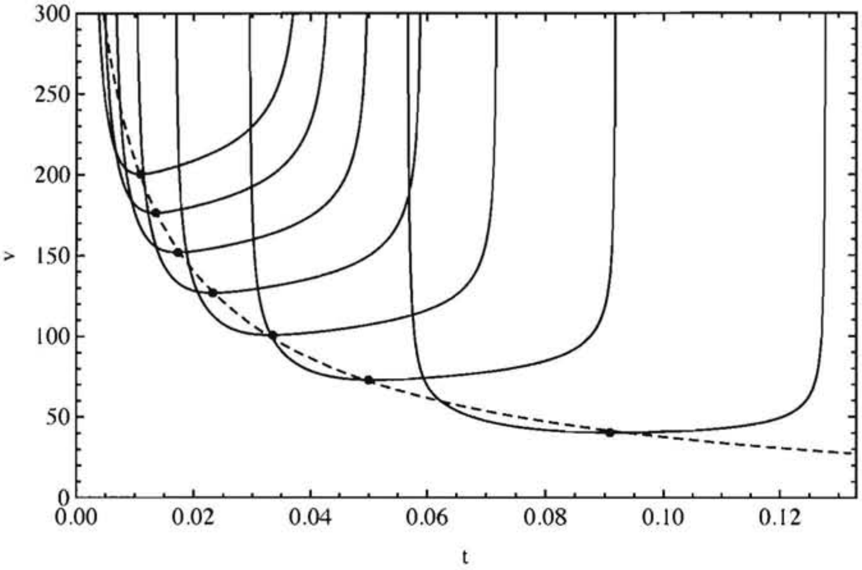


Figure 6: RTW speed curves for seven values of α. The minimum speeds (the points of zero acceleration) are sampled for further analysis.

Each of point sampled in Fig. 6 has a corresponding value of $\phi = \phi_\infty$ far ahead of the wave. These values are plotted in Fig. 7 as a function of α. The curve asymptotically approaches zero as α increases, decaying approximately as the inverse 3/2 power of α. Specifically, we find that at the largest computed value of α, ϕ_∞ is 1% of the unity burned-value. From this exercise we learn that at the largest computed value of α, the model assumptions are reasonably well satisfied at the minimum speed condition.

Figure 8 plots the speed points from Fig. 6 as a function of α. As α increases and ϕ_∞ decreases, the behavior looks to be approaching a straight line through the origin. One may argue that because alpha depends linearly upon q, and heat release is required to produce a wave speed, that $\tilde{V}[0] = 0$. Constrained from both sides, there is little choice for the function to be anything other than a straight line through the origin.

I therefore fit the data with the following fitting form, which exponentially relaxes to a straight line through the origin:

$$\tilde{V}_{fit}[\alpha] = a\,\alpha - b\,e^{c\,\alpha} = \tilde{V}[\alpha] - b\,e^{c\,\alpha}. \tag{18}$$

As noted in Eqs. 18, the best-fit line determined in this manner is $\tilde{V}[\alpha]$. Note that the value of a computed by the least-squares analysis is controlled by the relaxation rate. Therefore, the accuracy to which a can be determined depends on how well the assumed exponential relaxation law fits the numerical data points. Figure 8 shows the agreement to be excellent.

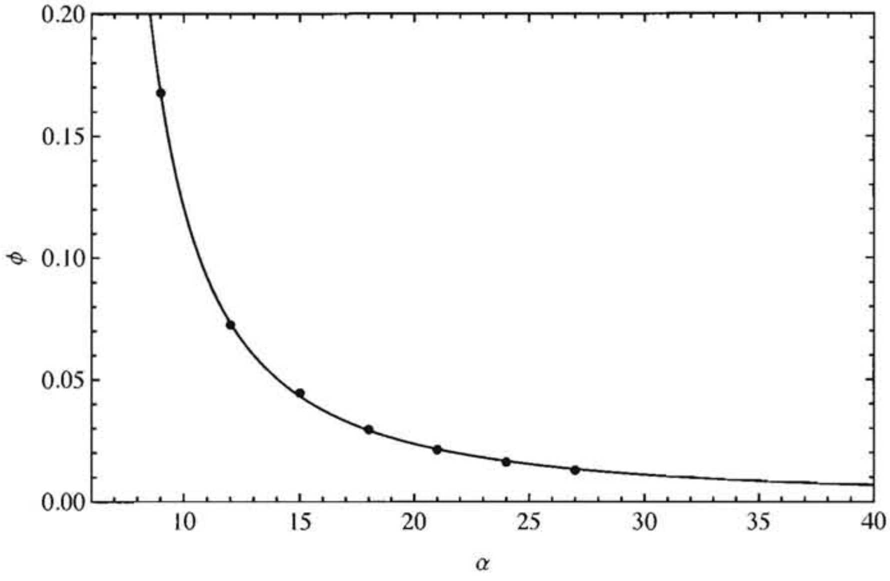


Figure 7: Plot of the dependence of dimensionless temperature ϕ_∞ far ahead of the wave, upon α. At the highest computed value of α, ϕ_∞ is 1% of the burned value.

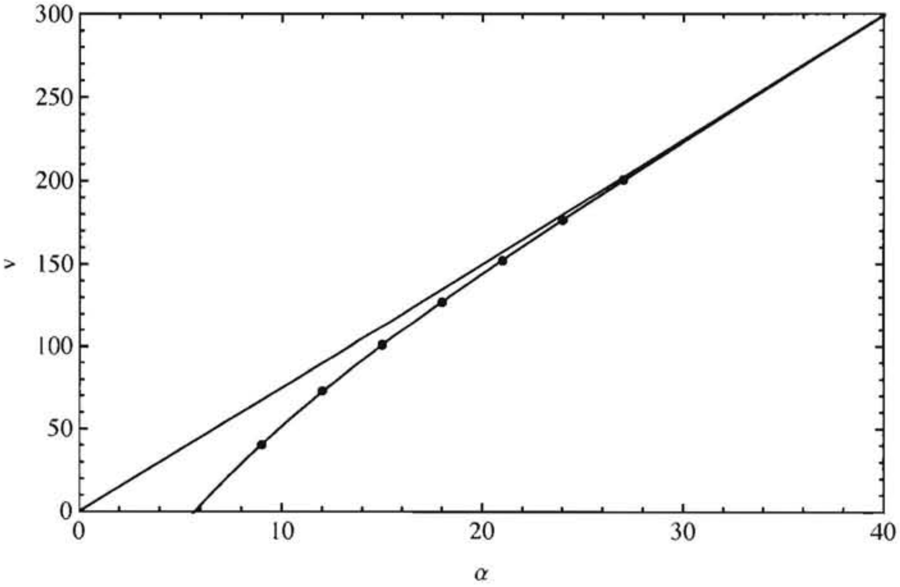


Figure 8: Plot of the dimensionless wave speed versus α. The trend looks to be approaching a straight line through the origin.

By this means we determine that $\tilde{V}[\alpha] = 7.48\,\alpha$. Thus we obtain the final wave speed result, which is

$$V = \frac{7.48\,\tilde{q}\,\sqrt{\kappa\, Z}}{\tilde{T}_0^2\, \mathrm{e}^{1/(2\,\tilde{T}_0)}}. \qquad (19)$$

Written in fully dimensional form, Eq. 19 is:

$$V = 7.48\,\sqrt{\kappa\,Z}\,\left(\frac{q\,T^{*}}{c\,T_0^2}\right)\exp\left[\frac{-T^{*}}{2\,T_0}\right]. \tag{20}$$

The argument is that Eqs. 19 and 20 hold for essentially all α-values in which a quasi-steady RTW is observed, the reason that the points in Fig. 8 deviate from the linear trend being that the calculation did not remain properly normalized as it proceeded. Thus, Eqs. 19 and 20 should hold generally, except where the upstream material is rapidly cooking off.

APPLICATION TO PBX 9501 AND PBX 9502

The parameters needed for numerical examples, collected from various sources, are listed in Table 1. HMX-based explosives in general, and PBX 9501 in particular, have been very well studied. Good data exists for the parameters that we need. Most importantly, Henson et al.[11] have developed a wide-ranging set of Arrhenius parameters, based on a variety of different classes of experiments. Unlike most parameter sets that were obtained for slow decomposition (and of dubious applicability for other conditions), Henson's parameter sets are applicable in the detonation regime.

Table 1: RTW-Relevant Parameters for PBX 9501 and PBX 9502

Class	Property	Symbol	Unit	PBX 9501	Ref #	PBX 9502	Ref #
Arrhenius Parameters	Activation Temperature	T^*	K	17,910	11	26,000	here[a]
	Pre-Exponential Factor	$\log[Z]$	log[1/s]	12.8	11	16	here[a]
	Specific Heat Release	q	kJ/g	5.6	12	3.6	12
VN Spike Conditions	Temperature	T_{vn}	K	2,580	13	1,567	14
	Pressure	P_{vn}	GPa	56.9	13	42.8	14
	Density	ρ_{vn}	g/cm^3	3.070	13	3.049	14
	Specific Heat	c_{vn}	J/(g-K)	2.1	13	2.1	14
	Thermal Conductivity	k_{vn}	W/(m-K)	2.5[b]	15	3.1[c]	15,16
	Thermal Diffusivity	κ_{vn}	m^2 /s	3.9×10^{-7}	mix[d]	4.8×10^{-7}	mix
	Dimensionless Heat	$\tilde{q}_{vn}$	----	0.15	mix	0.066	mix
	Dimensionless Temperature	$\tilde{T}_{vn}$	----	0.14	mix	0.060	mix
	Heterogeneity Parameter	α_{vn}	----	7.1	mix	18.1	mix
CJ Conditions	Temperature	T_{cj}	K	3000	13	3,126	14
	Pressure	P_{cj}	GPa	34.8	13	28.3	14
	Density	ρ_{cj}	g/cm^3	2.430	13	2.525	14
	Specific Heat	c_{cj}	J/(g-K)	2.1	13	2.2	14
	Thermal Conductivity	k_{cj}	W/(m-K)	1.9[b]	15	2.3[c]	15,16
	Thermal Diffusivity	κ_{cj}	m^2 /s	3.6×10^{-7}	mix	4.1×10^{-7}	mix
	Dimensionless Heat	$\tilde{q}_{cj}$	----	0.16	mix	0.063	mix
	Dimensionless Temperature	$\tilde{T}_{cj}$	----	0.17	mix	0.12	mix
	Heterogeneity Parameter	α_{cj}	----	13.7[e]	mix	30.1[e]	mix

[a] These parameters are deduced from internal evidence. [b] This value is for detonation products. In this model, thermal properties are the same for reactants and products. [c] Lacking PBX 9502 data under detonation conditions, this value is the 9501 value at detonation conditions, scaled by the 9502/9501 values at STP. [d] "mix" means that the parameter is a combination of other parameters, the sources of which have already been identified. [e] Value is based on unreacted material at the P_{cj}.

Let us first consider PBX 9501 (95 wt% HMX, 5 wt% binder). At the von Neumann (VN) spike, $\alpha = 7.1$. Examination of Fig. 2 indicates that the reaction behavior is substantially, though not entirely, homogeneous. Menikoff[13] has previously noted that PBX 9501 detonation is well predicted by a homogeneous Arrhenius rate law, and the present result is basically consistent with that result. Because PBX 9501 is a heterogeneous composite material, hot spots are generated in the shocked explosive. However, these hot spots and the heterogeneity that causes them would appear to have a minimal effect on the ensuing reaction. In such situations I say that heterogeneity is *incidental* in its importance, in that reaction proceeds in a similar way with or without it.

Note, however, that this HMX result is for a CJ wave. Values of α for convexly curved detonations will be higher. Because the CJ wave shows some signs of heterogeneity, weaker curved waves will evidently exhibit heterogeneous reaction. In a sufficiently large rate stick, for example, reaction will be largely homogeneous near the axis, and heterogeneous near the edges, with some sort of transition region in between. Thus, I would say that material heterogeneity is *incidental* near the center, and *essential* near the edge. HMX explosives are interesting in this sense, because they are "transitional forms". Primary explosives (PETN perhaps?) will exhibit incidental heterogeneity throughout a charge; whereas, IHEs (PBX 9502, as we shall show) will exhibit essential heterogeneity throughout a charge. By this means one can identify three classes of explosives with respect to heterogeneity effects in established detonations.

Although there is not much tendency for RTWs to develop in PBX 9501 (at least near the VN spike), we can nevertheless compute a wave speed using Eq. 19. The predicted VN value is 2505 m/s. In light of the discussion in Sec. 2, this number is a physically sensible value. Not all Arrhenius parameter sets give sensible values for V; rather, I attribute this success to the applicability of Henson et al.'s wide-ranging Arrhenius parameters. One need only examine PBX 9502 to realize that not all Arrhenius parameter sets give sensible values of V. Several workers have produced Arrhenius parameters for TATB-based explosives, with activation temperatures ranging from ~16,000 K to ~30,0000 K. The corresponding predicted wave speeds can range from O[10] m/s to O[10^5] m/s (plus or minus two orders of magnitude).

This behavior illustrates that, although I have argued that RTW speeds cannot physically exceed the sound speed in the reacted material, the formula Eq. 19 knows nothing of acoustic limitations. The speed is very sensitive to the Arrhenius parameters, and can take on most any value depending on the values of T^* and Z. On the other hand, this makes the speed formula of Eq. 19 a sensitive selector of Arrhenius parameters. When one plots the collection of available Arrhenius parameters in $\log Z$-T^* space, one finds that the collection lies on a straight line. This is the well-known *kinetic compensation effect*.

Restricting parameters to the line of "admissible" values, one finds that only a narrow range of the domain produces physically sensible values of V. In particular, the parameter set $\log Z = 16$, $T^* = 26{,}000$ K gives similar speeds as were predicted for PBX 9501. These are the parameters listed in Table 1, and which I shall use for examples. This parameter set lies somewhere in the middle of the collection of parameter sets that previous workers have proposed. Hence, the RTW wave speed provides a sensitive and sensible means of selecting between a large number of equally plausible Arrhenius parameter sets.

Using the parameters $\log Z = 16$, $T^* = 26{,}000$ K, we find that at the PBX 9502 VN spike, $\alpha = 18.1$. Examining Figs 3 and 4, we observe that this value puts the behavior solidly in the heterogeneous regime. α increases as the material flows through the reaction zone, to a value of ~30 at the CJ point. Clearly, α is also greater for a convexly curved detonation as noted in connection with PBX 9501. Thus, we conclude that heterogeneity is everywhere *essential* for a PBX 9502 detonation. This conclusion holds for any plausible value of T^*.

In computing α at the CJ state, I have assumed that the upstream material remains unburned; i.e., that the behavior is perfectly heterogeneous. To simply estimate the unburned temperature at the CJ state, I assume isentropic expansion with an isentropic exponent of 3. That is,

$$T = T_{vn} \left(\frac{P}{P_{vn}} \right)^{(\gamma-1)/\gamma}, \ \gamma = 3. \tag{21}$$

The temperature of unburned HE at the CJ state is determined by evaluating Eq. 21 at P_{cj}.

Because the temperature of unburned explosive upstream of the RTWs decreases through the reaction zone, their speed also decreases. With the aid of Eq. 21, we may (neglecting domain dilation at this point) estimate the magnitude of this effect. With the assumed Arrhenius parameter set, the estimated RTW speed at the VN point is 2356 m/s. The estimated speed at the CJ point is 350 m/s. Hence, in this example rate slows by a factor of seven through the reaction zone. In his review of experiments related to hot spots[17], B. Davis catalogs experimental evidence that hot spots (as he colorfully describes it), "pop and go out". He further notes that for unknown reasons, it is as if part of the explosive behaves as if it were dead (i.e., inert). The exponential dependence of the RTW speed on temperature provides a means by which these effects could occur.

The sensitive dependence of the RTW speed upon temperature may also be related to several other anomalous properties of TATB-based explosives. The PBX 9502 reaction zone has a narrow (HMX-like) region in which some reaction occurs promptly, followed by a very long tail. This property causes an upturn in the diameter effect curve at large stick sizes, and an upturn in the detonation shock dynamics (DSD) calibration curve at small curvatures. The reason for this effect is usually imagined to be directly related to TATB chemistry. Although this may very well be so, the notion that RTW propagation is exponentially sensitive to temperature provides an alternative explanation for a fast reaction start, followed by a long tail. At this point in time, TATB has rather unique sensitivity properties. Unfortunately, there are few other explosives with which to compare it. As additional IHEs are developed and tested, we may find that properties that have been assumed to be TATB chemistry-specific, are actually a generic attribute of explosives for which heterogeneity is fully essential.

Most reactive burn models use a constant specific heat release with a state-dependent burn rate. A sufficiently strong state-dependence of the rate can cause reactions to freeze on relevant time scales, such that they may not complete even when the flow has expanded to atmospheric pressure. When this is the case, rate effects result in a decrease in energy output. Thus, the two effects can be practically coupled in a way that is hard to separate. Depending on the particulars, the exponential temperature dependence of RTW propagation speed may manifest as a severe rate effect, causing reaction to freeze.

The practical difficulty with frozen reactions is that the effect depends on conditions. Whether a reaction is homogeneous or heterogeneous, the freezing process depends on the pre-detonated HE temperature. The reason is that reaction rates are highly state-sensitive. Explosive that is hotter before the detonation shock is also hotter after. It therefore burns faster and more completely prior to freezing. For a heterogeneous reaction, the freezing process also depends on the material microstructure, and hence the HE the material lot. The reason for this dependence is that different material structures lead to different values of the RTW number density, η. Higher η -values consume the reactants faster and more completely before reaction freezes.

CONCLUSIONS

I have illuminated the properties of reactive thermal waves, or "hot spot burn". I showed that curved RTWs do not propagate at constant speed, but approach steadiness as they burn outward. Planar RTWs have a steady traveling wave solution in the limit that cookoff of the upstream material is negligible. Otherwise their propagation is quasi-steady, with the wave speed depending on the current upstream temperature. I have derived an analytic expression for planar RTW speed, the most important feature of which is that the speed depends exponentially on the upstream temperature.

The degree of reaction heterogeneity induced by an individual supercritical hot spot depends on a single parameter, which I have called α. For α-values less than about 10, reaction is substantially homogeneous. For α-values greater than about 10, reaction is substantially heterogeneous. The more α is increased, the more heterogeneous reaction will be. The reasons are that 1) less reaction occurs ahead of the wave prior to bulk cookoff, and 2) RTWs propagate farther before bulk cookoff. For a given RTW number density η, more material is consumed via RTWs, and less by homogeneous reaction, as α increases.

The RTW speed is sufficiently sensitive to Arrhenius parameters that one is able to use it to substantially narrow the range of admissible parameters that lie on the kinetic compensation effect line. I have performed this exercise for TATB, and suggest that $\log Z = 16$, $T^* = 26{,}000$ K, are good values to use in the detonation regime.

The exponential dependence of the RTW speed upon temperature can potentially explain a number of non-ideal "reaction freezing" effects that have been observed and/or are suspected for insensitive explosives such as TATB. In particular, it explains the effect of detonation properties upon PBX 9501 material lot.

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