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TITLE PREDICTIVE MODELS FOR THERMAL HAZARDS

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PREDICTIVE MODELS FOR THERMAL HAZARDS

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Many self-heating accidents with energetic materials have occurred when operations that have been done safely on a small scale are attempted on a larger scale. They have also occurred when a material is heated for a longer time or to a higher temperature than is normal for its processing or storage, such as might be caused by equipment malfunction or power failure.

To prevent self-heating accidents, we must be able to predict the critical temperature for the size and shape of the material we are interested in. The critical temperature (T_c) is defined as the lowest constant surface temperature at which a material of a given size and shape will self-heat to catastrophic destruction. This can be burning, explosion, or detonation, and because it is related to heat flow, it is dependent on the geometry of the system. As size increases, the critical temperature decreases, as shown in Figure 1. The shape also affects the T_c, so that a sphere will have a higher T_c than any other shape with the same radius or half thickness, as shown in Figure 2 for PBX 9501, plastic-bonded explosive.

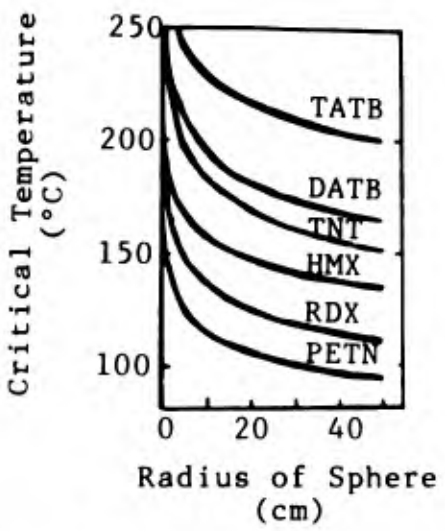

Figure 1. Effect of size on critical temperature.

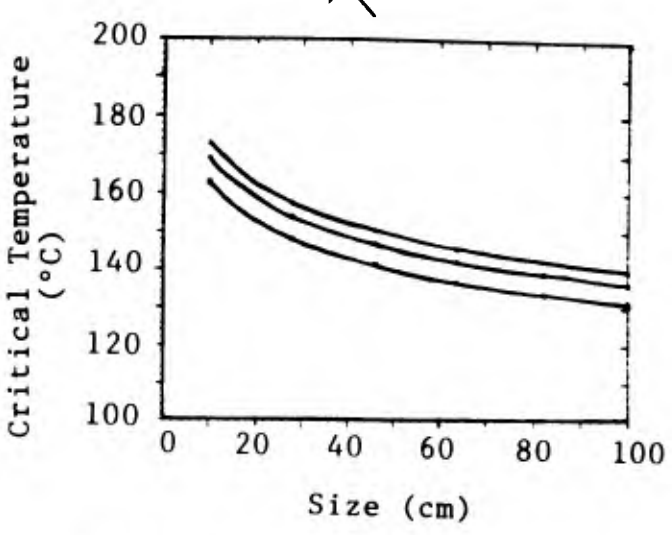

Figure 2. Effect of shape on critical temperature. Shapes shown are sphere (top), cylinder (middle), and slab (bottom).

The critical temperature can be calculated by the Frank-Kamenetskii[1] reactive-heat-flow equation for solid-state, unstirred systems,

$$\frac{E}{T_c} = R \ln\left[\frac{a^2}{\delta\lambda} \cdot \frac{\rho Q Z E}{T_c^2 R}\right] ,$$

or the Semenov[2] equation for liquid, stirred systems,

$$\frac{E}{T_c} = R \ln\left[\frac{V}{S\beta} \cdot \frac{\rho Q Z E}{T_c^2 R}\right] ,$$

where T_c = critical temperature, Kelvin
E = Arrhenius activation energy, cal/mole
Z = pre-exponential (frequency factor), s^{-1}
R = gas constant, 1.9872 cal/K mole
a = radius of sphere or cylinder, or half-thickness of slab, cm
ρ = density, g/cm^3
Q = heat of reaction, cal/g
δ = shape factor; 3.32 for sphere, 2.72 for l = d cyl., 0.88 for an infinite slab
λ = thermal conductivity, cal/°C s cm^2
V = volume, cm^3
S = surface area, cm^2
β = heat flow coefficient of vessel, cal/°C s cm^2

In order to calculate the critical temperature, we need to know the kinetics of the decomposition. We use a differential scanning calorimeter (DSC) to measure the rate of heat evolution, from several samples at dif-

ferent isothermal temperatures. This rate of heat production is proportional to the absolute rate of the total chemical reactions at any given instant, as follows:

$$\frac{dq}{dt} = Q\frac{d\alpha}{dt} = kQf(\alpha) \quad ,$$

where Q = heat of reaction

α = fraction decomposed at any time

k = chemical rate constant

f (α) = the applicable rate law.

The DSC rate curve will give us the rate of heat production as a function of time. If we calculate the area under the curve with Simpson's rule we can find the fraction decomposed at any given time, α, by dividing the partial area to that time, a, by the total area, A, as shown in Figure 3. We can then calculate $d\alpha/dt$.

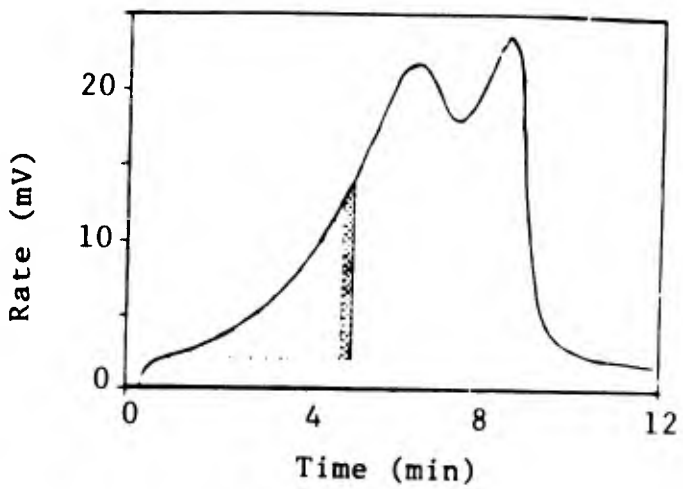

Figure 3. Rate curve.

Partial area, a

Change in area, $\frac{\Delta\alpha}{\Delta t}$; $\lim_{t \to 0} = \frac{d\alpha}{dt}$

Total area under curve, A, is calculated using an extrapolated final baseline.

To find the rate constant, we must use a rate law that will linearize the data for the part of the reaction that represents catastrophic self-heating. Most computer software programs use a normal rate law for the decomposition. A first-order rate law assumes maximum rate at the beginning, as shown in Figure 4. Most explosives, however, are complex, and decompose more nearly according to an autocatalytic-type rate law as shown in Figure 5, where the heat evolution builds up to a peak after intermediate products have been formed.

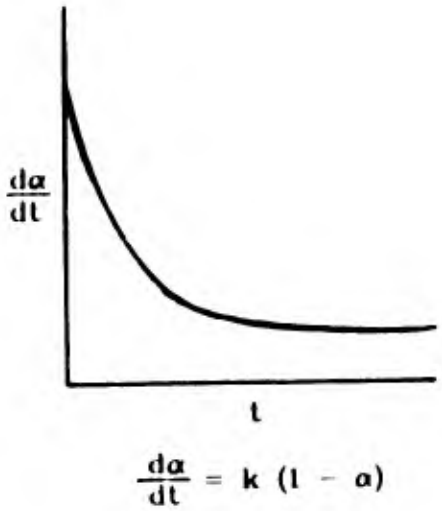

Figure 4. Idealized first-order rate curve.

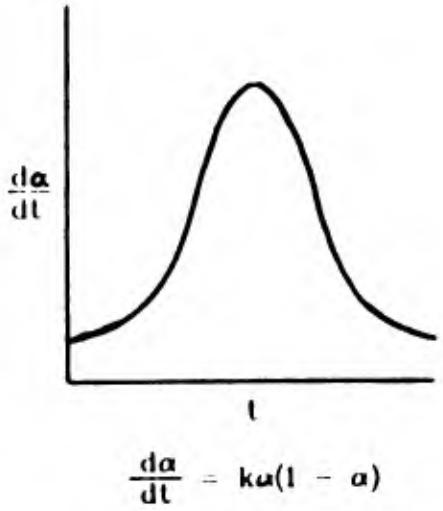

Figure 5. Idealized autocatalytic-type rate curve.

The total heat evolution may be expressed by the equation

$$\frac{d\alpha}{dt} = k_1 + k_2(1-\alpha)^n + k_3\alpha^p(1-\alpha)^q \quad ,$$

where each term may represent several simultaneous or sequential reactions. For thermal hazards predictive models, we use the global heat, since it is the rate of the total heat evolution that will determine whether the decomposition will be catastrophic.

The rate curve for triamino trinitrobenzene (TATB) is shown in Figure 6. If we use its data to calculate the values necessary for an autocatalytic rate law plot, we get the curve shown in Figure 7.

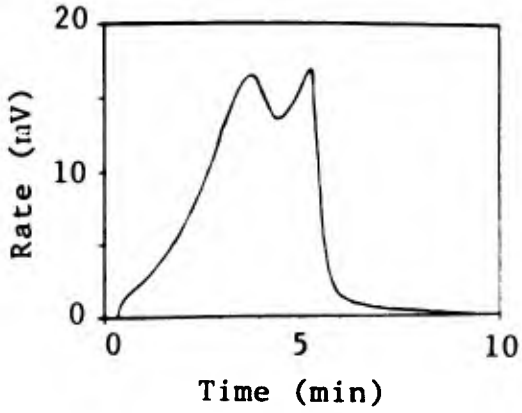

Figure 6. Isothermal DSC rate curve for TATB at 630 K.

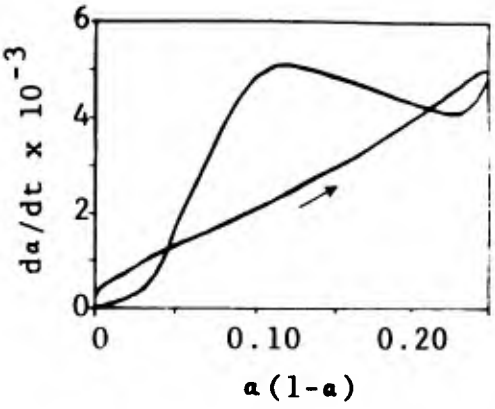

Figure 7. Autocatalytic-type rate law curve for TATB. The curve folds back on itself at $\alpha(1-\alpha) = 0.25$.

The slope of the linear portion is the rate constant, k, for that temperature.

To be valid for our calculations, the rate constants found from runs at different isothermal temperatures must also be from data linearized by the same rate law and for the same per cent decomposition. Otherwise we will not be comparing rate constants for the same decomposition mechanism, and an Arrhenius plot will not be valid.

Occasionally, rate constants for energetic materials can be calculated from normal rate laws. We then find the linear section from a plot such as that shown in Figure 8. The slope of the linearized segment will be the order, and ln k for that order can be found by extrapolating to 0. Figure 9 shows an order plot for Composition B, a mixture of 59.5/39.5/1 RDX*/TNT/wax. Again, the order at different isothermal temperatures must be the same, or

*Cyclotrimethylene trinitramine

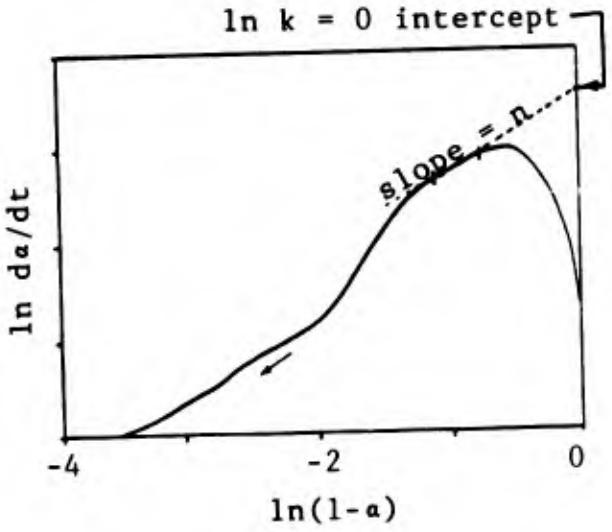

Figure 8. Order plot. Positive slopes represent data from the decay portion of the rate curve.

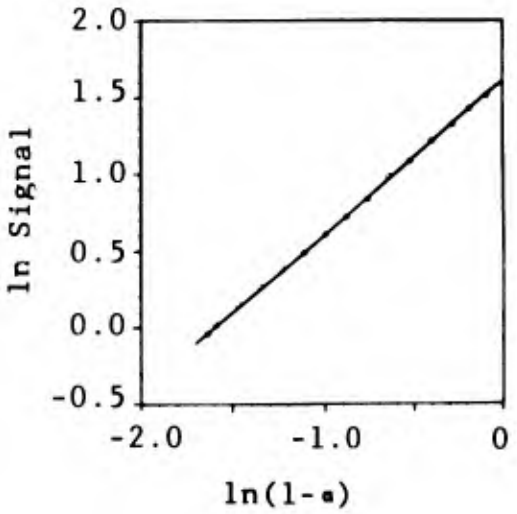

Figure 9. Order plot for Comp B at 500 K. The experimental order is 1.0.

nearly so, for the Arrhenius plot of the rate constants to be valid. When the orders at different temperatures are different, either the mechanisms have changed, or different parallel reactions have become predominant at the new temperatures.

A function might be found that would linearize the data throughout the decomposition, but for energetic materials with different decomposition mechanisms, such a function would have little chemical validity.

After we know the rate constants from the different isothermal runs, as calculated from any rate law that has chemical meaning, an Arrhenius plot can be made, as shown in Figure 10 for Comp B. The activation energy and pre-exponential are determined from the slope, which is equal to -E/R.

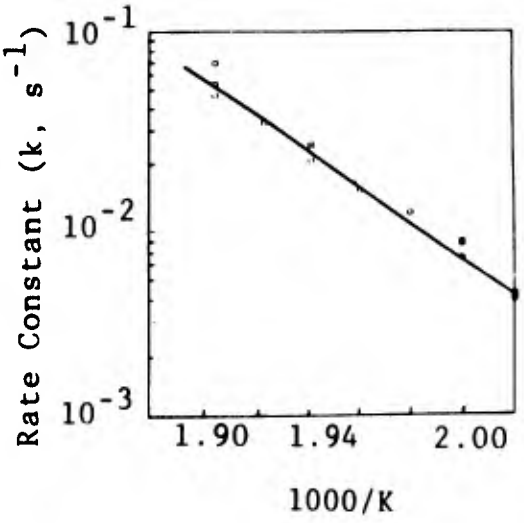

Figure 10. Arrhenius plot for Comp B, obtained from first-order data.

As may be expected, linear segments from different parts of the rate curves may give different rate constants, thus different sets of values for E and Z. Only one set will accurately predict the critical temperature for all sizes and shapes, so we must verify that the values we have chosen are the ones that represent the mechanisms that control self-heating.

The thermal properties of an explosive may differ greatly from batch to batch. The overall rate of the chemical reactions that occur during the induction time is determined by the number and energy of high-free-energy zones present. These may be caused by such things as crystalline imperfections and impurities. Figure 11 shows the differences in the rate curves of several kinds of cyclotetramethylene tetranitramine (HMX).

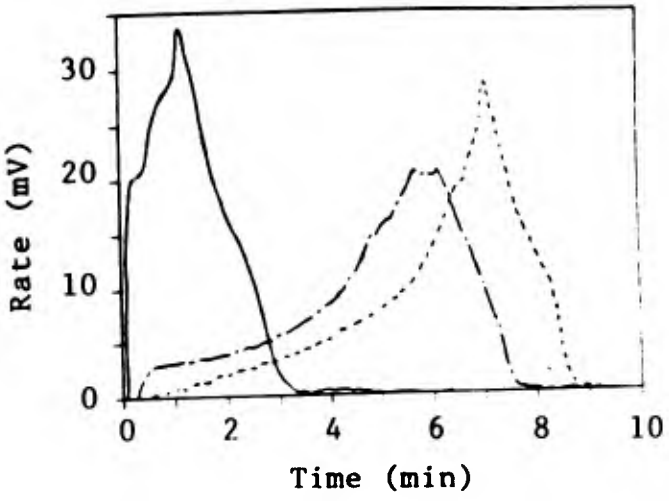

Figure 11. Isothermal rate curve data for three samples of production-grade HMX. Samples approximately 1 mg, run at 545 K.

We use a separate, small-scale laboratory test* to verify our results. A small sample, usually about 40 mg, is sealed into an empty blasting cap, and its thickness is measured. This sample is lowered into a molten metal bath at a constant, known temperature, and the time to explosion is measured. This test is repeated at different temperatures until we have found the temperature below which no explosions will occur.

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*The test is a modification of the one described by Henkin and McGill[3].

We can calculate the critical temperature for this size and shape with our DSC values for E and Z in the Frank-Kamenetskii equation. If the calculated T_c equals the experimental T_c, we feel we can make predictions for other sizes and shapes with some confidence, and this becomes our predictive model. If the predicted and experimental temperatures do not agree, however, we may not have calculated our kinetics values properly, or there may be errors in the other variables. A discrepancy may also indicate a significant pressure effect. The DSC tests are done at atmospheric pressure under a nitrogen purge gas, and the time-to-explosion test, while not able to witnstand high pressures, confines the gases up to several atmospheres.

When the predictive model needs further verification, or when there is no predictive model and information is needed about whether a material will self heat catastrophically at a given temperature, a large-scale test can be done. We use a pair of 1-liter heating mantles around liter flasks of castable explosives, or a pair of machined hemispheres of explosives if they will not melt at the test temperature. Thermocouples are placed at several positions in each mantle, and the temperature controllers are adjusted so that the hottest spot in each mantle controls its temperature. Thermocouples may be placed in the center of the sample if it is desired, and recorders can be attached to the thermocouples to chart the temperature excursion as the sample heats. The explosive assembly is placed in a 6-ft steel-walled containment vessel, and brought to a predetermined isothermal temperature as quickly as possible. It is then left until the sample self heats, which may be as long as several weeks if the experimental temperature is very near the critical temperature.

The small-scale time-to-explosion test is also good for ranking explosives in order of thermal stability. The compatibility of materials in formulations can also be easily checked, as illustrated by the HMX-Pb mixtures in Figure 12.

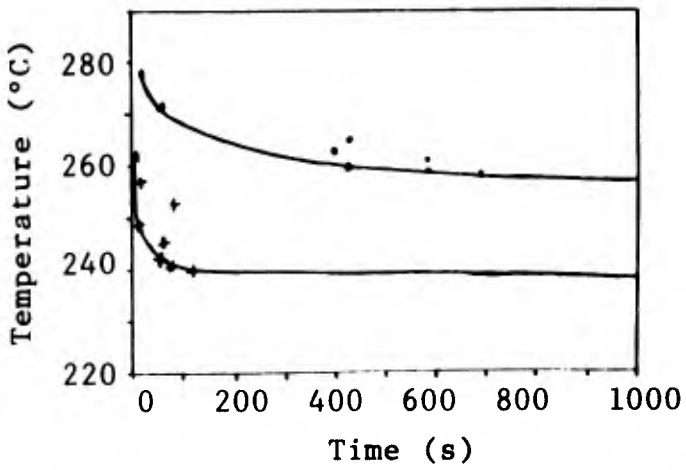

Figure 12. Critical temperature data for HMX (top) and HMX/Pb 50/50 vol% (bottom).

This test can also be used as a quality control test. Times to explosion may be affected by crystalline defects in the material, or particle sizes, even when the critical temperature may not vary significantly. Impurities and additives such as are found in fertilizer-grade ammonium nitrate can cause a difference of about 100° in the critical temperature at these small sizes, as well as a shorter time to explosion at the same temperature. Such decreases might cause an unacceptable decrease in the safety margin for processes conducted near the critical temperature.

REFERENCES

1. D. A. Frank-Kamenetskii, Diffusion and Heat Transfer in Chemical Kinetics, Plenum Press, New York, NY, 1969.

2. N. N. Semenov, Chemical Kinetics and Chain Reactions, Oxford University Press, London, 1935.

3. H. Henkin and R. McGill, Ind. Eng. Chem., 44 (1952) 1391.