LAL-81-9 C.3

March 1981

THERMAL HAZARDS OF EXPLOSIVES

Raymond N. Rogers

Los Alamos
Los Alamos National Laboratory
Los Alamos, New Mexico 87545

An Equal Opportunity Employer Operated by the University of California

UNITED STATES
DEPARTMENT OF ENERGY
CONTRACT W-7405-ENG. 36

INTRODUCTION

How fast and how far can a high-performance military airplane fly before its own weapons get hot enough to destroy it? The answer to this question depends on the weapons' location and thermal stability. A weapon stored outside an airplane causes shock wave interactions with generation of considerable heat, whereas a weapon stored in a bomb bay does not cause this problem.

Explosives are high-energy materials. They can self-heat to ignition or explosion from the heat generated in flight, hot guns, and accidental fires, as well as from the heat required for their fabrication. To handle high-energy materials safely, we must be able to predict their response to heating. Developing methods to predict heating response has entailed some extremely interesting chemical work at the Los Alamos National Laboratory. The chemical principles of hazards predictions also can be used to predict the effects of age on explosives; that is, at what age will a weapon fail to function as planned or become dangerous?

The thermal safety of any device involving high-energy materials depends on the balance between the rate at which the material generates heat and the rate at which heat flows from the device (Fig. 1). This balance depends on the shape and size of the device, its thermal conductivity, and the chemical reaction rates in its high-energy material.

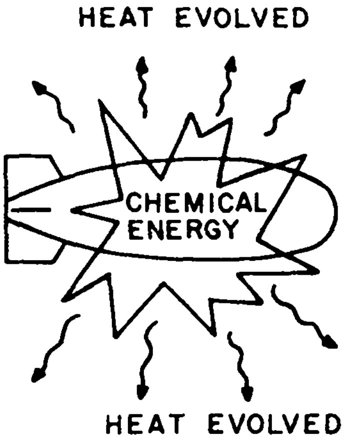

Fig. 1.
A weapon will self-heat to explosion if the chemical energy produced by decomposition of the weapon's high-energy material cannot escape as rapidly as it is formed.

Chemical reactions occur at some rate at every temperature above absolute zero, but these rates usually change very rapidly with temperature change. Given enough time, all high-energy materials will self-heat to ignition or explosion at *some* temperature. Predicting this temperature is somewhat like predicting the critical mass of a fissionable material. The lowest temperature at which a high-energy material of a given shape and size will self-heat to ignition or explosion is called its critical temperature. Figure 2 shows that the critical temperatures of explosives of different thermal stability vary with size. The curves suggest that the results of safety experiments on one particular size and shape cannot be applied to other sizes and shapes without using a mathematical model to make a "translation." Theoretically, a sphere of TNT that is 1 km (0.6 mi) in diameter and weighs 906 megatons would self-heat to explosion spontaneously at normal room temperature. Less stable materials can become hazardous at much smaller sizes.

The most important factor determining the rate at which heat escapes from a high-energy material or device is its thermal conductivity, which can be measured by standard methods. However, measuring the chemical factors that determine the heat production rate is more difficult.

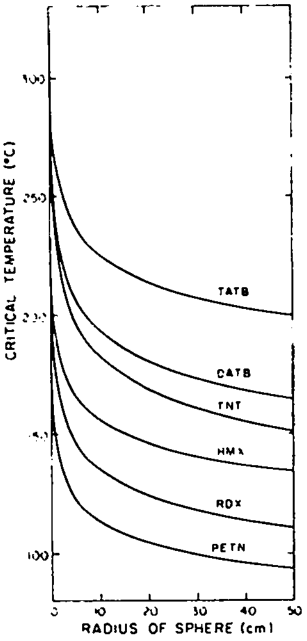

Fig. 2.
Critical temperature varies with size in all explosives. TATB is the "insensitive explosive" used in new US nuclear weapons to improve safety; DATB has been used in several air-to-air rocket systems; HMX is the most powerful explosive produced in large amounts; RDX is an important military explosive; and PETN is used in military and commercial detonators and blasting caps.

CHEMICAL REACTIONS AND HEAT

Most methods that measure chemical reaction rates involve periodic measurements of the unreacted material or selected reaction products. However, when questions about self-heating are asked, it seems only logical to measure heat.

All chemical reactions involve heat. A specific amount of energy is required to activate the molecules to make the reaction possible, and a specific amount of energy is evolved from each chemical reaction. The difference between the activation energy and the evolved energy determines the "heat of reaction," which can be positive or negative. Some reactions require heat and some reactions produce it. For our purposes, a useful fact concerning chemical energy is that the rate at which it appears is proportional to the rate of the chemical reaction.

Chemical reaction rates usually change drastically with temperature change. In the simplest reactions, the energy required to activate the molecules can be determined by measuring how much the chemical rate varies with temperature change, and the activation energy can be used to predict the rates at all other temperatures. However, explosives react by such complex routes that the observed activation energy does not represent the exact amount of energy required to activate a specific molecule. Still, the observed activation energy provides us with a useful predictive model for rates at other temperatures.

The activation energy required for a pound of normal explosive is about equal to the food energy in a very small slice of pumpkin pie, but the reaction heat is about equal to the food energy of half the pie. The startling effect of high-energy materials is due to the speed with which the energy can appear.

MEASUREMENT OF RATES FOR EXPLOSIVES

Using a differential-scanning calorimeter (Fig. 3), we determine the chemical reaction rates by measuring the rates at which heat evolves. This instrument compares the temperature of an explosive sample with the

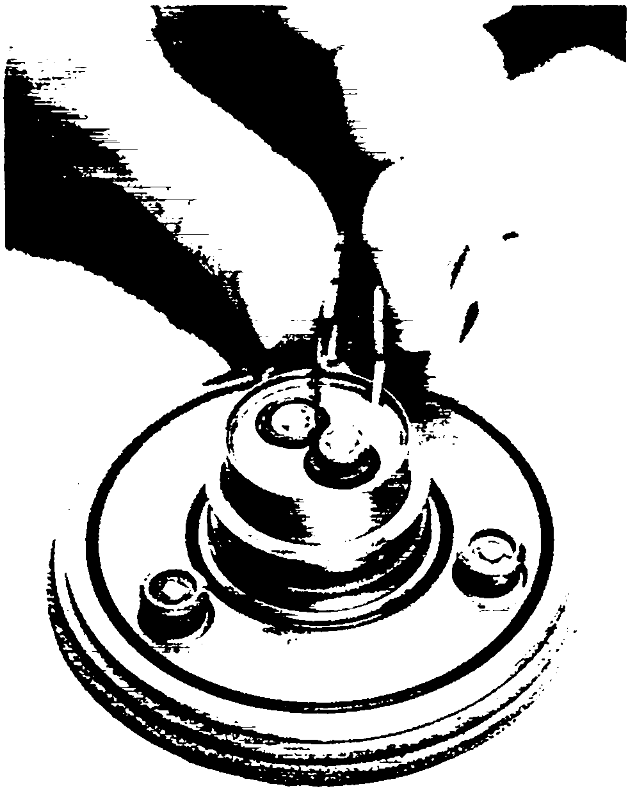

Fig. 3.
A very small sample of explosive encapsulated in an aluminum cup is placed in the differential-scanning calorimeter.

temperature of an inert material and keeps the two temperatures exactly the same. The energy required to keep the sample and the reference at the same temperature is measured. If the explosive sample produces heat, energy is supplied to the reference to make its temperature the same. The amount of energy required will be proportional to the explosive's reaction rate.

Figure 4 shows two curves obtained with the same explosive but at different constant temperatures. A difference of only 10°C greatly affects the rate at which energy is produced and at which the reaction approaches completion. Computer analysis of similar curves, made over as wide a temperature range as possible, will give the activation energy for the overall reaction of the material.

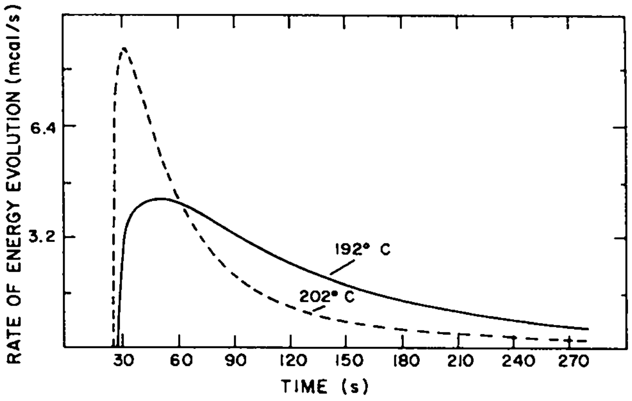

Fig. 4.
Differential-scanning calorimeter rate curves for a cellulose nitrate composition at two temperatures. Increasing the temperature only 10°C (the dotted line) more than doubles the reaction rate.

We need only two sets of equations to calculate the critical temperature. One set predicts the heat capacity and heat flow of the explosive-containing assembly, and the other set predicts the rate at which heat is generated by chemical reactions. The equations cannot be combined into one to predict critical temperatures for all sizes and shapes of all chemical compositions, but some special solutions can be obtained for specific sizes of many shapes and compositions.

TESTING PREDICTIVE MODELS

Although a mathematical predictive model can predict critical temperatures for different sizes and shapes of a high-energy material, it would be too dangerous to bet a human life or expensive equipment on unconfirmed theory. Therefore, we use several methods to test our predictive models.

We have developed an independent laboratory-scale method for measuring directly the critical temperature of high-energy materials. After placing the weighed material in empty aluminum blasting-cap shells and pressing the samples to a known and measured size, shape, and density, we drop a sample into a preheated liquid-metal bath (Fig. 5) and measure the time to explosion. By continuing to reduce the temperature of the bath and using new samples, we eventually find the lowest temperature at which an explosion occurs. This is the critical temperature for our test-assembly size and shape.

Because the predicted critical temperature for the time-to-explosion test can be calculated from the theory-based mathematical model, we can compare the predicted and measured values. If the two values agree, we can use the predictive model with some confidence.

Fig. 5.
A blasting-cap shell with an explosive sample is inserted into the blast shield before being dropped into the liquid-metal bath.

Table I shows that agreement is quite good for common explosives.

We also have tested the predictive models against much larger experiments, but they must be done at a firing site and are quite expensive. The experimental results confirmed the predictions for the systems we have tested.

TABLE I

PREDICTED AND MEASURED CRITICAL TEMPERATURES[a]

Explosive	Measured Critical Temperature (°C)	Predicted Critical Temperature (°C)
HMX	253-255	253
RDX	215-217	217
TNT	287-289	291
PETN	200-203	196
TATB	331-332	334
DATB	320-323	323

[a] Values apply *only* to the size and shape of the laboratory scale time-to-explosion test; all other sizes and shapes will be different.

CONCLUSIONS

We have developed small-scale methods for determining the reaction rates of explosives that make it possible to predict safe temperatures for using them, and we have developed methods for testing the accuracy of these predictions.

Each different size and shape of each different explosive has its own critical temperature. We must be able to predict these critical temperatures before high-energy materials can be used safely.

Mini-Review
readers are encouraged
to correspond directly
with the author.