Cookoff

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The term “cookoff” is a relatively inelegant descriptor of a very complicated series of events. However, it has entered the vernacular, and when it is used, it connotes a process that would be difficult to describe with another single term. The process begins with a thermal source that raises the temperature above ambient, where presumably the kinetic processes leading to decomposition of the energetic material are, for all intents and purposes, zero. The thermal source can be self-produced, as in the center of a well-insulated, large volume of energetic material, or it can arise from an external event such as a fire. The heating can be rapid or very slow, or anything in between. The energetic material can be homogeneous, or it may have been damaged, either through thermal expansion and chemical processes or mechanically. As a result, the gases produced by the increased chemical reaction may either be confined to the immediate vicinity or allowed to permeate throughout a larger volume. The gases carry both thermal and chemical energy and thus the outcome of the heating event can be significantly affected, or, as we show later, even completely determined by their mobility.

Once the thermal source is created, two things can happen. First, the energy can be dissipated through conduction, convection, or radiation. This is why explosives are metastable. Even though they are constantly reacting, as described by the Arrhenius kinetics, the rates are so low at ambient temperatures that any thermal energy produced is dissipated faster than the kinetics can accelerate. Alternatively, this balance can be in favor of the kinetics and the reaction rate can accelerate.

Should the thermal source result in an accelerating chemical reaction, several outcomes are possible. If the material has a very small volume, it can react rapidly, and yet produce only small amounts of gas before all of it is consumed. If the material is large and unconfined, any gas that is produced may escape through fissures or interconnected pores, relieving pressure and providing a pathway for further cooling and subsequent extinguishment of the reaction. If the material is heavily confined, either by itself (inertial confinement) or by
a case or container, then the pressure will continue to build, the surrounding material will fracture creating more surface area available for reaction, and the temperature will continue to rise as more and more explosives become involved.

If the reaction continues, it can either build, through a complicated set of steps, to a detonation or it can merely burn rapidly producing an explosion, or it can burn slowly releasing its energy over a relatively long time, resulting in very little damage or consequence. There are a seemingly infinite number of important steps and considerations in the evolution of this process. One way of representing these is found in Fig. 7.1a, b. Fault trees of this nature are constructed to guide the thought process in analyzing potential accidents and abnormal events. They are also useful in designing numerical models and experiments to ensure that all significant aspects of the problem are being addressed. They also illustrate the complex nature of the area that we are dealing with. The outcome of any given thermal event is determined by many complicated and, in some cases, poorly understood factors.

Thus, cookoff refers to any situation in which bulk explosive is heated either directly to ignition (sometimes referred to as fast cookoff) or to a temperature at which relatively slow exothermic reactions eventually generate heat faster than it is removed by dissipative transport processes, leading to self-heating to ignition (slow cookoff).

These events split naturally into two quite distinct stages, with different timescales and dominant physics and chemistry. During the preignition (heating) stage, which may last from seconds to days, external heating of the explosive leads to relatively slow processes such as phase changes, slow mechanical and chemical damage, and largely solid-state chemical decomposition. At some point, ignition occurs, by which we mean a transition to faster, and generally much more exothermic, gas-phase chemistry. If the explosive is confined, high pressurization rates will result, with accompanying high-strain-rate deformation of both the explosive and the confinement, and the possibility of compaction and shock wave formation that may lead to a transition from deflagration to a higher order event such as detonation. The post-ignition event may be over in milliseconds or even in microseconds, and is complicated considerably by the thermally damaged state of some or all of the explosive charge; to understand the evolution of the post-ignition reaction, we must first characterize this state, which may be far different than the original, pristine material.

This chapter will explore the field of cookoff on small and large scales. We will confine ourselves mainly to secondary explosives. The mechanisms that are important to the process, that is, damage, DDT, kinetics, initiation sources, etc., are covered in other parts of the book. As described in the introductory chapter, all initiation mechanisms can be reduced to the thermal event. In general, secondary explosives will not react, even when taken to extremely high pressures or subjected to large strains, as long as the material is not heated in the process. As Henson has pointed out in his chapter on