SENSITIVITY OF EXPLOSIVES

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CONTENTS

I. GENERAL

A. INTRODUCTION

The practical problem of the sensitivity of explosives can be viewed as one of reliability and of safety; consequently its solution must meet two requirements. First, an explosive must be detonable reliably whenever necessary. Second, and perhaps more urgently important, it must not explode accidentally. The need to know how to explode explosives when and only when desired is tantamount to the need of knowledge of their behavior in any practical situation. The field of sensitivity of explosives thus properly includes all effects of externally imposed physical conditions on the behavior of explosives and hence is of exceedingly large scope. Of direct interest, however, are only those conditions which may normally be encountered in practice. The aim of this review is a discussion, from a unified point of view, of the fundamentals underlying the practical problem.

General, qualitative notions of sensitivity are commonplace. The well-known fact that some explosives detonate more easily than others is the basis of the conventional division of all explosives into two broad classes, *primary explosives* and *high explosives.* Primaries are usually thought of as explosives which can be detonated by a hot source such as a resistance bridge wire; by contrast, high explosives would be those which can be detonated only when in contact with, or in the vicinity of, another detonating explosive charge. This division according to behavior, while sometimes convenient, is arbitrary and cannot be made rigorous. It appears that, given proper conditions, all explosives can be detonated starting from a purely thermal source. It is also known that, under other conditions, most explosives can burn without detonating; differences in the sensitivity of various explosives are of degree, not of kind. Moreover, there are high explosives, for instance PETN, which approach primaries in detonability. Consequently, a further subdivision of high explosives (also an arbitrary one) is made in practice to take care of explosives which are less sensitive than the primaries, but too sensitive to

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be used in large amounts in field work. These are termed "boosters." The normal explosives train designed to detonate a large amount of explosive is constructed accordingly; a detonator consisting of a small charge of a primary explosive, initiated thermally, transmits the detonation to an intermediate amount of booster which, in turn, detonates the main charge of an insensitive high explosive. A typical primary explosive such as lead azide is so sensitive that one would normally not use it in quantities larger than a few grams and often much less. A typical booster is Tetryl, which would be used in amounts of perhaps 100 g., although considerably larger amounts can be handled. The most widely known high explosive is TNT. With a deal of care an explosive as insensitive as TNT can be safely used in practically unlimited quantities. Thus years of practice have provided a crude framework for the classification of explosives as to sensitivity.

A closely related type of material is the *propellant.* The two most common classes of propellants are *double-base propellants,* composed of nitroglycerin, nitrocellulose, and varying amounts of additives, and *composite propellants,* which are mixtures of oxygen-rich compounds (oxidizers) and various energy-rich fuels. Propellants are, in fact, explosives, but they are formulated with a different intention: it is their function to burn in a controllable fashion and, ideally, not to detonate in any circumstance. In practice the ideal is hard to attain; hence the problem of sensitivity of propellants, in spite of the different emphasis on function, is essentially the same as that of explosives; whether the intention be to bring a charge to detonation exactly when desired (explosive emphasis) or to keep it from detonating at all times (propellant emphasis), it is imperative that one know the conditions under which detonation will develop. In consequence, although discussions of the sensitivity of explosives are sometimes meant to concern mainly the behavior of high explosives (and this primary intent will be retained in this review), any such discussion will in the main be applicable to propellants and also to primary explosives. One restriction will be imposed here: primary explosives, being almost invariably inorganic salts, are chemically rather different from high explosives and many conventional propellants, which are largely organic materials. Those special aspects of initiation of primary explosives which can be related to their peculiar physicochemical properties (ionic and crystalline structure, sensitivity to radiation, tendency to form metallic nuclei, etc.) are outside the province of this review. The subject has been dealt with at some length in a Discussion on Initiation and Growth of Explosions under the leadership of F. P. Bowden (13).

B. DEFINITIONS AND SCOPE[2]

In the forthcoming discussion there will be repeated occasion to use a number of specialized terms; inasmuch as nomenclature in current usage is not com-

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[2] This footnote contains a list of the symbols used in this review, definitions of the subscripts, and a list of the explosives referred to.

List of symbols

a = reaction zone length (cm.)
A = constant defined by equation 12 (cm. sec.$^{-1}$ atm.$^{-1}$)
B = constant defined by equation 12 (dimensionless)
$c(p)$ = sound velocity defined by equation 13 (cm. sec.$^{-1}$)
C = heat capacity (cal. g.$^{-1}$ deg.$^{-1}$)
D = detonation velocity (cm. sec.$^{-1}$)
E = energy (cal. g.$^{-1}$)
E_a = activation energy (cal. mole^{-1})
k = specific surface reaction rate (cm.^{2} sec.$^{-1}$)
n = number of moles
p = pressure (atm.)
q = rate of heat evolution (cal. cm.$^{-3}$ sec.$^{-1}$)
Q = heat of reaction (cal. g.$^{-1}$)
r = characteristic linear dimension (cm.)
R = gas constant (cal. mole^{-1} deg.$^{-1}$)
$\mathcal{R}$ = linear burning rate (cm. sec.$^{-1}$)
S = surface area (cm.^{2})
t = time (sec.)
T = temperature (°K.)
u = particle velocity (cm. sec.$^{-1}$)
U = shock velocity (cm. sec.$^{-1}$)
V = volume (cm.^{3})
x = space coördinate (cm.)
Z = frequency factor of a homogeneous first-order reaction (sec.$^{-1}$)
Z' = frequency factor of a surface reaction (cm.^{3} sec.$^{-1}$)
α = heat transfer coefficient (cal. cm.$^{-2}$ sec.$^{-1}$ deg.$^{-1}$)
δ = parameter defined by equation 6 (dimensionless)
λ = thermal conductivity (cal. cm.$^{-1}$ sec.$^{-1}$ deg.$^{-1}$)
ρ = density (g. cm.$^{-3}$)
σ = velocity defined by equation 13 (cm. sec.$^{-1}$)
τ = induction period (sec.)

Subscripts

cr = critical condition
exp = explosion
H = shock (Hugoniot) condition
i = ideal
0 = initial or ambient condition
r = reactant
s = surroundings

List of explosives

DINA = diethylnitramine dinitrate
EDNA = ethylenedinitramine
Explosive D = ammonium picrate
HMX = cyclotetramethylenetetranitramine
PETN = pentaerythritol tetranitrate
RDX = cyclotrimethylenetrinitramine
Tetryl = ethyltrinitrophenylnitramine
TNT = trinitrotoluene
Amatol = NH_4NO_3/TNT (60/40)
Composition A = RDX/wax (91/9)
Composition B = RDX/TNT/wax (60/40/1)
Pentolite = PETN/TNT (50/50)
Tritonal = TNT/aluminum (80/20)

pletely uniform, it is appropriate that those most frequently used be defined explicitly. To that end consider a hypothetical case of an explosive in which the chemical reaction is originally started by an external energy source; let the reaction grow in violence until the extreme regime of detonation is attained. The process of build-up can then conveniently be divided into four stages of development.

The first stage, termed *initiation*, is one in which the reaction has not yet released sufficient energy for self-propagation and hence is dependent on an external source of energy. If the latter is removed before the completion of the initiation stage, the reaction will die out.

Initiation is followed by the second stage, *deflagration*. Deflagration is a self-sustained reaction in which the energy is transmitted from the burning to the unburnt layers of the fuel by means of transport properties, a relatively slow process (Section II,B,3). The linear deflagration rate can be considered to be a function of ambient pressure only; consequently, steady states are attainable at constant pressures. Specifically, for condensed explosives the linear deflagration rate is a monotone increasing function of pressure, a fact which plays an important role in the self-acceleration of explosive reactions.

The third stage, transition from deflagration to detonation, is the stage during which the reaction accelerates from the slow transport-determined steady state to supersonic speeds. In condensed explosives the velocity of propagation during transition to detonation must increase by a factor of about a million.

The fourth stage, *detonation*, is again a steady regime, but in detonation the energy liberated in the chemical reaction is transmitted to the unburnt layers of explosive by means of shock waves. While transport phenomena no doubt play a part in the propagation of detonation, an excellent first approximation which fully accounts for properties such as detonation pressure, velocity, and energy, i.e., the Zeldovich–von Neumann–Doering theory, was developed on the basis of hydrodynamics alone (136, 96, 41). In most condensed explosives detonation propagates at velocities of 5 to 8 km./sec. The corresponding pressures are about a quarter of a million atmospheres. Detonation velocities (D) are somewhat dependent upon the charge diameter; they increase with increasing diameter asymptotically to a value D_i, called ideal detonation. Metastable subdetonation regimes (the so-called "low-order detonations"; see Section III,C) differ essentially from the hydrodynamically defined steady-state detonation.

If in the first stage the external energy is supplied with the express purpose of starting a deflagration (i.e., a pressure-controlled burning), such a process is more properly termed *ignition*, a concept of special importance in propellant technology. Initiation is a more embracing term applicable to a variety of situations. For all of the above four stages of development are not necessarily well defined in every experiment (or accident!). For instance, in a situation in which the energy of initiation is supplied as a strong externally imposed shock, the deflagration stage is nonexistent, or at any rate so fleeting that it is not practical to speak about it. It is thus evident that the concept of initiation is inherently tied to the type of initiating stimulus, a point which will be discussed further on in this section.

The above classification is recognized to be closely akin to Bowden's three-stage division into initiation, growth, and explosion (17). Indeed, Bowden himself makes clear that impact-initiated explosions, which he studied very extensively, start as deflagrations and only occasionally develop into detonations. The term "explosion," however will not be used here, because it is an ill-defined concept; it can mean either detonation or an arbitrary point during the transition stage at which the reaction has become noisy and destructive. Nevertheless, the term does have a practical value. From the point of view of safety, if life and property are at stake, it matters little whether a destructive reaction is a steady-state detonation or not; the word explosion describes it fully for the purpose.

The unified approach adopted in this review will assume that all initiation is ultimately thermal. More precisely: every initiating stimulus (shock, impact, electric discharge, and the like) serves to heat up the explosive, or a portion thereof, initially at a temperature T_0, to an elevated temperature T. It will be assumed here that T and the length of time the explosive is exposed to T are the two variables sufficient to account for initiation[3]; furthermore, that the same is true of the deflagration, transition to detonation, and detonation stages which arise and propagate when, and only when, T is sufficiently high to maintain rates of chemical reaction requisite for the three respective phenomena. At the present state of knowledge it does not seem necessary to presuppose the existence of nonthermal factors other than catalysis and chain propagation, which are an integral part of the thermal theory of reaction rates. (Since, however, the total energy output of an initiating agent may be insufficient to initiate the body of a condensed explosive in a homogeneous manner, it does frequently become necessary to seek mechanisms which allow the concentration of energy into small local regions, usually referred to as "hot spots.") It thus becomes clear that the problem of the

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[3] A third factor influencing the reaction rate, density, is important in gaseous combustion where it varies considerably with temperature and pressure; in homogeneous solids and liquids it is nearly constant.

sensitivity of an explosive is fundamentally one of chemical kinetics.

So reduced, the field, while conceptually clear, nonetheless remains sorely unexplored. For although even the basic knowledge of the kinetics of the decomposition of explosives is far from satisfactory, this is only one of two problems at hand; the other is the mechanism of degradation of the energy of the stimulus into heat, which must be known quantitatively before the chemical kinetics of the reaction launched by the stimulus can be studied.

It is the latter problem which is responsible for the lack of unity in studies of sensitivity. Since the mechanism of degradation into heat, among other things, obviously depends on the nature of the stimulus, it has become customary to recognize different *types of sensitivity*. One speaks of heat sensitivity when the initiating stimulus is direct application of heat, but also—and even more frequently—of sensitivity to shock, impact, radiation, or friction. Only when the type of sensitivity, i.e., the exact manner of initiation, is specified is it possible to define quantitative sensitivity scales; the quantity on which a particular scale is based can be, for instance, the minimum shock pressure needed to initiate an explosive in a shock test, or the minimum height of fall of a hammer in an impact test. Thus, instead of a single property of sensitivity, practical explosives technology has been forced to deal with an entire set, each property in the set being defined by the appropriate type of stimulus. The essence of the problem is that there is not sufficiently firm correlation among different sensitivity scales.

It is, of course, not surprising that practice should fail to provide a basis for the definition of sensitivity as a property of an explosive. Indeed, from what was said above it is clear that the sensitivity of an explosive (or propellant) is defined precisely to the extent that the characteristics of its thermal decomposition are known; but even when these are known, they are not useful until conversion of the energy of the stimulus into heat can be assessed quantitatively. The evaluation of any one experiment and hence the entire field of sensitivity thus naturally falls into two parts: the question of thermal sensitivity, which is a fundamental problem of chemical kinetics, and the question of degradation of the stimulus into heat, which is a complex applied problem entailing the nature of the stimulus, of the explosive, and of its surroundings. Figure 1 relates schematically the proposed four-stage classification to both the fundamental and the applied problem.

The two steady states, deflagration and detonation, are not a part of the sensitivity problem proper. They have been discussed extensively elsewhere (70, 118). The real problem of sensitivity centers around the transient phenomena of initiation and of transition to detonation. While the initiation stage is specific to the type of experiment (i.e., the physical and chemical nature of the stimulus, the explosive, and the surroundings), the transition stage can be discussed on the basis of the nature of the explosive alone, independent of the type of experiment.

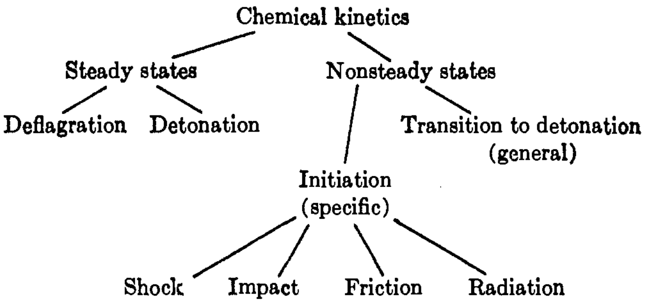

FIG. 1. Classification of explosive reactions.

The forthcoming discussion is in three sections. Section II deals with the fundamental question of the thermal decomposition of explosives. Section III is a discussion of the general problem of the transition from deflagration to detonation. Section IV takes up two specific (applied) problems of initiation, the gap test and the impact test. The gap test is a relatively simple kind of nonthermal initiation. The impact test, on the other hand, is quite complex to analyze, but it is so widely used that it rather demands explicit mention. Friction testing is not discussed separately, because it is seldom used and not at all well explored (15, 84, 94, 95). Irradiation by light, x-rays, energetic particles, or ultrasonics, as mentioned previously, has been specifically applied to inorganic primaries only; hence it is beyond the scope of this review.

II. THERMAL DECOMPOSITION OF EXPLOSIVES

A. THERMAL EXPLOSION THEORY

Description of the thermal behavior of explosives, which underlies all considerations of explosives reactions, is provided by a combination of the theories of transport properties and of chemical kinetics. While a completely general approach to the problem would be of altogether forbidding scope, there exist meaningful tractable idealizations. The one discussed here will assume a homogeneous isotropic solid undergoing a first-order exothermic chemical reaction and exchanging heat with chemically inert surroundings. Restriction to solid reactants minimizes the significance of diffusion and convection within the fuel, which will therefore be neglected, but no restrictions need be placed upon the state of aggregation of the surroundings: a gross term representing Newtonian cooling of the explosive boundary can be included under appropriate conditions to take care of heat exchange with the surroundings. In addition, it will be assumed that the thermal conductivity and the heat capacity of the explosive are constant; that the amount of the reactant consumed prior to thermal explosion is negligible[4]; and finally that there is no autocatalysis of the chemical reaction. The last two assumptions, in effect, mean restriction to initial stages of the reaction. Systems of somewhat more general validity have been treated, e.g., those dealing with gases or including corrections for the amount of reactant consumed (51, 52), but the one chosen here will suffice to illustrate the principles. The effect of autocatalysis and lack of homogeneity of explosive reactions will be discussed in subsequent sections.

The aim of the thermal explosion theory is the knowledge of the temperature of the system as a function of both time and location. The information is provided by the solution of the equation

$$c\rho\frac{\partial T}{\partial t} = \lambda\nabla^2 T + q \tag{1}$$

Physically, equation 1 states that there is a balance of the heat evolved in the chemical reaction, the heat conducted away from the site of the reaction and the increase in the temperature of the system. It is the term q which both determines the explosive properties of a reactant and is the source of mathematical obstacles to finding the solution of equation 1. This is so because the peculiar nature of explosive reactions requires a mathematical expression for q which will allow a very rapid change of reaction rate within a narrow temperature range; the conventional two-constant Arrhenius term satisfies the requirement, providing the exothermicity of the reaction, Q, is sufficiently high:

$$q = \rho Q Z e^{-E_a/RT} \tag{2}$$

The exponential dependence of the evolution of heat upon temperature, besides rendering equation 1 nonlinear and hence difficult to solve, accounts for the existence of concepts such as ignition, ignition temperature, induction period, limits of inflammability and, indeed, of the concept of "explosion" itself, which, as described in the preceding section, can be defined no more rigorously than by the requirement that the reaction rate become sufficiently high. This fundamental point, of course, is implied in every theoretical treatment of thermal explosion, but it has been brought out especially explicitly in Russian scientific literature (52, 80). In particular, Frank-Kamenetskiĭ has shown (52) that the quantitative requirement for a homogeneous thermal reaction to be explosive is $E_a \gg RT$. Since for reasonable temperatures RT is about 1 kcal., while E_a for chemical reactions is usually measured in tens of kilocalories, the inequality will in general be valid for the problem at hand.

The quantitative theory of thermal explosions, which is equivalent to solutions of equation 1 under various boundary conditions, was developed piecemeal, mostly in the 1930's (52, 99, 112, 121, 122). The theory was originally developed for gaseous systems; application to condensed explosives is more recent (100). Since, on account of its nonlinearity, equation 1 cannot be solved in a general manner, the solution consists of a series of approximations which must be rather drastic, yet such that they conform to the physical reality in limiting cases at least. Several such approximations were treated in detail by Frank-Kamenetskiĭ (52) and recently were discussed critically by Gray and Harper (60).

1. Stationary approximation

The case which has received considerable attention is the stationary treatment, that is, the case in which the space distribution of temperature does not vary with time, $\partial T/\partial t = 0$. Consequently, equation 1 reduces to

$$\lambda\nabla^2 T + \rho Q Z e^{-E_a/RT} = 0 \tag{3}$$

For three geometries which have been treated in stationary approximation—an infinite plane-parallel slab of thickness $2r$, an infinitely long cylinder of radius r, and a sphere of radius r—equation 3 can be written

$$\lambda\left(\frac{\partial^2 T}{\partial x^2} + \frac{m}{x}\frac{\partial T}{\partial x}\right) = -\rho Q Z e^{-E_a/RT}; \quad |x| < r \tag{4}$$

The parameter m assumes values 0, 1, and 2 for the slab, the cylinder, and the sphere, respectively.

Frank-Kamenetskiĭ (52) solved equation 4 for the slab ($m = 0$) analytically by expanding the exponent E_a/RT in a Taylor series around the boundary temperature T_0 and neglecting terms higher than first order. The approximation is valid if $T - T_0 \ll T_0$, which is equivalent to $E_a \gg RT_0$. Under these conditions the temperature distribution is as sketched in figure 2. The curves show different stationary temperature distributions within the slab which arise from different

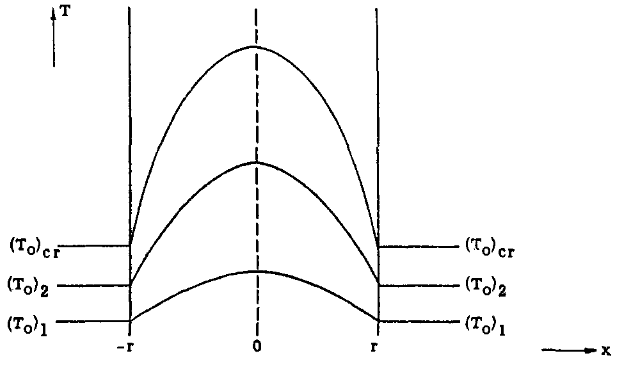

FIG. 2. The Frank-Kamenetskiĭ model of one-dimensional steady-state self-heating in explosives.

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[4] It has been estimated (8) that during the thermal induction period the amount of the explosive reacting is 5–10 per cent.

specified boundary (i.e., ambient) temperatures T_0. The solution of equation 4 shows that a stationary state is possible only if the parameter

$$\delta = \frac{\rho QZ}{\lambda}\frac{E_a}{RT_0^2}r^2e^{-E_a/RT_0} \tag{5}$$

does not exceed a critical value δ_{cr} which depends on the geometry of the explosive charge only; evidently, this will be true if T_0 is kept below a critical value for a given r. Once the δ_{cr} is exceeded, the heat evolved can no longer be conducted to the surroundings rapidly enough to maintain stationary temperature gradients within the explosive; the corresponding ambient temperature is, by definition, the explosion temperature $(T_0)_{exp}$. Frank-Kamenetskiĭ obtained an analytical solution of equation 4 for the slab ($m = 0$) and showed that $\delta_{cr} = 0.88$. He also obtained the critical values $\delta_{cr} = 3.32$ and $\delta_{cr} = 2.00$ by numerical integration of the spherical and the cylindrical geometries, respectively.

Chambré (26) developed a method by which geometries other than the slab can be solved in terms of elementary functions and confirmed analytically Frank-Kamenetskiĭ's values of δ_{cr} for the cylinder and the sphere. Chambré's method was extended by Enig (46) and Thomas (120), who integrated equation 4 for a hollow infinite cylinder. As should be expected, the parameter δ_{cr} increases (and consequently the sensitivity to thermal explosion decreases) rapidly as the ratio of the inert hollow diameter to the cylinder diameter increases. For example, when the diameter of the hollow is equal to r, δ_{cr} is as high as 13.9.

Frank-Kamenetskiĭ's stationary-state treatment stipulates two physical conditions. The first one is that the boundary offer no thermal resistance. If, in addition, the thermal conductivity of the explosive is very large—or, which in effect is the same, the reaction is very slow—the process becomes isothermal. The limiting isothermal condition is one about which conventional texts on chemical kinetics are written and which, explicitly or tacitly, is assumed in interpreting all but a very few measurements of chemical kinetics.

The second condition, $RT_0/E_a \ll 1$, has been shown by Frank-Kamenetskiĭ to be equivalent to $T - T_0 \ll T_0$, which means that there must be no large increase in temperature of the reactant above the surface temperature prior to explosion. Whether the condition is approached closely or not will obviously depend on the magnitude of activation energy E_a. A numerical integration performed without introduction of the approximation (47) reveals that the approximation is good for reasonable values of E_a and T_0. For typical values, $E_a = 35{,}000$ cal./mole and $T_0 = 500°$K., the exact values for δ_{cr} are 0.905, 2.063, and 3.429 for the slab, the cylinder, and the sphere, respectively. As RT_0/E_a decreases, δ_{cr}, of course, approaches the limiting values of the approximate computation.

An alternative approach to the stationary problem, developed by Semenov (112), assumes that the reacting explosive is at a uniform temperature higher than that of the surroundings, $T > T_0$, and that it loses heat to the surroundings by Newtonian cooling (figure 3).

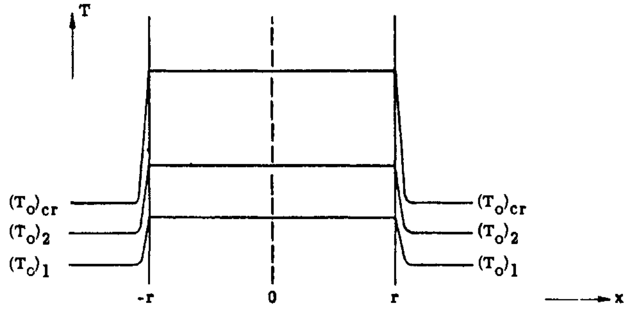

FIG. 3. The Semenov model of one-dimensional steady-state self-heating in explosives.

The energy balance is then

$$VQ\rho Ze^{-E_a/RT} = \alpha S(T - T_0) \tag{6}$$

The corresponding critical condition is very simple:

$$T - T_0 = \frac{RT^2}{E_a} \simeq \frac{RT_0^2}{E_a} \tag{7}$$

i.e., no stationary state can be maintained if the temperature rise in the reactant is larger than RT_0^2/E_a. Semenov's approximation obviously presupposes the heat transfer within the reactant to be large compared to the rate of heat evolution; this means, in effect, large thermal conductivity of the reactant or a slow chemical reaction. If, in addition, the heat transfer across the boundaries becomes large, $T - T_0$ will become small and isothermal condition is again approached, this time from a physically different starting point.

The application of the above considerations to practical problems is immediate. The Frank-Kamenetskiĭ approach, requiring unhindered heat transfer across the boundaries, will be a good approximation for (*a*) a gaseous reactant enclosed in a vessel, (*b*) a solid or liquid reactant of relatively low thermal conductivity cased in a material of high conductivity and of sufficient thickness, e.g., an explosive in a heavy metal casing, and (*c*) a solid reactant immersed in a stirred fluid. In view of the very large difference between the densities of a gas and a solid, (*a*) is the case of relatively large product $(\rho C)_s$ of the wall and, consequently, the relative magnitudes of λ_s and λ_r do not matter much; the condition is satisfied even for surroundings of relatively low λ_s, such as glass (although, of course, more perfectly for a metal). Theoretical treatments of gaseous systems, however, must generally include convection. The work of Rice, Allen, and Campbell (99) is a good experimental test for equations pertinent to case (*a*). In case (*b*) heat capacities and densities of the reactant and of surroundings are of the same order of magnitude so that, given a sufficiently large mass of the wall to absorb the heat, the boundary condition depends on the relative magnitudes of thermal conductivities only. The condition $(\mathrm{d}T/\mathrm{d}x)_s = 0$ will be satisfied for a finite heat flux, $-\lambda(\partial T/\partial x)$, theoretically only if λ_s is infinite, practically if $\lambda_s \gg \lambda_r$. In case (*c*) the surroundings are kept approximately isothermal by forced convection.

Semenov's alternative approach (high λ_r) may be expected to apply in the case of a solid reactant surrounded by a gas. Groocock's work with lead azide (63) provides an experimental example of the condition.

Thomas (120) showed that the stationary problem, equation 4, can be solved by imposing the more general boundary condition

$$\alpha(T - T_0) - \lambda\frac{\partial T}{\partial x} = 0$$

of which the Frank-Kamenetskiĭ and the Semenov approximations are special cases. The implications of such a treatment are discussed by Gray and Harper (60).

2. Nonstationary treatment

If the restriction of a stationary regime is removed, it must be replaced by other approximations. Frank-Kamenetskiĭ (52) discusses the nonstationary system by assuming a uniform reactant temperature and Newtonian surface cooling:

$$VC\rho\frac{\partial T}{\partial t} = VQ\rho Ze^{-E_a/RT} - \alpha S(T - T_0) \qquad (8)$$

The case also was treated by Gray and Harper (60), who used special approximation methods.

While such an approach represents a considerable advance beyond Semenov's stationary approximation (equation 6), it is well to point out that any method contingent upon infinite diffusivity $\lambda/(\rho C)$ of the reactant and allowing for a surface cooling mechanism, will still be of limited practical validity. For in this nonstationary system, the temperature of the reactant increases until explosion occurs. Since the thermal conductivity of the reactant can never be infinite, a small thermal gradient will arise, which, on account of the exponential dependence of the evolution of heat on temperature, far from being smoothed out, is apt to be magnified.

A simpler model results if the reaction is assumed adiabatic. This is the limiting case of equation 8 as the heat transfer to the surroundings decreases:

$$C\frac{\mathrm{d}T}{\mathrm{d}t} = QZe^{-E_a/RT} \qquad (9)$$

Here, the temperature T of the reactant will be uniform regardless of the magnitude of the thermal conductivity of the reactant. The requirement, however, is that there be infinite heat resistance at the boundary. Adiabatic condition can be approximated (*a*) by bounding the explosive by a good thermal insulator or (*b*) by continuously increasing the wall temperature so that it always equals that of the explosive (Section II,B). The solution of equation 9 is

$$t_{\mathrm{exp}} \equiv \tau = \frac{C}{QZ}\int_{T_0}^{T_{\mathrm{exp}}} e^{E_a/RT}\mathrm{d}T \simeq \frac{C}{QZ}\,\frac{RT_0^2}{E_a}e^{E_a/RT} \qquad (10a)$$

$$\ln \tau \simeq \frac{E_a}{RT_0} + \text{constant} \qquad (10b)$$

where τ is the delay to explosion (induction period). Form 10b can be used for the determination of the activation energies of the decomposition of an explosive from measured delays to explosion at specified initial temperatures. Equations 10, of course, can be applied only when the system is truly adiabatic, a requirement which has not always been fulfilled in practice (Section II,B).

3. General case

In order to solve equation 1 without approximations subject to specified boundary conditions, one has to resort to numerical procedures. G. B. Cook (27, 28) treated two problems by means of calculations with a digital computer. First is the case of a slab of solid explosive one face of which is in contact with a constant-temperature bath. In the second case the explosive is subjected to a time-dependent heat pulse. In the two respective cases the time to ignition and the critical condition for ignition are given as functions of physical parameters of the system.

A calculation similar to the first case recently has been done by Zinn and Mader (138) for a semi-infinite slab, an infinite cylinder, and a sphere, and compared with experimental data for the cylindrical shape. In spite of the fact that the mathematical model neglects fusion (the explosion temperature is usually above the melting point of the explosive), agreement between the calculation and the experiment is reasonably good.

B. RATES OF REACTIONS OF EXPLOSIVES

Despite a fair measure of attention, the chemical kinetics of the reactions of explosives has defied a unified explanation perhaps more than any other phase of the sensitivity problem. This, of course, is unfortunate, because thermal explosion theory (Section II,A), fundamental to all explosive phenomena, can become quantitative only when the necessary experimental parameters are furnished.

Measurement of the gross rates of decomposition of explosives at relatively low temperatures (say 150–

200°C.) does not present any special difficulties, but the simplest interpretation—namely, breakdown of the rate expression into a frequency factor and an exponential term—has not been accomplished satisfactorily even for common explosives. The case of Tetryl, a high explosive, may serve as an example. Roginsky (105), using Farmer's (49) data, calculated the activation energy for thermal decomposition to be 52.0 kcal./mole with the corresponding frequency factor for a first-order reaction of $10^{22.5}$ sec.$^{-1}$; Robertson's (102) values for the same explosive are $E_a = 38.4$ kcal./mole, $Z = 10^{15.4}$ sec.$^{-1}$; those of Cook and Abegg (31) are $E_a = 34.9$ kcal./mole, $Z = 10^{12.9}$ sec.$^{-1}$; Henkin and McGill (65) find the activation energy as low as 14 kcal./mole. The range of experimental data for other explosives is not necessarily so large, but widely different values are so common that it has become customary to speak about "high" values (E_a about 50 kcal./mole, Z about 10^{20} sec.$^{-1}$) and "low" values (E_a about 35 kcal./mole and a normal frequency factor Z of about 10^{13} sec.$^{-1}$) of the kinetic parameters.

The wide scatter of chemical kinetic parameters can to a limited extent be accounted for by the fact that the measurements are being done under diverse physical conditions. The methods can be divided into those which attempt to approximate isothermal conditions and those which attempt to approximate adiabatic conditions (see Section II,A). Any experimental deviation from the two ideals means that expressions for concepts such as activation energy are introduced into mathematical formulas which do not properly describe the physical situation at hand. The results may well differ from each other and from the real values.

1. Isothermal kinetics

Isothermal kinetic measurements (31, 49, 101, 102, 103, 104, 135) require working at relatively low temperatures, not above 200°C. for sensitive high explosives such as Tetryl, RDX, EDNA, or the like, and not above 300°C. for insensitive ones such as TNT; at higher temperatures the rate of evolution of heat becomes so high that it cannot be conducted away in time to keep the system isothermal. Under these conditions high explosives are often (but by no means always) apt to yield low chemical kinetic parameters, i.e., a normal frequency factor and an activation energy appreciably below 40 kcal./mole. The work of Robertson (104) and of Cook and Abegg (31) shows that, at higher temperatures, both E_a and Z increase. In both papers this is interpreted to be the evidence for autocatalysis. In particular, Robertson offers the comparison of the thermal decomposition of RDX in air and in ether solution; in air the activation energy is 47.5 kcal./mole and in ether, where less catalysis should be expected, 41 kcal./mole.

Superficially it may appear that, whatever the results, high-temperature measurements will be more useful in explosives technology, for in most instances data on chemical kinetics have to be applied in the high-temperature regions associated with explosions and detonations—so high, indeed, that direct measurements are all but impossible. Cook and coworkers (30, 33) argue that this, in fact, may not be so, because at very high temperatures autocatalysis will disappear and consequently the low-temperature noncatalytic data are the ones to be extrapolated to detonation conditions. If they are not available (or if the reaction exhibits autocatalysis even at the initial stages of the low-temperature reaction), it is proposed to adopt a uniform procedure of assuming a small standard entropy of activation (−3.2 e.u.) and then calculating the activation energies directly from rate data. This is in agreement with Robertson's suggestion (104) that, in the absence of autocatalysis, the entropy of activation will be rather small and the frequency factor normal. Interpretation of the kinetics of explosives by the assumption of a normal frequency factor has recently been urged also by Serbinov (113), who finds that data taken and interpreted over a very wide range of temperatures and pressures warrant such a procedure. This would place practically all activation energies of high explosives between 30 and 36 kcal./mole. Indeed, it may be argued that explosives are by definition substances which exhibit similar kinetics under similar circumstances, since the remarkable fact is that there are almost no other chemical properties which they would possess as a class; even the organic high explosives alone are drawn from all three major groups, aliphatic, aromatic, and cyclic compounds.

While the procedure has a measure of attractiveness, because it offers a unifying hypothesis, it rests on a slim foundation. Moreover, a specific argument against it arises from the attempts at correlating impact sensitivity (Section IV,B) with the data for slow decomposition (129). It was shown that the ordering of explosives by the impact test is the same as the ordering of their reaction rates under impact conditions (about 500°C.), while at lower temperatures the reaction rates bear different relationships to each other. If the frequency factors were the same, this could obviously not be so.

2. Adiabatic kinetics

Adiabatic data can be obtained by one of two procedures. First, it is possible to set up the experiment in such a way that the temperature of the surroundings is maintained equal to the temperature of the sample throughout the run (64). Tested in such an adiabatic furnace, two pure high explosives, TNT and DINA, were found to have activation energies of 37 and 35.5 kcal./mole, respectively, and approximately normal frequency factors; a somewhat impure sample of

RDX, however, had an activation energy of 57.2 kcal./mole and a correspondingly high frequency factor. The advantage of the method over isothermal measurements is that the rate data can be obtained from initial stages of the reaction alone.

The second procedure rests on an approximation. If the ambient temperature is high, the exponential heat-generating term overwhelms the linear heat-exchange term, and equation 8 reduces to equation 9 (Section II,A); conformance of the experimental induction periods with equation 10b then can be taken as a test of the adiabatic condition (subject to important qualifications of absence of autocatalysis or complex kinetics). Most kinetic data interpreted to have been taken under approximately adiabatic conditions (15, 100, 113, 123) come from impact tests (Section IV,B); this is the case in which the reaction can be completed in as little as 10^{-4} sec., presumably with little attendant thermal conduction. The values of activation energies range widely from about 20 to about 50 kcal./mole.

The interpretation that a reaction is adiabatic because it is rapid entails a major difficulty. If the reaction is to proceed adiabatically, the initial temperature T_0, uniform throughout the reactant, must be so high that the thermal conduction during the run can be neglected. Now if T_0 is to be attained by thermal conduction from the surroundings, the requirement is evidently in conflict with the attendant requirement that T_0 adjust itself uniformly throughout the sample practically instantaneously. Thus the adiabatic condition can be fulfilled only if either the experiment is specifically designed to be adiabatic, such as the work of Gross and Amster (64), or the initial temperature adjustment does not depend on conduction. The latter may or may not be true of shock and impact experiments, depending on whether the reaction in the compressed explosive proceeds homogeneously at a uniform temperature or from locally hot regions. Hot spots themselves may be approximately adiabatic, but the entire system, even if it is adiabatic in the usual sense that there is not appreciable heat exchange with the surroundings, is not so in the sense of equations 9 and 10, which require uniform temperature distribution. Techniques employing the rapid conductive heating of explosive boundaries (11, 53, 54, 65, 130) are also not adiabatic, but are subject to a special set of boundary conditions (138).

Finally, it must be pointed out that even experiments in which the activation energy is obtained from equation 10b by measurement of induction periods preceding the explosion need not be adiabatic at all. The work of Robertson (103) and of Henkin and McGill (65) would appear to fall in that category. The range of induction periods over which equation 10b holds is often a matter of seconds, so that the experiment can hardly be adiabatic; Robertson has shown that it can actually be isothermal simply by assuming the condition for explosion to be accumulation of a critical concentration of autocatalyst. Henkin and McGill consider Semenov's chain reaction theory (112) to be a possible alternative to a purely thermal explanation of the linear dependence of log τ on $1/T_0$.

Thus, it is well to keep in mind that even if thermal conditions are adequate, autocatalysis and chain reactions may still afflict kinetic experiments and greatly complicate their theoretical interpretation. Nonthermal effects are certainly present during induction periods which may run for minutes (11, 53). This must be so especially since, for some primary explosives at least, induction periods can be broken up into two or more stages separated by long intermissions (hours and even days so that the possibility of accumulation of heat is completely out of the question), and yet discontinuous periods of heating are essentially additive, their sum approximating the one-stage induction period (61, 125). A theoretical analysis of such *presensitization* or *memory* effects has been given recently by Hess and Ling (67).

3. *Surface burning*

If an explosive is initiated with large amounts of its surface exposed, its main decomposition is not likely to be homogeneous, but surface burning. Steady-state surface combustion, termed deflagration, is a complex process established by a balance of the reaction rate, thermal conduction, diffusion, and radiation in which reaction kinetics is usually not the only rate-controlling factor. Geckler (55, 56) and Huggett (70) have made surveys of the fundamental problems of the deflagration of solids.

The empirical characteristics of the controlled burning of explosives and propellants under high pressures have been known for some time (83, 118), but attempts to study detailed deflagration mechanisms have been made only recently (3, 86) as a result of an increasing interest in solid propellants. In steady-state deflagration the temperature of the burning surface or at the site of the reaction can evidently not be varied arbitrarily, but such variation can be accomplished indirectly through changes in pressure. Thus in the studies of surface burning it is often best to take the ambient pressure as the independent variable. A general theory connecting the thermodynamic, chemical kinetic, transport, and radiation properties of deflagration would involve extremely complicated mathematics, but models which allow determinations of the surface temperature, reaction rate, etc., have been proposed for specific propellant systems (24, 93, 106, 110, 116). If the linear regression rate is expressed by kinetics of the Arrhenius type, the models usually require a small overall activation energy (about 10 kcal./mole).

In the absence of general fundamental laws it is common practice to treat surface-burning rates through their measured dependence on pressure. The most frequently adopted law for the linear burning rate which can serve over limited pressure ranges, is:

$$\mathcal{R} = \mathcal{R}_0 + Ap^B \tag{11}$$

where $\mathcal{R}_0$, A, and B are empirical constants. Burning rates of common explosives and propellants are of the order of magnitude of 1 cm./sec. at 100 atm. Typical values of B range between 0.5 and 1. The limiting low-pressure rate, $\mathcal{R}_0$, is usually small (or zero) and is often neglected at higher pressures.

4. Summary

Since the many attempts by widely differing methods have failed to produce an authoritative set of chemical kinetic parameters for use in explosives technology, it does not appear meaningful to include a table of numerical values. Probably the largest portion of the activation energies of homogeneous reactions, obtained under both isothermal and adiabatic conditions, is contained between 30 and 40 kcal./mole, which one may therefore consider typical for the purpose of estimates of order of magnitude. Quite a few others were reported as high as 55 kcal./mole; a few as low as 20 kcal./mole. Values even lower than these must almost certainly be ascribed to incorrect interpretation of experimental conditions. Activation energies of surface reactions, on the other hand, which are normally controlled by transport effects must be expected to be much lower, probably no more than 10 kcal./mole. Some application of this crude distinction to practical problems will be made in later sections.

III. TRANSITION FROM DEFLAGRATION TO DETONATION

A statement of the problem of transition from steady-state deflagration to steady-state detonation can be based directly upon definitions of the two regimes (Section I,B). Deflagration is described by the dependence of the linear burning rate, $\mathcal{R}$, on ambient pressure (equation 12). If one allows the ambient pressure to increase—for example, by burning a solid or a liquid fuel under confinement—the linear rate $\mathcal{R}$ will also increase, but as long as the functional relationship between $\mathcal{R}$ and p remains the same, one is still dealing with deflagration. Burning-rate data for high explosives are not available beyond several kilobars, but if these are extrapolated to pressures as high as those which arise upon complete burning of an explosive under rigid confinement (up to 100 kbar, depending mostly on the density of the explosive), one obtains deflagration velocities of the order of magnitude of 10 meters/sec. Thus even under such extreme conditions deflagration pressures remain several times and deflagration velocities hundreds of times below those of detonation. It follows that detonation is not simply deflagration proceeding under pressure, but it has its own distinct mechanism of propagation. This does not mean that one must exclude the possibility of applying the concept of surface burning to both deflagration and detonation (see Section III,C); it does mean that the mechanism of energy transfer by which fresh layers of the fuel are activated must be different in the two regimes. Transition from deflagration to detonation is transition from a burning mechanism propagated by transport phenomena to a burning mechanism propagated by shock waves.

A. TRANSITION IN GASES

The prominent features of the phenomenon in gases, where it can be observed directly by means such as schlieren photography, have been known for a long time (40, 78). If deflagration is initiated near the closed end of a tube, the flame will in general accelerate; under conditions leading to detonation, a shock wave, termed the *precursor shock*, will form and initially outdistance the subsonic flame; during later stages either the flame accelerates sufficiently to merge with the shock or, frequently, detonation starts some distance ahead of the flame. Reflections from the walls and collisions of shocks play prominent parts, because the duration of the experiment is often such that the disturbances can traverse the reaction tube several times. A one-dimensional mathematical treatment of the process was done by Jones (77). A detailed theoretical analysis of flames, compression waves, and shock waves, based on recent experimental data (109), was made by Oppenheim and Stern (97).

In order to explain the phenomenon of transition, one must postulate a mechanism for a large increase in the linear rate of deflagration; it is generally agreed (18, 137) that, in gases, such mechanism can be provided by turbulence. Indeed, the early work of Shchelkin (114, 115) demonstrated that the process of transition is shortened drastically if the walls of the reaction tube are made rough.

B. THE PRECURSOR SHOCK IN SOLIDS

The shift of attention to the problem of transition to detonation in condensed explosives, about a decade ago, was occasioned by the awareness that the problem may be pertinent to the proper functioning of large rocket propellant grains, and was given additional impetus by the scientific approach to shock-initiation (Section III,D). From initial qualitative suggestions of Kistiakowsky (81, 82) and Ubbelohde (124) there developed the hypothesis of precursor shock, which postulates a sequence of events rather analogous to that which occurs in gases. One may distinguish three steps: (*a*) rapid increase in pressure behind the burning front, which sends compression waves through the front and into the unburnt explosive; (*b*) formation of the precursor shock, due to coalescence of compression waves, in the unburnt explosive ahead of the flame; and (*c*) shock-initiation of the detonation reaction. The sequence will occur only if there is confinement of the gaseous product; the rigor of confinement requisite for transition to detonation will be determined by the strength of the shock necessary to initiate the detonation reaction.

The hypothesis is borne out by quantitative studies of the burning of explosives under confinement. Maček and Gipson (59, 87) have shown that for fairly sensitive cast high explosives (pentolite and DINA) the experimentally determined distance between the point of ignition of deflagration and of the development of steady-state detonation (usually 5 to 20 cm.) coincides with the distance necessary for the precursor shock to form from compression waves if the process of shock formation is computed on the basis of a one-dimensional model of surface burning of a homogeneous solid under confinement. Furthermore, experimental evidence indicates that, prior to the development of steady-state detonation, compression fronts of increasing strength run ahead of both the deflagration and the low-order detonation front (Section III,C); velocities of the compression fronts and of the low-order detonation are about 2 km./sec. Essentially similar evidence was presented by Griffiths and Groocock (62) on the basis of experiments with low-density granular PETN, RDX, and HMX.

The one-dimensional precursor shock mechanism is sketched in figure 4. Following ignition (at origin) there is a relatively protracted period during which the pressure is so low that the waves $c(0)$ remain very nearly sonic and the entire charge of explosive essentially uncompressed. The significant acceleration begins at the time t_1, when the amplitude of compression waves emerging from the deflagration front becomes appreciable; the ensuing growth of a full-fledged detonation wave takes typically less than 100 microsec. The compression waves converge into a precursor shock in a region in the x–t plane determined by the rate of increase of pressure of the product gas which, in turn, depends on the burning rate law, the geometry of the system, and the equation of state of the product gas in a manner discussed further on in this section. The region of shock formation, represented in figure 4 for simplicity by a single point S, can then be constructed by the method of characteristics (38). The pertinent velocities are

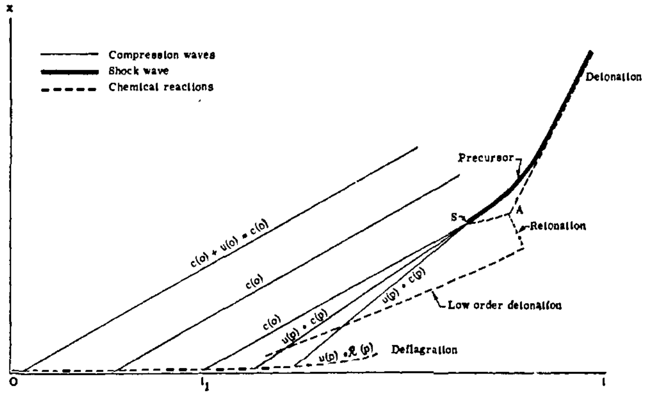

FIG. 4. One-dimensional precursor shock mechanism of transition from deflagration to detonation in solids.

$$u(p) = \sigma(p) - \sigma(o) \qquad (12)$$

$$\sigma = \int \frac{c(p)\,d\rho}{\rho} \qquad (13)$$

$$c(p) = \sqrt{\frac{dp}{d\rho}} \quad \text{(isentropic)} \qquad (14)$$

Velocity of the deflagrating boundary separating the solid charge from the product gas is $u(p) + \mathcal{R}(p)$. At any appreciable pressure $\mathcal{R}(p)$ is negligible.

The central point of the precursor shock mechanism is that the shock wave formed at the point S is assumed to cause detonation in a manner entirely similar to initiation in shock-testing (Sections III,D and IV,A). Chemical reaction is initiated at S. This is so despite the fact that points of lower values of x have been exposed to high pressures for a longer time. It has been speculated in connection with gaseous systems that the effect may be due to lateral transport losses. While such losses will inevitably occur to some extent in all real systems, initiation of a reaction in the shock-formation region ahead of the deflagration point can be accounted for on the basis of one-dimensional hydrodynamics alone. For the compression process, shown in figure 4, consists of two regions. Up to the point S the flow is that of a simple (isentropic) compression wave. Beyond S the flow is no more a simple compression and, consequently, there is an increase of entropy across the shock front. The corresponding compression energies are:

$$E_{\text{isent}} = -\int p\,dV,\ x < x(S),\ t < t(S) \qquad (15)$$

$$E_{\text{H}} = \frac{1}{2}\,p_{\text{H}}\left(\frac{1}{\rho_0} - \frac{1}{\rho_{\text{H}}}\right),\ x \geq x(S),\ t \geq t(S) \qquad (16)$$

The shock-compression energy given by equation 16 (the Hugoniot equation) is always larger than the corresponding isentropic compression energy. For reasonable equations of state of solid explosives and for pressures of the order of 10^4 atm., the discontinuous increase in energy (and temperature) at the point S may be about 20 per cent (140); the resulting increase in reaction rate will be manifold. A consequence of the fact that shock-initiation occurs ahead of other reaction fronts (deflagration and low-order detonation) is that the precursor shock mechanism requires a backward-moving detonation front—a *retonation*—to propagate from the point S. Such a front was observed photographically by Griffiths and Groocock (62).

The cause of failure of less sensitive explosives to undergo transition to detonation (58) within a limited time and under limited confinement may be either a low burning rate, in which case the rise in pressure is slow and no precursor shock can form within a reasonable distance, or a low sensitivity to shock. In the latter case the shock may form, but cannot attain sufficient strength before rupture of the casing quenches the chemical reaction. Estimates of the actual time delay between rupture and quenching involve the multi-dimensional problems of the motion of the wall and of propagation of rarefaction waves toward the center of the charge.

As in the case of gaseous systems, the sequence of transition events detailed above presupposes a mechanism of rapid increase of burning rate. In the simple case of a cast solid the mechanism can be provided by the pressure dependence of laminar deflagration rate (87). In most practical cases, however, the explosive is probably not homogeneous. At the present time it appears doubtful whether adiabatic compression of occluded gas has any profound effect, but the existence of cracks and pores does furnish an increased burning surface area, and, if porosity is sufficiently high, it may allow important flow of hot reaction products. Porosity has been found to have a strong influence on the detonability of explosives and propellants (2); indeed, it has been demonstrated in experiments on the burning of explosives under confinement (119, 127) that a significant increase of pressure will occur only when a mechanism of burning within cracks and interstices becomes possible. Several possible mechanisms of flame acceleration (such as increase of burning surface because of porosity, the effect of radiation, and energy transfer in irregular burning) and the part they play in transition to detonation were discussed qualitatively by Andreev (4, 5) a number of years ago.

Quantitatively, the problem can be treated as regressive surface burning with a given initial volume. The pressure-time history of the partly or completely confined deflagration can then be derived on the basis of the balance of pressure increase from deflagration and pressure decrease from venting (if any). Assuming the process to be isothermal and making use of the surface burning law (equation 11), one obtains:

$$\frac{\mathrm{d}p}{\mathrm{d}t} = \frac{\partial p}{\partial n}\frac{\mathrm{d}n}{\mathrm{d}t} + \frac{\partial p}{\partial V}\frac{\mathrm{d}V}{\mathrm{d}t} \tag{17}$$

$$\frac{\mathrm{d}n}{\mathrm{d}t} = \frac{\rho_0}{M}\frac{\mathrm{d}V}{\mathrm{d}t} - u(p)S'\frac{n}{V} \tag{18}$$

$$\frac{\mathrm{d}V}{\mathrm{d}t} = S\mathcal{R} = S(\mathcal{R}_0 + Ap^B) \tag{19}$$

Here n, M, and V are the number of moles, the molecular weight, and the volume of the product gas, ρ_0 is the density of the solid, S is the surface burning area, and S' is the exhaust area; $u(p)$ is the egress speed of the product gas. If $\mathrm{d}p/\mathrm{d}t = 0$, the problem is the one of rocket motor burning. The criterion of burning instability, on the other hand, is given by the requirement that $\mathrm{d}p/\mathrm{d}t$ be positive. The requirement is always fulfilled in the special case of complete confinement. In that case $S' = 0$, and equation 17 becomes

$$\frac{\mathrm{d}p}{\mathrm{d}t} = \varphi(p)\frac{\mathrm{d}V}{\mathrm{d}t} = \varphi(p)S\mathcal{R} \tag{17'}$$

where

$$\varphi = \frac{\rho_0}{M}\frac{\partial p}{\partial n} + \frac{\partial p}{\partial V}$$

depends on the equation of state of the product gas. Integration of equation 17′ yields the pressure-time history:

$$t(p) - t(p_0) = \int_{p_0}^{p} \frac{\mathrm{d}p}{\varphi S(\mathcal{R}_0 + Ap^B)} \tag{20}$$

For explosives, equation 20 has been shown to approximate an exponential dependence of pressure on time (87).

The value of the precursor shock mechanism is that it allows the complex problem of transition to detonation, in the first approximation, to be dealt with as a sequence of two simpler processes, formation of a shock in an essentially inert medium and initiation of detonation by shock discussed in Section III,D. The problem of detailed causes of the acceleration of burning in specific systems and of consequent formation of compression and shock waves is the least studied aspect of the transition process.

C. GRAIN BURNING AND THE LOW-ORDER DETONATION

There is no doubt that the granular structure of explosives plays an important part in the propagation of both detonation and subdetonation waves. For instance, it was found long ago (72) that charges composed of large particles detonate at lower velocities than those composed of smaller particles. Such observations are consistent with the theory that grains of explosives react by surface burning rather than by adiabatic homogeneous thermal decomposition: grain surfaces are exposed to high temperatures of compression of interstitial gas and, once its surface is ignited, every grain deflagrates under shock pressure until consumed. The inside of the grain is, of course, also compressed, but its temperature remains much lower. Extrapolation of rates of linear deflagration to detonation pressures on the basis of the grain-burning mechanism gives the right order of magnitude for the velocity of detonation if one assumes a reaction zone less than 100 grain layers thick, which is not unreasonable.

There are earlier discussions of surface burning (7), but it was the quantitative work of Eyring and coworkers (48) on the mechanism of nonideal detonation waves that established the close connection between the concept of grain burning and the propagation of metastable regimes of velocities much higher than those of deflagration but lower than the steady-state detonation. Such intermediate regimes, commonly termed "low-order detonations," are frequently observed during the transition to detonation. The time required to consume a spherical grain is

$$t_b = \frac{3r_g}{kr_m} \tag{21}$$

where r_g is the grain radius, r_m is the molecular radius, and $k = Z' \exp(-E_a/RT)$ is the specific reaction rate. The combination of such grain-burning kinetics with a quantitative treatment of nonideal detonations (48) gives the following relation between the ideal and nonideal detonation velocities (based on the so-called "curved front theory"):

$$\frac{D_j}{D_i} = 1 - \frac{Ka_j}{X} \tag{22a}$$

$$\frac{a}{a_j} = \frac{D_i}{D} \exp \frac{E_a}{RT} \left(\frac{D_j^2}{D^2} - 1 \right) \tag{22b}$$

where the subscript i refers to the *ideal* detonation, subscript j to any *steady* detonation, a is the reaction zone length, X is the charge diameter, and K is a constant (about 0.5). Equations 22 give two propagation velocities for every charge diameter, a "low-order" and a "high-order" detonation (the high-order regime is the hydrodynamically defined steady-state detonation); furthermore, reasonable velocities are obtained only if E_a/RT is not too far from unity. This means that the grain-burning theory demands activation energies for subdetonation and detonation reactions which are essentially lower than those of homogeneous explosive reactions (*cf.* Section II,B). Cawsey, Farrands, and Thomas (23) applied the curved-front theory to their data on pressed Tetryl and obtained an activation energy of only 2-kcal./mole. Such a low value is difficult to reconcile with unimolecular decomposition; it appears more likely to refer to physical processes, such as evaporation or diffusion, which are prominent in heterogeneous surface reactions.

Whatever its detailed mechanism, the low-order detonation possesses the following characteristics (23, 33, 48, 59, 107, 108, 137):

(*1*) Its velocity of propagation is neither very reproducible nor strictly constant, but it usually appears to be somewhat less than the sonic velocity in the explosive. Values between 1 and 2.5 km./sec. have been reported.

(*2*) Its reaction is very incomplete. Possibly the reaction merely skims the surface of the grains without penetrating into any depth. Consequently, pressures developed remain relatively low.

(*3*) It can be established more easily in porous low-density charges than in high-density charges.

(*4*) To persist for an appreciable time (say several microseconds at least) it must be initiated by a shock of quite critical strength. If the shock strength is somewhat less than critical, the result is failure; if it is somewhat more, high-order detonation develops very rapidly. Consequently, low-order detonation can be established by shocks of carefully limited strength, for instance, by employing detonators without "boostering" charges (23, 33), but even more easily in thermally initiated charges which go over into detonation by the spontaneous shock mechanism (Section III,B): in the latter case the compression waves grow continuously and hence necessarily pass through the critical strength.[5] Indeed, it was found (59) that even in high-density cast explosives, initiated thermally, the occurrence of a remarkably long low-order detonation (up to 80 microsec.) is wholly reproducible. By contrast, transition from low- to high-order detonation takes no more than a few microseconds.

Finally, it must be pointed out that, as predicted by equations 22, at large values of the ratio of reaction zone length to the charge diameter the low-order and the high-order detonation branches merge. The effect was studied (107) with ammonium nitrate explosives which have relatively long reaction zones. Near the failure diameter of the charge the detonation velocity (2–3 km./sec.) is very sensitive to geometric parameters, and it becomes difficult to distinguish the low from the high regimes; hence the oft-reported variation in the velocity of detonation of such insensitive explosives. Military explosives, on the other hand, are almost invariably used in diameters considerably above critical, so that the two velocity branches are widely separated, the upper steady state being the commonly observed one.

D. SHOCK-INITIATION OF DETONATION

Compression of explosives by a hydrodynamic shock wave initiates a chemical reaction in the shocked region; if the reaction rate exceeds a certain critical value which depends on both the properties and the geometry of the explosive, the energy released in the reaction reinforces the shock wave and, after a transient interval of build-up, steady-state detonation results. If the reaction is quenched by rarefactions before it can reinforce the shock, failure results. Shock-initiation of detonation can be realized experimentally either indirectly, by allowing a precursor to form within the

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[5] The author is indebted for this observation to Mr. R. H. Stresau.

explosive charge (Section III,B), or directly by an externally supplied shock wave. The latter experiment, more controllable and studied more extensively by far, is always some sophisticated version of gap testing (Section IV,A), wherein a strong shock wave from a donor charge is attenuated in an inert barrier before impinging upon the acceptor charge. Such arrangements permit quantitative observation of the last stage of the transition process, the growth of the shock into steady-state detonation.

For the sake of simplicity this discussion will assume unidimensional hydrodynamics of a condensed medium, either homogeneous or granular. The two major practical problems attending unidimensional experiments are generation of a plane shock wave and elimination of side rarefactions. Reasonably plane waves can be obtained by means of explosive lenses (29). While lateral rarefactions can be eliminated by use of large donor charges, opaque explosives require special techniques for observing the portion of the explosive undisturbed by such rarefactions (20, 71, 88). External confinement of the system is not feasible, because in studies of the build-up of detonation from a shock wave the pressures impressed upon the acceptor material are for conventional explosives almost never less than 5 kbar and often more than 100 kbar, a magnitude greatly in excess of the ultimate strength of materials.

The information sought in shock-initiation experiments is the shock pressure and duration in the acceptor, the two variable parameters determining build-up (or failure). Neither can be measured directly. Shock pressures are commonly obtained from simultaneous measurements of shock and particle velocities. Similar data can in principle serve to determine the pressure profile in and behind the detonation front (42, 89), but such determinations are both difficult and uncertain. The field of unidimensional shock-initiation, one of vigorous activity at the present time, recently has been reviewed by Jacobs (71).

The commonly accepted explanation of the mechanism of one-dimensional shock-initiation (71) is well documented by a large number of accurate and very carefully planned experiments at the Los Alamos Scientific Laboratory and elsewhere, both for solid (20, 88, 111) and for liquid (21, 22, 25, 37) explosives. An idealized version of the mechanism is sketched in figure 5. The shock entering the acceptor at origin O gives rise to an elevated temperature, which in turn induces a chemical reaction at the interface of the explosive and the inert barrier. For an induction period τ the reaction rate remains negligible and the interface travels to the point A at the particle velocity u; meanwhile the impinging shock propagating at the velocity U has progressed into the explosive along the path OB. The time τ—about a microsecond—is so short that both paths OA and OB are approximately linear. After the induction period τ a detonation reaction proceeds from A to B. Since this reaction travels through a precompressed medium, its velocity D' (usually 9–12 km./sec.) is higher than that of steady-state detonation D; it overtakes the shock wave and merges with it into steady state detonation at B.

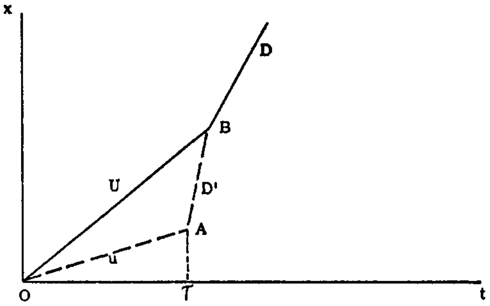

FIG. 5. One-dimensional shock-initiation of a condensed explosive.

For a given incident shock pressure p_H, the two velocities U and u—as well as the density and the energy of the compressed material—can be obtained from the three hydrodynamic conservation equations and the equation of state of the explosive:

Conservation of momentum $$p_H = \rho_0 u U \qquad (22)$$

Conservation of mass $$U\rho_0 = (U - u)\rho_H \qquad (23)$$

Conservation of energy $$E_H = \frac{1}{2} p_H \left(\frac{1}{\rho_0} - \frac{1}{\rho_H}\right) \qquad (16)$$

Equation of state $$E = E(p, \rho) \qquad (24)$$

In order to evaluate the delay τ, one must also know the kinetics of the explosive reaction induced by the incident shock as well as the relation

$$T = T(E) \qquad (25)$$

Under the conditions assumed in the discussion of the thermal theory (Section II,A), the delay then is:

$$\tau = \frac{C}{QZ}\int_{T_H}^{T_{\exp}} e^{E_a/RT} \mathrm{d}T \simeq \frac{C}{QZ} \frac{RT_H^2}{E_a} e^{E_a/RT_H} \qquad (26)$$

The steady-state detonation velocity D can, in principle, be calculated from the thermodynamic-hydrodynamic theory (118). The same theory will be valid for the calculation of D' if one replaces the initial state, normally at ambient conditions p_0, ρ_0, E_0, by the shocked state (p_H, ρ_H, E_H).

The idealized one-dimensional mechanism of build-up of detonation from a strong externally imposed shock wave entails neither low-order detonation nor retonation (Sections III,B and III,C), because the region below the line OA in figure 5 is inert medium (the corresponding region below the line SA in figure 4 is explosive). The backward detonation which is often observed in shock-initiation experiments (called "hook" effect because of its appearance in a smear camera record) is a two-dimensional phenomenon.

Slight but significant deviations from the idealized scheme shown in figure 5 have been reported (20, 21). It was observed that shock velocities U are never quite constant: they decrease in liquid and increase in solid explosives. The observation can be explained readily on the assumption that in liquids the reaction is a homogeneous one, while in solids it is surface burning. Thus in liquids one has to deal with adiabatic kinetics (Section II,B), which require activation energies of perhaps 30–40 kcal. and hence exhibit a pronounced induction delay closely resembling the idealized pattern which stipulates that for $t < \tau$ the rate is quite negligible and at $t = \tau$ it goes to completion practically instantaneously. The shock, not being reinforced during the induction period, decays slightly. The surface reaction in solids, on the other hand, requires much lower activation energies (Sections II,B, III,C), the induction period is less pronounced, partial reaction starts almost immediately upon entry of the shock into the acceptor, and the energy so released reinforces the shock wave which accelerates more smoothly into steady-state detonation. The low activation energy mechanism also explains the fact that granular solid explosives are more detonable than the liquid ones, although their homogeneous activation energies are not conspicuously lower.

The experimental evidence concerning the occurrence of the hypervelocity wave D' in solids shown in figure 5 is not uniform. Such an effect should be observable only to the extent that there is an experimentally discernible induction period τ. Indeed, the question of detailed mechanism of growth of a shock to detonation in solids, which is evidently more complex than the corresponding process in liquids, allows ground for speculation. If the activation energy of the governing process is so low that an appreciable amount of explosive energy is released throughout the transient predetonation interval, there will be considerable intensification of the incident shock along the path OB and both paths OA and OB will curve upward. The situation would thus present some features of a new shock-formation stage, and one should not *a priori* exclude the possibility of either initiation of detonation reaction near the shock front or a short (one-dimensional) retonation from the shock front to the interface.

There are several theoretical treatments of homogeneous shock-initiation. Hubbard and Johnson (69) carried out a high-speed digital computer analysis in which they considered the effect on an hypothetical explosive charge of a hydrodynamic shock of specified strength and duration (a "square wave"):

$$\begin{aligned} p &= 0 && \text{for } t = 0 \\ p &= p_H && \text{for } 0 < t < t_2 \\ p &= 0 && \text{for } t > t_2 \end{aligned}$$

The value p_H was arbitrarily set to be 100 kbar; the time t_2 was varied (about 1 microsec.). This pressure–time relationship is converted by means of equations 24 and 25 into a hydrodynamic time–temperature curve. The criterion of shock-detonability is established by a comparison of the t vs. T_H curve and the corresponding τ vs. T curve defined by equation 26 for various values of T. (On account of a large assumed activation energy, 40 kcal./mole, the induction delay τ was sharply defined.) Shock-initiation of detonation occurs only if the two curves cross. Similar results were obtained by a different computational scheme recently presented by Enig (46). The scheme contains separate equations of state for the condensed medium and the product gas and includes, besides hydrodynamics and chemical kinetics, also transport properties.

The *a priori* computations, in view of oversimplified equations of state and of uncertainties in the values of physical properties at high temperatures and extremely high pressures, give qualitative information only. Chaiken (25) showed that the salient features of shock-initiation of homogeneous condensed materials—the induction delay τ and the hypervelocity detonation D' (see figure 5)—can be accounted for also quantitatively in a semiempirical fashion.

Campbell and coworkers (21) have successfully applied the computational treatment of Hubbard and Johnson, which employs homogeneous kinetics, to shock-initiation data in liquids. It can be shown, however, that if one attempts to apply such a treatment to solids, the computed dependence of detonability on pressure is much too strong. This adds to the evidence that, in solids, the governing rate process has a low activation energy.[6] Still further evidence supporting the grain-burning theory of growth of detonation is furnished by shock-initiation of low-density granular PETN (111); it was found that the shock pressure required for detonation is independent of the shock temperature of the interstitial gas. This is understandable if the governing factor for the growth of detonation is not the shock temperature, but the subsequent surface decomposition rate. For the efficiency of surface burning depends on the rate of heat transfer from the deflagration flame to the solid surface (see references in Section II,B,3); an increase of pressure, causing larger amounts of heat to be transferred to the unit area of the solid, increases decisively the surface regression rate. By contrast, the temperature of the gas adjacent to grain surfaces prior to the establishment of surface deflagration, although essential for the ignition of the

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[6] The term "activation energy" as applied to interphase initiation must be interpreted loosely and with caution, because even in the absence of shock waves the process involves a combination of chemical and of transport phenomena (Section II,B,3); the shock wave introduces additional hydrodynamic problems associated with transitions across contact discontinuities which have not yet been explored to any appreciable extent.

grains, has little effect on the propagation of deflagration and growth of the shock to detonation.

There is interesting experimental evidence that single crystals of explosives can be initiated either homogeneously or heterogeneously. Holland, Campbell, and Malin (68) showed that strong shocking of a crystal of PETN, a quite sensitive explosive, follows a homogeneous pattern of growth to detonation analogous to that in liquids. Adams, Holden, and Whitbread (1), on the other hand, initiated single crystals of the less sensitive RDX by shocks of marginal strength (about the 50 per cent point; see Section IV,A) and found that whenever detonation occurs, it starts only after the shock has traversed the crystal and then propagates back into the shocked explosive. (The experimental arrangement was not one-dimensional.) While it was thus clearly shown that detonation always started at the interface of the acceptor and the adjacent material (regardless of the properties of that material), the detailed mechanism of initiation at the contact discontinuity is not clear (see Section IV,A). It would appear that the same crystal may have two different critical shock strengths, a higher one for homogeneous and a lower one for interfacial initiation. It is still within the realm of speculation whether the shock which initiates the interior of a crystal is sufficiently strong to do so strictly homogeneously or whether the process begins at crystal imperfections.

An essentially different mechanism of growth of detonation from a shock is being advanced by Cook and coworkers (30, 32, 36). The mechanism is the outgrowth of the theory according to which thermal conductivity associated with shock waves in explosives is so large that it plays a paramount part in the mechanism of both formation and propagation of detonation. The inert material interposed between the donor and the acceptor in the shock test is assumed to transmit the pressure wave from the donor, but not the thermal wave. The pure shock impinging upon the acceptor not only initiates a chemical reaction, as in the more conventional explanation, but it also induces a high-electron-density metallic state in the acceptor, rendering it extremely conductive. The heat evolved by the reaction after an induction period is thus enabled to flow exceedingly rapidly across the shocked material to the shock front, whereupon the heat pulse and the shock merge into steady-state detonation. The rapid heat pulse, termed "flash-across," is qualitatively analogous to the hypervelocity wave *AB* in figure 5, but it has been reported to propagate much faster (up to 100 km./-sec.). An increase of electrical conductivity of the solid explosive behind the shock front is an observed fact (10), but its quantitative consequences (71), as well as the interpretation of the photographic evidence of high electronic density phenomena supporting the heat-pulse theory (39), are the matter of some controversy.

The summary progress of pure shock testing in the last decade or so is impressive. It has become possible to generate and apply plane shock waves of known pressures and in geometries which yield essentially unidimensional data. However, methods of simultaneous calibration of the duration of shock—hence of total impulse imparted to the acceptor—are still lacking. Theoretical analysis of the pressure profile behind a one-dimensional detonation has been done in principle (117), but its application to shock tests would require equations of state of both the detonation products of the donor charge and of the inert (solid) barrier, as well as a treatment of propagation of shocks across at least two discontinuities. As far as theoretical treatment of the chemical reaction in the acceptor is concerned, it appears that one can with some confidence assume that liquid explosives under *strong* shock conditions are homogeneous for the purpose of reaction kinetics. Solids almost certainly are not so, and one can hardly hope to construct a realistic working model of growth and propagation of steady-state detonation in granular explosives, analogous to the work of Hubbard and Johnson (69), based directly on the Arrhenius type kinetics. A theoretical attempt would have to include both surface kinetics of the type discussed in Section II,B and the correct amount of exposed surface per unit mass of explosive as determined from grain size and bulk density.

IV. PRACTICAL SENSITIVITY TESTS

A. THE GAP TEST

The method of shock-initiation across inert barriers was suggested by Muraour many years ago (91), but the first systematic study of the phenomenon by means of smear photography was carried out by Herzberg and Walker during World War II (66). Since that time several explosives research laboratories both in the United States and abroad have adopted and standardized it as a practical test of sensitivity (2, 19, 30, 34, 35, 43, 73).

The *gap test*, sometimes called the *booster test*, is an experimental arrangement wherein the shock from a detonating donor charge is attenuated through an inert "gap" to the strength barely sufficient to initiate detonation in the acceptor. Most commonly used gap materials are plastics or metals. For given donor and gap materials and for fixed geometries of both the donor and the acceptor the gap thickness which gives the marginal shock strength, termed the "gap value" or the "50 per cent point," is a quantitative measure of the sensitivity of the acceptor to shock; sensitive explosives have a high and insensitive ones a low gap value. A practical way of determining the gap value of the explosive under test is to vary the gap until one arrives at two thicknesses n and n' such that thickness n always results in detonation of the acceptor and thickness n' always in failure; the gap value then is $(n + n')/2$. Plots of the location of the shock front vs. time in the acceptor are concave upward for gaps smaller and downward for gaps larger than the 50 per cent point (19). Although for reasonably short acceptors the only unambiguous way of determining the outcome of a particular shot (detonation or failure) is just such a measurement of velocities of propagation in the acceptor, it has been found satisfactory for routine testing to judge the result from the mechanical damage to a witness plate placed at the end of the acceptor. The gap values, under reasonably carefully controlled conditions, are quite reproducible and remarkably sharp; n and n' frequently do not differ by more than a fraction of a millimeter. Table 1 lists gap values for a number of explosives and propellants obtained in the U. S. Naval Ordnance Laboratory gap test (figure 6). Absolute numbers obtained in another gap test (different geometry, different gap material) will differ, but the ordering of explosives, which defines a relative shock sensitivity scale, will usually be the same.

TABLE 1

The U.S. Naval Ordnance Laboratory Gap Test (Fig. 6)

Material	Cast or Pressed	Density *g./cc.*	Gap Value *cm.*
DINA	Cast	—	8.39
RDX	Pressed	1.640	8.20
Pentolite	Cast	1.684	6.70
Tetryl	Pressed	1.615	6.63
EDNA	Pressed	1.551	6.35
Composition B	Pressed	1.663	6.05
Composition A	Pressed	1.59	5.34
Composition B	Cast	1.704	5.24
TNT	Pressed	1.569	4.90
Amatol	Cast	—	4.12
Explosive D	Pressed	1.593	3.81
TNT	Cast	1.60	3.50
Tritonal	Cast	1.75	2.90
Double-base propellant	—	—	0.88
Composite propellants	—	—	<0
Ammonium nitrate	Pressed	1.615	<0

The description of fundamental processes occurring in the gap test is essentially that of growth of a strong shock to detonation; indeed, the test is reproducible and amenable to analysis precisely because it approaches rather closely the idealized behavior outlined in Section III,D. The principal disparity between the existing gap tests and the ideal is their geometry; they are so subject to side rarefactions (caused by too low ratios of the diameter of the acceptor to the length of the gap–acceptor assembly) that attempts at unidimensional analysis must be definitely ruled out. In most routine gap tests the shock wave from the donor is not plane and the diameter of the acceptor is several times smaller than its length. Since it has been found empirically that such relatively long acceptors are needed for unambiguous indication of detonation or failure, it is clear that gap testing is an essentially two-dimensional process. The tests, of course, could be redesigned so that build-up to detonation would be opposed by rear rarefactions only, but the change would not be practical: first, because it would make the procedure prohibitively elaborate and expensive and, second, because the primary purpose of the test is to provide detonability data under practical military and commercial conditions, which are almost never one-dimensional. The alternative approach, a two-dimensional hydrodynamic study, entails cumbersome mathematics which can be handled only with high-speed computers; some two-dimensional computation work has been started (98). Much empirical knowledge of nonunidimensional shock initiation across gaps has been gathered in a number of exploratory nonstandardized tests (10, 30, 44, 50, 75, 90, 128, 132, 134). It has been shown that steady-state detonation in the acceptor always forms at a distance from the gap which increases with increasing gap thickness. Shock-initiation occurs first in the interior of the acceptor. Detonation (Sections III,B, III,D), on the other hand, is observed on the surface of the acceptor.

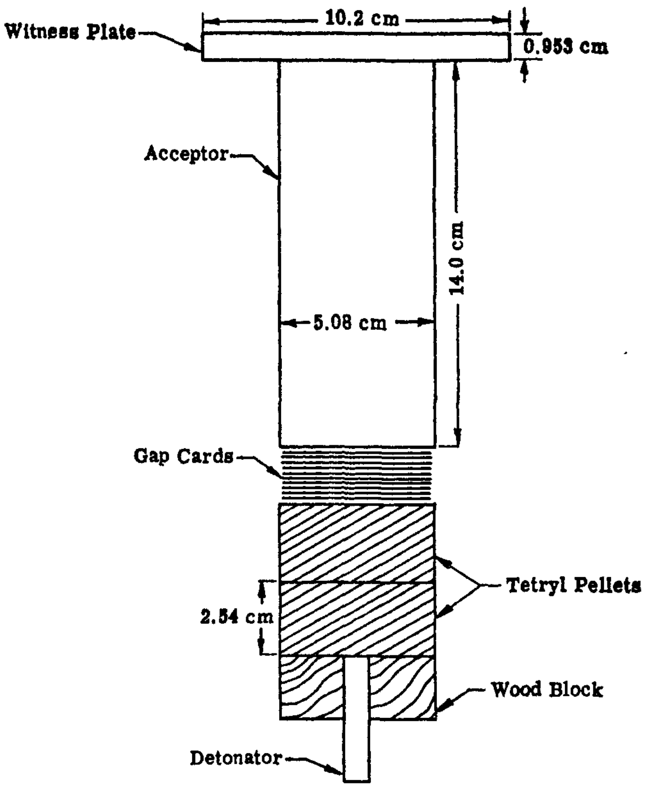

FIG. 6. The Naval Ordnance Laboratory gap test for solids. The gap consists of a varying number of cellulose acetate "cards," 0.25 mm. thick. The witness plate is steel.

Besides the geometry of the acceptor, the physical nature of the lateral boundary plays a part in determining the gap value. The obvious effect of the wall is to confine the acceptor and thus decrease side losses: the heavier the confinement, the higher the gap value. However, it is becoming evident that confinement alone does not fully explain the experimental results. Testing of the effect of the confining material at the U.S. Bureau of Mines (57) indicates that stronger confinement does not necessarily enhance the detonability of explosives and vice versa. A more complete explanation must take into account the effect of lateral interactions of shock waves with the surroundings. If the confining material has a higher shock impedance (ρU) than the acceptor, a reflected lateral shock will propagate from the interface into the acceptor; if the surroundings have a lower impedance, a lateral rarefaction is reflected. It appears that, in some cases at least, either type of discontinuity may sensitize the acceptor. The role of a contact discontinuity in the initiation of detonation by shock already has been mentioned in the discussion of initiation of single crystals (Section III,D). Nonunidimensional shock testing must therefore be done with controlled physical properties (mass, density, compressibility) of the surrounding material.

Increase of the initial temperature of the acceptor increases the gap value of liquid explosives (9, 22, 43), because it increases the shock temperature. The effect of initial temperature in solids is more complex, and an explanation must include not only the thermal, but also the mechanical properties of the acceptor (2). Interstitial gas and gas pockets at the gap–acceptor interface (111) when shocked create very hot centers, but their effect on shock sensitivity does not appear appreciable (Section III,D).

Simultaneous measurements of the shock and the particle velocities in the gap allow determination of shock pressure, $p = \rho u U$, in the gap; hence any given gap test can be calibrated so that gap values are translated into minimum shock pressures necessary to initiate an explosive. Such calibrations have been reported (2, 19, 36, 73), but they must not be considered absolute calibrations of the sensitizing stimulus, first, because even when the pressure in the gap is known, pressure in the acceptor will depend on the shock impedances of the gap and the explosive and, second, because there is still no assessment of either durations of the shock or lateral interactions with the surroundings.

B. THE IMPACT TEST

The initiating stimulus in the impact test is provided by the drop, from a known height, of a hammer on the sample of the explosive. The sample, usually a small fraction of a gram, may be placed on a steel anvil and covered by a cylindrical steel striker, which is struck by the fall of the hammer. The test differs essentially from the gap test, because its pressures (several hundred, or up to several thousand atmospheres) are much lower and its time scale (hundreds of microseconds, depending on the length of the hammer) much longer. Impact sensitivity rating of an explosive is defined by the drop height which gives a 50 per cent probability of explosion. The first attempts at the ordering of explosives by impact go back to the turn of the century (79, 131); the procedure has since that time been adopted as a practical standardized test by many laboratories in several countries. The history of the test was reviewed recently by Koenen, Ide, and Haupt (85).

Since the results of the impact test are subject to much larger fluctuations than those of the gap test (Section IV,A), the method of arriving at the 50 per cent point must be given some care. A widely used statistical procedure for the determination of standard deviations and of the 50 per cent point was devised at the Explosive Research Laboratory, Bruceton, Pennsylvania, during World War II. Even when such a well-defined procedure is adopted, there is still an uncertainty in judging the outcome of a single test, because the criterion of the test—explosion—is not a defined concept (Section I,B). The usual indication of explosion is an appreciable amount of noise; this means that the test is counted positive if there is ignition of the sample followed by an indefinite degree of acceleration of the explosive reaction. The British investigators sometimes use as a criterion the amount of gas evolved under impact. High explosives seldom, if ever, detonate in the impact machine.

Table 2 lists the 50 per cent points obtained at the U.S. Naval Ordnance Laboratory for several explosives and propellants. The quantitative ordering is the same as in the gap test (it also agrees with field experience) for high explosives, but not for propellants. Indeed, the point has been made (2) that none of the standard propellants, which are considered safe in practical

TABLE 2

The U.S. Naval Ordnance Laboratory Impact Test

(2.5 kg. hammer weight, 35-mg. sample, No. 12 tool with sandpaper)

Material	50% Impact Height *cm.*
PETN	13
Composite propellant	15–41
RDX	24
HMX	26
Double-base propellant	28
EDNA	34
Pentolite	38
Tetryl	38
Composition A-3	60
Composition B	60
Tritonal	107
Amatol	116
TNT	200
Ammonium nitrate	>320

work, could be justified from the safety point of view if the impact test were the standard.

While the fundamental processes occurring in the gap test can be described starting from the extensively studied pure shock-initiation, there is no such simple first approximation applicable to the impact test. So many variables must be considered that it is generally agreed that impact tests are not sufficiently well understood to serve as a firm criterion of sensitivity. Yet, while most workers in the field entertain and admit misgivings about the reliability of established impact tests,[7] impact machines continue to be used quite extensively. This is so, first, because results of impact testing do, in a general way, agree with the notion of sensitivity derived from field experience, at least for primary and high explosives, and, second, because the impact test is very simple to perform. Obviously then, it would be very desirable to know how to control the variable factors and thus reduce the uncertainty of results so that it would become possible to impact-test and thereby classify a new explosive authoritatively rather than merely with a vague probability. However, without the knowledge of both the conditions which obtain in the sample of explosive under impact and the manner in which explosives react to such environment, impact testing remains a crude art of limited usefulness.

Only a very brief mention of some variables which must be controlled will be made here. The most important one, of course, is pressure. Given the elastic constants of the anvil and the striker, metal-to-metal impact pressures can be calculated (92), but these pressures may change drastically when an explosive substance, usually pulverized, is introduced under the tool. The same is true of the very important pressure-time diagram of the process. Since the temperature of the compressed sample is almost certainly not uniform, its distribution must also be known, and if the sample has a low density, its volume may change appreciably.

In addition to the thermodynamic properties, one must consider exchange of both mass and energy with the surroundings. Lateral escape of the sample from its initial volume may become very important, depending on the geometry of the tool and the mechanical properties of the sample. From the thermodynamic point of view, confinement of the sample must have a sensitizing effect, but it is known from experience that explosions may occur precisely during (and presumably because of) the flow of the sample; this indicates that properties such as viscous heating and friction matter as well. Rapid extrusion of explosives through crevices has long been known to lead to explosions. More recently, it has been reported that adding wax to explosives, a standard desensitizing procedure, may actually increase impact sensitivity, because it increases fluidity of the sample (6). Many geometries and other minor variations of the impact tool have been attempted with the aim of increasing reproducibility and reliability of the results. Such empirical variations have added little to the knowledge of the fundamentals, although there are partial practical results. For instance, it has been found at the U.S. Naval Ordnance Laboratory that good results are obtained if the sample is placed on a sheet of sandpaper; this is interpreted to mean that the procedure minimizes the effect of uncontrolled parameters such as hardness and thus allows correlations of the test with the chemical properties. Durations of impact are so long that, in addition to mass flow one may have to consider also heat flow to the surroundings, governed by thermal conductive properties of the explosive and the surroundings (Section II,A).

Despite the great complexity of the subject, remarkable attempts at a scientific evaluation were made during and immediately after World War II mostly by British investigators (15, 16, 17, 100, 123, 126, 135), who developed nonroutine impact tests. The extensive study, predominantly with sensitive primary explosives, gave a general phenomenological description of impact-initiation. Typically, the entire process occurs within an interval of the order of magnitude of 10^{-4} sec., which can be divided in three parts: (*a*) the initial delay before a visible reaction; (*b*) the slow flame stage (propagation velocities of 10–50 m./sec.); (*c*) explosion. Explosion may propagate at velocities of several meters per second, or as high as 2 km./sec.; hence it may be a form of low-order detonation (Section III,C). It has also been shown quite convincingly that initiation occurs at small hot spots rather than homogeneously throughout the body of the sample. Experiments in which grit particles of melting points between 400° and 600°C. were admixed to the sample show that hot-spot temperatures necessary to initiate explosions are about 500°C. The exact mechanism of formation of hot spots is not clear. It was suggested that they may be due either to adiabatic compression or entrapped gas bubbles or to internal friction. The former mechanism recently has been questioned (12, 139) on the ground that, for typical heat-transfer properties, compression of bubbles in the impact test is not adiabatic, but more nearly isothermal. It has been pointed out, however, that bubbles may be very effective if they contain drops or particles of combustible materials; the impact may cause small drops and particles to be spalled off into the bubble, where they ignite and burn rapidly (76).

Hot spot considerations show that impact explosions are governed by the thermal properties of explosives. Bowden and Gurton (15) correlated delays to explosion

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[7] According to F. P. Bowden (14), "hitting a solid with a hammer . . . is perhaps an experiment more proper to a carpenter than to a physicist."

with chemical kinetic data on the assumption that reaction within the hot spot is adiabatic. Wenograd (129) made a more extensive study of the connection of the 50 per cent impact heights and rates of explosive decomposition for high explosives, and showed that there is a reasonable correlation if the reaction is assumed to take place at 500°C. (*cf.* Section II,B). Such correlations show that, although the exact mechanism of initiation by impact is not known, the process almost certainly obeys the laws of thermal theory; it is complex and poorly reproducible only because testing conditions are so.

C. COMPARISON OF THE TWO TESTS

The gap test is better defined than the impact test, because (*a*) the initiating stimulus is more reproducible and (*b*) the criterion of the test, detonation, is well defined: the gap test measures detonability, which is a specific form of sensitivity. The weaker stimulus in the impact test apparently makes it more sensitive to minor variations (condition of tool surfaces, angle of impact, inhomogeneity of the sample, etc.); moreover, the criterion of explosion—ignition followed by an arbitrary extent of growth toward detonation—is somewhat ambiguous. The two tests do not measure the same property and should, in general, be expected to give different results. In particular, fuels of low detonability and high ignitability will be rated relatively sensitive by the impact test and insensitive by the gap test; this, of course, is the exact case of propellants. Indeed, propellants which cannot be detonated at all in reasonable dimensions (possibly because the fuel and the oxidizer are separated and not able to diffuse toward each other within reasonable reaction zone times) may have high sensitivity to impact.

It follows that there can be satisfactory correlation of the two tests only for substances whose mechanisms of both the ignition and the transition to detonation are similar. It has been common practice to make such correlation among explosives. A comparison of tables 1 and 2 justifies the procedure and, to the extent that this can be done, either test gives a fairly good indication of sensitivity. The two scales are comparable, but since the impact test is experimentally simpler, it is more widely used. While it is realized that explosives and propellants cannot be meaningfully rated on the same impact-test scale, it is becoming routine to rate propellants among themselves on a separate scale. This should be done with caution, because propellants are of so widely different compositions that their reaction mechanisms are not necessarily similar. For instance, high-energy double-base propellants contain so much high explosive that they may have properties intermediate between those of a typical propellant and those of a typical explosive. While such intermediate compositions can certainly be meaningfully evaluated by the gap test, the results may not be very useful, because in the case of a propellant one is not so much interested in its detonability as in its tendency toward deviation from the controlled burning rate.

In conclusion, it may be mentioned that shock testing approaches impact testing in the limit of low pressure and (for some impact tool geometries) high confinement. Hence initiation by weak nonunidimensional shocks, such as those generated by detonators without "boostering" charges (23, 33, 133), is a field intermediate between initiation by shock and initiation by impact. Each case has to be studied separately, but it is fairly clear that as pressure decreases, nonuniform heterogeneous initiation becomes more important. Liquids, for instance, can be considered homogeneous only above a certain pressure level, which may be taken to define the limit of a "strong" shock (Section III,D).

V. SUMMARY

The sensitivity of an explosive has been defined (85) as the minimum amount of energy that must be imparted to the explosive, within limited time and space, to initiate explosive decomposition. The definition is meaningful and can serve as a basis of quantitative fundamental treatments provided the imparted energy is thermal and provided its initial distribution in time and space is known. The accuracy of treatments of thermal explosion (Section II,A) is then limited mainly by the accuracy of chemical kinetic data. If the initiating energy is not supplied directly as heat, there is the additional requirement of quantitative assessment of conversion of the stimulus into heat. Since the process of growth of detonation necessarily entails shock waves, the conversion of the mechanical energy of a shock wave into heat is a most important problem in studies of sensitivity. This means that, in addition to chemical kinetics, one must know the equation of state of the explosive under very high pressures. One-dimensional problems of shock formation and shock-initiation have been treated theoretically.

Both chemical kinetics and the equation of state must, of course, be known for a fundamental appraisal of initiation and growth of explosion in routine gap and impact tests and, in addition, one must be able to calibrate the initiating stimuli. The two specific, and only partially solved, problems of the gap test are the determination of the total initiating impulse, $\int p\,dt$, and the effect of lateral interactions. (The latter can be eliminated if the experimental arrangement is unidimensional, but routine gap tests are not.) Both problems can, in principle, be solved by hydrodynamic methods; the practical problem is measurement under extremely high transient pressures. In the impact test the pressures are such that the total impulse of the stimulus can be measured, but mass and energy losses in all three dimensions are so pronounced that a determination of the portion of energy absorbed by the sample is not possible. Moreover, the effects of heterogeneity and consequently the energy distribution during the test are less well known than in the gap test. Thus, while gap testing is becoming a science, impact testing remains essentially an art.

Practical correlations and empirical definitions of sensitivity scales are possible for substances whose physical properties and mechanisms of explosion do not differ excessively.

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