Although explosives have been known for over a thousand years, the science of explosives is still very young. We are only beginning to understand the nonlinear interaction between chemistry and fluid mechanics that produces the rapid energy release known as detonation. The science of high explosives is basically a coupling of chemistry and fluid mechanics. While each of these fields is in itself quite well-developed and sophisticated, high-explosives science is surprisingly primitive. The fluid-mechanical phenomenon of detonation is reasonably well understood, but the detailed chemical reactions and thermomechanics that cause a detonation are still largely a mystery. For many explosives, even the final chemical composition after detonation is not known accurately and the reaction mechanisms are only guessed at. Similarly, while it is clear that some of the most energetic explosives would not detonate at all were it not for their nonuniform mechanical response to shock waves, the micromechanics of explosive materials is not nearly so well understood as that of metals.

There are two basic reasons why the science of explosives is relatively undeveloped, and an understanding of them indicates why the next decade is likely to produce a dramatic increase in our understanding. First, as is obvious, measurements in the interior of a detonating explosive are extremely difficult. Whereas experimental methods have existed for many decades that can characterize chemical reactions under normal conditions, they are of little use under the extremes of temperature and pressure generated in explosives. Similarly, standard techniques to study the mechanics of flow in metals are of little use when the relevant stress and strain rates produce a violent reaction in the studied material. As a result, few academic institutions have deemed it fruitful to establish a research program in explosives.

The second reason is that applications of explosives technology in the past have not placed a high premium on understanding the details of the detonation phenomenon. Most explosive applications are in the fields of excavation, mining, or conventional munitions. All of these have well-established, albeit crude, “rules-of-thumb” as regards quantities and configurations of explosive required to accomplish the task. Hence there has been little pressure to establish an extensive industrial research base.

Recently, however, there has been a significant increase in both the capability and motivation for expanded research in explosives science. Modern instruments, particularly those employing lasers as probes, have made it possible to selectively investigate chemical phenomena on time scales of less than 100 picosecond. Such measurements are
stimulating a rapid growth in experimental and theoretical techniques that should soon be applied to explosives. The need for understanding the details of the energy release in explosives is also increasing rapidly. Explosive systems are being demanded that function with increased precision and efficiency and at the same time maximize safety. For example, in situ retorting of oil shale or chemical mining of scarce minerals will require blasting techniques that can produce a preselected distribution of small cracks or fragments rather than just a displacement of the ore to facilitate mechanical mining. As another example, modern munitions are increasingly reliant on the ability to focus the energy from explosives to defeat well-protected targets such as tanks and armored vehicles. Designs of such systems are so sophisticated that a giant computer is needed to optimize them, and the behavior of the explosive must be quite accurately predicted. This combination of demand for a refined explosive technology and the availability of new research tools should produce a dramatic improvement in the state of explosives science. In this article we review our understanding of explosives as it has evolved by bursts and starts from the turn of the century to the present. We begin with empirical observations and trace the development from simple to more complex fluid-dynamical models of energy release and propagation.

Because the time scales for energy release are so fast, the simplest model that ignores all details of the chemistry has been remarkably successful in predicting the performance of many explosives presently in use. But the more complex models give us insight into the nonlinear interaction between chemistry and fluid dynamics that is at the heart of the detonation process.

Detonation Physics

Our understanding of explosives begins with empirical observations. Figure 1 shows a block of explosive as it detonates. The detonation wave spreads out from the point of initiation almost like a Huygens construction. The wave velocity is supersonic and almost constant for a particular explosive, but it varies from one explosive to another, depending primarily on the composition and density of the explosive. For most explosives, the detonation velocity is affected little by the time it has run, the size and shape of the block, or the curvature of the detonation wave front. Because the detonation wave velocity is faster than the velocity of sound in the explosive, the material in front of the wave is absolutely unaffected until the detonation wave passes through it. In particular, a second detonation wave in the block propagates independently of the first wave until the two intersect.

The wave front is the moving surface that separates explosive material in motion from stationary material. In solid or liquid explosives, the pressures just behind the front are very high, a few hundred thousand atmospheres (a few tens of gigapascals), and the temperatures are from 2000 to 4000 K.

The high temperatures and pressures are produced by the very rapid release of chemical energy in the explosives. Typically the chemical reaction is 90% complete in $10^{-6}$ to $10^{-8}$ second. The energy goes into the motion of the explosive products, creating the high pressures and temperatures necessary to drive the reactions. In other words, the inertia of the explosive itself provides the confinement necessary to maintain the conditions for the fast chemical reaction rates and the self-sustaining propagation of the detonation wave. The distinguishing feature of detonation is the self-inertial confinement of the chemical reaction. Thus, there is an intimate relationship between chemistry and mechanics, and neither can be treated as an independent process in a realistic detonation model.
Fig. 3. Radiograph of detonating Composition B explosive, taken with the PHERMEX flash x-ray machine. The detonation wave, which has advanced from the initiation point up through the conical plane wave lens (see Fig. 7) and almost to the top of the Composition B blocks, appears as a light streak across the radiograph. Light areas on x-ray pictures indicate high density, darker areas indicate low density. The high density remains of the plane wave lens also appear as a very light area.

Above the detonation wave is a thin layer of unreacted explosive. Below the detonation wave we can see various waves in the explosive product gases: a wishbone wave from the gap between the two blocks, rarefaction waves from the air gaps around the tantalum foils, and the reflected shock wave hardly visible in the remains of the plane wave lens. The foils mark distinct mass points in the explosive. The spacing between them decreases as the explosive is compressed by the passage of the detonation wave.

With current instrumentation we can only follow the motion of an inert material driven by explosive or follow the positions of the shock front and other waves. Pulsed x-ray photographs can show positions of matter or waves, and cameras and electrical contacts can record what happens at accessible surfaces. (See Fig. 3.) This very limited information makes the interpretation of measurements depend heavily on theory and models.

Detonation phenomena experimentally and the necessity of inferring an explosive’s material properties and chemical reaction rates from theoretical models and indirect measurements. For example, there is no way to take a sample of material from the reaction zone to see how the chemistry is progressing. There is no way (yet) to study the chemicals and their reactions at the conditions of pressure and temperature in the detonation reaction zone in any sort of laboratory apparatus. Pressure gauges, velocity gauges, and thermometers for the study of conditions in explosions are being developed, but are not yet satisfactory. In addition to experimental difficulties like making electrical connections that are not destroyed by the violent motions of the explosive products, the massive apparatus perturbs the flow so much that the system is changed and the measurement is meaningless. Perhaps developments, particularly in laser spectroscopy, will eliminate these difficulties,
Fig. 2. Plot of pressure versus distance for a detonation wave. The shock wave, at the right, is the leading element of the detonation wave. The explosive behind it, heated by the sudden compression, begins its chemical reaction there. Pressure falls as the reaction proceeds, and reaction is finished at the point marked final state. Behind that point are a rarefaction and a constant-state region; they reduce the pressure and particle velocity to match the motion of the external confinement, shown here as a piston. The reaction zone, between the shock wave and the final state, is a subsonic flow region; energy liberated in it can flow forward to drive the shock wave. The region behind the final state is a supersonic flow region; neither energy released there nor any perturbing waves can move forward to affect the reaction zone or the shock.

The explosive and the inert material it drives are usually solids, but the detonation pressures are so high that material strength may be neglected and the propagation of energy may be understood through the equations of reactive fluid dynamics. Furthermore, energy transport by heat conduction, viscosity, and radiation is negligibly small compared with the transport by motion. The theoretical basis for treating one-dimensional detonation (the ZND theory) is a fluid-dynamical model that was arrived at independently by Zeldovich, von Neumann, and Doering. Figure 2 shows a plane, steady, unsupported detonation wave predicted by the ZND theory. The detonation, initiated by a pressure pulse from the piston at the left, is called unsupported because the piston velocity is less than the fluid or particle velocity of the explosive products. The detonation front is a shock wave, supersonic relative to the material ahead of it, so no signal precedes it. Compression heats the explosive, and rapid chemical reaction follows. Finally, reaction is complete, and the product gases expand as an inert flow. The inert flow of the explosive products is affected by the surrounding inert materials. In other words, the inert flow must match the boundary conditions provided at the left of Fig. 2 by the piston and at the right by the final state of the explosive products at the end of the reaction zone.

The speed of the chemical reaction rates and the seemingly independent propagation of the detonation front lead naturally to a division of the problem into two parts: (1) the study of the chemical reaction zone where the detonation process goes on and (2) the study of the acceleration of inert components, such as the metal of a hand grenade or the expansion of the explosive gases after the reaction is finished. Although the two parts are interrelated, until recently they have been treated as separate problems.

In most practical cases, the chemical reaction zone is so thin compared to the size of the explosive charge that its length is neglected completely in explosive performance calculations. We assume that the reaction takes place instantaneously at the detonation front and calculate the expansion of final explosive products as they push whatever material may enclose them. If this idealized calculation is compared with measurements, the effect of finite reaction zone length (or finite time of chemical reaction) appears as a small rise in pressure or velocity at the detonation front.

In many cases, this simple way of treating detonation phenomena is sufficient for determining the equation of state of the explosive products and for calculating the inert flow and explosive performance. However, modern applications of explosives have stimulated attempts to treat the entire problem as a whole, to learn in more detail the chemical reaction rates in the reaction zone and how they are affected by changes in the boundary conditions, by the addition of new materials, and by the effects of inhomogeneities and transverse waves. These details became important in applications of nonideal explosives, such as TATB and other insensitive high explosives, that have relatively long reaction times.

Our methods may baffle the newcomer to the field unless he or she recognizes the difficulty of studying det-
A Simple Theory

An explosive’s performance or usable energy is determined by the expansion of product gases following completion of the chemical reaction in the explosive. Thus, to calculate performance we must know the state (pressure and particle velocity) of the materials at the end of the reaction zone and their equation of state, that is, how the pressure varies with the particle velocity of the product gases during adiabatic or free expansion. With no direct measurements of these material properties nor fundamental theory to help us, how do we proceed?

The usual practice has been to apply a simple fluid dynamical model of detonations known as the CJ theory. This generalization of the theory of shock waves provides a framework for inferring the relevant material properties from standard detonation experiments. It relates the detonation wave velocity to the properties of the gases behind the detonation wave front.

The CJ theory assumes that all chemical energy is released at the detonation front so the reaction zone in Fig. 2 has no thickness. The detonation wave is thus approximated by a self-sustained supersonic wave traveling through the explosive at constant velocity. We are interested in determining four quantities: the velocity of propagation \( D \), and the pressure \( p \), density \( \rho \), and particle velocity \( u \) behind the wave front.

For shock waves in inert materials, the three equations of conservation of energy, momentum, and mass across the shock front, the so-called jump conditions, are sufficient to determine the shock velocity \( U \) in terms of the variables \( p \), \( \rho \), and \( u \).

In the CJ theory for detonation waves, the jump conditions apply, but because energy is released at the front, making the wave self-propagating, an additional condition is needed to determine the detonation wave velocity \( D \). The condition, postulated by Chapman and Jouguet around the turn of the century, is known as the CJ condition. Before discussing it, we review the jump conditions for simple shock waves and show how chemical energy release in explosives complicates the analysis of the conditions behind the wave front.

A plane shock wave propagating in a medium initially at rest is shown in Fig. 4. We use \( U \) for wave velocity, \( u \) for particle velocity, \( p \) for pressure, \( \rho \) for density, and \( E \) for specific internal energy. Subscripts 0 and 1 indicate the regions before and after passages of the shock, respectively. Velocities are positive for motion to the right.

We treat a tube of area \( A \) for a period \( t \). During the period \( t \), the wave front, moving at velocity \( U \), passes over a mass of material equal to \( \rho_0 AUt \). During the same period, the fluid element located at the wave front at \( t = 0 \) moves a distance \( ut \), so material passed over by the wave front is now within a volume \( A(Ut – ut) \), and its mass is \( \rho_1 A(U – u)t \). Its quantity has not changed, so we equate the two expressions for the mass. Canceling \( At \), we obtain

\[
\rho_0 U = \rho_1(U – u_1).
\]  

The passed-over material is accelerated to velocity \( u_1 \), so its momentum changes from zero to \( \rho_1 AUt_0 \). The force acting on the material (if \( \rho_0 \) is assumed negligible) is \( p_0 A\), and it acts for a time \( t \), so the impulse is \( p_0 At \). Equating the impulse and the change of momentum (and again canceling \( At \), we obtain
\[ p_1 = p_0 U u_1. \]  

The internal energy changes by \( p_A U t (E_1 - E_0) \), the kinetic energy changes by \( 1/2 \rho_p A u_1^2 \), and the work done on the material is the force times the distance, \( p_A u_1 t \). The change in energy and the work done are equal, so we equate them. Canceling \( A t \) and dividing by \( p_0 U = p/u \) from Eq. (2), we obtain the conservation of energy equation

\[ E_1 - E_0 = 1/2 u_1^2. \]  

Equations (1), (2), and (3) are called the Rankine-Hugoniot shock relations, or the jump conditions. The Rankine-Hugoniot relations along with an equation of state for the material (an expression for \( E \) in terms of \( p \) and \( u \)) define a smooth curve in the \( p-u \) plane called the Hugoniot curve. The curve describes all the states of the material that can be reached by the passage of a single shock wave. The Hugoniot curve is steeper than isotherms and isentropes for the material.

The jump conditions, Eqs. (1) - (3), derived under the assumption that the material has no strength, are often applied to metals because the material strength is small relative to the shock forces and the shear forces quickly relax to zero. This approximation is good at high pressures, but the deviations may be large at low pressures.

Although we don’t have a theoretical equation of state for the shocked material, we know empirically that the relationship between the pressure \( p \) and the particle velocity \( u \) on the Hugoniot curve is described adequately by a few terms of the series expansion

\[ \gamma_1 = \rho_0 (c u_1 + s u_1^2 + \ldots), \]  

where \( c, s \), and the coefficients of higher powers of \( u \) are constants. These constants are determined experimentally. In this simple approach that treats the shocked material as a nonviscous fluid, the Hugoniot curve given in Eq. (4) is a complete statement of the important material properties. Comparison with Eq. (2) shows that the velocity of the shock wave in the material is given by the expansion

\[ U = c + s u_1 + \ldots. \]  

Thus, the constant \( c \) is the sound speed since a very weak wave, with \( u \), negligible, propagates with velocity \( c \).

For a fixed shock-wave velocity \( U \), Eq. (2) describes a line in the \( p-u \) plane along which momentum is conserved, called the Rayleigh line. The slope of the line is given by \( U \) times the initial density \( \rho_0 \).

Figure 5 shows the Hugoniot curve for a particular material and the Rayleigh line for a particular shock velocity \( U \) and initial density \( \rho_0 \). The intersection of the two curves gives the state of the material behind the wave front with shock velocity \( U \).

Now we turn from shock waves in inert material to detonation waves in explosives. We are going to ignore the thickness of the reaction zone and approximate the detonation wave by the discontinuity shown in Fig. 4. Now the material to the right is unreacted explosive, and the material to the left is completely reacted explosive products.

The jump conditions apply just as they do for shock waves, but the Hugoniot relation describing the final state of explosive products behind the detonation wave front has an additional term reflecting the fact that energy is released as the chemical bonds are rearranged. The Hugoniot relation becomes

\[ \gamma_1 = \rho_0 (nQ + c u_1 + s u_1^2 + \ldots). \]  

Here \( Q \) is the specific chemical energy of the explosive, and \( n \) is another material constant to be determined experimentally. The Hugoniot curve for an explosive is shown in Fig. 6, along with the Rayleigh line that is just tangent to it. We compare Figs. 5 and 6 to illustrate the differences between inert materials and explosives. An inert material has a minimum shock velocity \( U = c \), representing a sound wave with zero pressure, and a unique shock wave pressure and particle velocity for any faster wave. Notice that the Hugoniot curve for the explosive does not pass through \( p = 0 \). The explosive has a minimum detonation wave velocity, but the pressure at that velocity is not zero but large, and for any higher shock velocity the Rayleigh line and the Hugoniot curve intersect at two points rather than one so that the final state for the shocked explosive is not uniquely determined by the jump conditions and the equation of state.

In the late 1890s, Chapman, in England, and Jouguet, in France, eliminated this ambiguity. They studied the propagation of waves in the flows that might follow a detonation front and made the plausibility argument that an unsupported detonation proceeds at the minimum detonation velocity, which is the
unique velocity given by the Rayleigh line tangent to the Hugoniot curve. This is called the CJ condition.

The selection of the unique minimum velocity is in agreement with the observation that detonations have a well-defined velocity, determined by the composition and density and little affected by any external conditions. The plausibility is increased because simple thermodynamic arguments show that the CJ point is a sonic point. That is, the detonation velocity \( D \) at that point is given by

\[
D = c' + u',
\]

(7)

where \( c' \) is the local sound velocity and \( u' \) is the local particle velocity. Thus, any signal, such as energy liberated at that point, propagates forward at the wave velocity, just keeping up with the front and not overrunning it. Farther back in the rarefaction region the flow is supersonic, and any signal falls farther and farther behind the front, so the pressure decrease in that region does not interfere with the propagation of the detonation wave.

Thus, the simple theory gives a prescription for the final state of reacted explosive behind the detonation front—namely, the CJ point on the Hugoniot curve.

Determining the CJ Point and Hugoniot Curve

The CJ point is the starting point for calculations of inert flow behind the detonation front. This point is determined by measuring the detonation velocity and the Hugoniot curve for a
given explosive.

During the 1950s, W. E. Deal of Los Alamos carried out an extensive experimental program to determine the Hugoniot curves [the constants in Eq. (6)] for several explosives. Because computing power was very limited, Deal had to design experiments that could be analyzed by using pencil and paper. He simplified the required analysis by using plane detonation waves in the experiment.

Figure 7 shows the plane wave lens for Deal’s experiment and Fig. 8 shows the diagnostic part. The plane detonation wave in the explosive reaches the inert material simultaneously over the interface and drives a plane shock wave through the inert material. The free surface of the inert material moves upward, driving the shim against the Plexiglas and compressing and heating the argon in the gap to produce a brief flash of light. The free surface moves only a very short distance to close the two outer gaps, but it moves an extra distance d to close the center gap. The film of an experiment recorded with a smear (or streak) camera is shown in Fig. 9. Measurement of the time offset between the flash from the outer gaps and the flash from the center gap gives the time it took the free surface to move the distance d. Division of the distance by the time gives the free-surface velocity.

How does measurement of the free-surface velocity of the inert material determine the CJ point and Hugoniot curve in the explosive? The analysis involves determining the pressure and particle velocity of the inert material at its interface with the explosive. Deal did this through a series of experiments with thinner and thinner plates of inert mate-

![Fig. 7. Plane wave lens generates a plane wave from the point of initiation. It is made of a cone of slow explosive, with detonation velocity $D_s$. The conical surface is covered with a layer of fast explosive, with detonation velocity $D_f$. Initiation is at the point apex of the cone. After a time, the detonation wave in the fast explosive arrives at point F, and the detonation wave in the slow explosive at point S. If the cone angle $A$ is chosen so that $\cos A = D_s/D_f$, points S and F will lie in a plane. Because the fast explosive initiates the slow explosive as it proceeds, the detonation wave in the slow explosive is plane at every level. The lens can be used to initiate a plane wave in the test explosive for the experiment.]

![Fig. 8. The Plexiglas block assembly used by Deal for measurement of free-surface velocity of an explosive-driven plate. The argon gaps produce a flash of light when they are closed by the moving inert material. The time of flight of the inert material across the gap d is measured by the camera.]

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Fig. 9. Smear camera record showing seven records of free-run time of a metal plate accelerated by explosive. Free-run time is measured from each pair of side traces down to the corresponding central plate arrival time.

Fig. 10. Experimental values of free-surface velocity imparted to 24ST aluminum plates by Composition B explosive as a function of plate thickness. The line is the linear least squares fit to the data. The intercept of the fit with the ordinate corresponds to the free-surface velocity of a zero-thickness plate.
Above the CJ point, the curve corresponds to the reflected shock Hugoniot curve for the explosive. Below the CJ point, it is an expansion isentrope. The CJ point, the intersection of the Rayleigh line with the curve in Fig. 11, is determined by measuring the detonation velocity in the explosive.

The measured curve in Fig. 11 differs slightly from the Hugoniot relation defined by Eq. (6). However, with some assumptions about the behavior of the explosive products, we can use the measured curve to determine the coefficients in that equation.

This method to determine the equation of state for an explosive obviously requires many experiments. Moreover, the experiments are very expensive. As computers became powerful enough to calculate the motion of metal driven by explosive products, workers in the field tried to devise less expensive ways to obtain the information. A group at the Lawrence Livermore National Laboratory (Kury, Hornig, Lee, McDonnel, Ornellas, Finger, Strange, and Wilkins) developed a method known as the cylinder test. They filled a cylindrical copper tube with explosive, detonated it at one end, and carefully measured the expansion of the copper wall. Figure 12 shows a flash silhouette photograph of such an experiment. Only the short section of the tube at the top remains unexpanded. The Livermore group compared their experimental data with a calculation using an assumed equation of state for the explosive and adjusted the equation-of-state parameters to obtain good agreement. This approach yields all the data below the CJ point in Fig. 11 with one relatively inexpensive experiment. The analysis must be done.

Fig. 11. Plot of pressure and particle velocity obtained from zero-thickness free-surface velocity measurements for Composition B explosive. The CJ point must lie on the Rayleigh line for the measured detonation velocity; it is determined from the line's intersection with a smooth curve. The points above the CJ point determine the reflected-shock Hugoniot curve, and those below determine the expansion isentrope for the explosive products.
Fig. 12. Silhouette flash photograph of a cylinder test. The explosive charge, 300 mm long and 25 mm in diameter, was encased in a copper tube with 2.5-mm wall thickness. Explosive in the tube has been detonated at the bottom and is accelerating the copper outward. A very short section of undisturbed tube can be seen at the top. Measurements of the shape of the copper wall can be used to compute the expansion isentrope of the explosive products. Shock waves in the surrounding gas can be seen around the tube.

carefully, but the two-dimensional calculation, while neither cheap nor easy, is less expensive than the plate experiments.

Performance of Explosives

As one can easily imagine, there has been a tendency to avoid long calculations by using the experimental measurements of cylinder-wall velocity directly to rank explosives in order of their performance for accelerating metal. This is a mistake. Consider a series of explosives with fixed energy per unit volume but with various densities. In experiments, the energy released by chemical reaction is partitioned between the explosive products and the copper wall. Obviously, the lower the density of the explosive, the more energy is transferred to the copper. The lowest density explosive will rank highest. This ranking is correct if the explosive is used to expand the tube. But suppose the explosive must collapse the tube. In this case, the explosive is applied as a layer on the outside of the tube. Now the confinement effect of the tube is gone, and the inertia of the explosive product gases provides the confinement for energy transfer to the copper. In this imploding configuration, there is an optimum density for the explosive. If the explosive is too light, its products, containing almost all the kinetic energy, will fly off at very high velocity. If it is too heavy, both the metal and product gases will move slowly, and less than the optimum fraction of the energy will be transferred to the copper. Therefore, calculations are necessary to determine the optimum-density explosive to achieve the best
performance in any particular configuration of explosive and inert material.

Today, the performance of explosive systems for most practical applications is calculated by using the CJ point and equations of state determined from free-surface velocity and cylinder tests. Most engineering calculations neglect the reaction zone length and calculate only the inert flow. The calculations are very accurate when they are done correctly, but they have subtle problems. C. L. Mader, of Los Alamos, discusses many aspects of detonation calculations in his book, Numerical Modeling of Detonations, a volume in the Los Alamos Series in Basic and Applied Sciences.

The Reaction Zone

The assumption that the reaction zone is small compared with distances of interest can be violated in two ways: the charges can be abnormally small, or the explosives can have abnormally long reaction zones. Explosive logic (computers for extreme environments that use explosive to "make and or gates") is an application using extremely small charges, and one in which the length of the reaction zone must be taken into account. Accurate modeling of the reaction zone is important in applications using insensitive high explosives that have long reaction times. These applications include design of nuclear weapons and studies of in situ retorting methods. The discovery that TATB and nitroguanidine (NQ) are extraordinarily safe explosives, with accidental initiation between 100 and 10,000 times less likely than for common military explosives, was of great interest to weapon designers. Although accidental initiation of explosive cannot produce a nuclear explosion, it can result in the scattering of toxic and radioactive nuclear material. Consequently, insensitive high explosives are used in nuclear weapon design. These explosives are safe in part because their chemical reactions proceed more slowly than those of other explosives. Slow chemical reactions mean long reaction zones.

Explosives used for blasting also have long reaction zones. For economy and safety, some are made from coarse granular ammonium nitrate (a source of oxygen) coated with hydrocarbon fuel. The physical separation of fuel and oxidizer means that the components must diffuse into each other. Because the diffusion is slow, the reaction zone is very long. Until recently, blasting was done with the guidance of simple tests, but with no detailed computer calculations. However, new in situ retorting methods for oil shales and coal require precise fragmentation of the rock. Los Alamos, Livermore, and others are doing experiments and calculations to try to solve some of the problems. The relatively small charges of these materials used at laboratory firing sites don’t stay together long enough for the reactions to go to completion. Therefore, to scale measurements of small charges up to the large sizes required for blasting, we must understand the chemical reaction rates and their dependence on boundary conditions.

The ZND Theory

Present Laboratory efforts to model the reaction zone are built on theories developed during the war years. About 1940, the theory of detonation was extended independently, but in almost ex-
Fig. 14. An experimental assembly for measuring particle velocity with the magnetic probe technique. The motion of the aluminum foil (75 µm thick) between the explosive and the Teflon in the nonuniform magnetic field induces about 150 mV in the single-turn pickup coil. The voltage is recorded during the interval, about 1 µs, between the time when the foil starts to move and the time when the shock wave reaches the coil and destroys it. The voltage record can be unfolded to give foil velocity versus time.

.. exactly the same way, by Zeldovich in Russia, von Neumann in the United States, and Domb in Germany. The ZND theory, describing a steady reaction zone with a finite chemical reaction rate, took some of the mystery out of the CJ theory. In the ZND theory, the front of the detonation is a shock wave where the pressure and temperature rise, but where little or no reaction occurs because the time is so short. Behind the shock wave, the explosive reacts at high pressure and temperature until all of it is changed into product gases. To make the equations tractable, the ZND theory also assumes that the reaction zone is steady; that is, it maintains exactly the same form as it moves through the explosive. The shock wave in Fig. 3 is unchanged, but instead of a single state (pressure and particle velocity) behind it, there is a continuous range of states described by a new variable \( \lambda \), \( 0 \leq \lambda \leq 1 \), that marks the progress of the chemical reaction. The assumption that the reaction zone is steady, however, reduces the problem to the kind already considered. Equations (1), (2), (3), and (6) apply between the initial state and any selected state in the reaction zone. Equation (6), of course, must be changed to represent the heat released up to that point. If \( \lambda \) is the fraction of material already reacted, it is also the fraction of heat already released. The replacement for Eq. (6) is

\[
\lambda = \rho_0 (n\lambda Q + cu_x + su_t^2 + ...) ,
\]

where the subscript \( \lambda \) indicates the point in the reaction zone where \( \lambda \) has that value. The coefficients \( n, c, s, \ldots \), are also functions of \( \lambda \). Figure 13 is a plot of curves represented by Eq. (8). The Hugoniot curve marked \( \lambda = 0 \) for the unreacted explosive at the detonation front is just like the Hugoniot curve for an inert material shown in Fig. 5. As chemical reaction proceeds toward \( \lambda = 1 \), the state in the reaction zone is represented by points along the Rayleigh line between N and CJ.

The pressure-distance curve for the ZND detonation was shown in Fig. 2. The shock wave at the detonation front in Fig. 2 raises the pressure to point N in Fig. 13. As the reaction proceeds, the pressure falls until it reaches point CJ, where reaction is complete. (This point is marked “final state” in Fig. 2.)

The new feature of the ZND theory is the reaction zone and, in particular, the high pressure at the detonation front. The fall in pressure caused by chemical reaction is contrary to almost everyone’s intuition. When von Neumann’s report detailing his new theory was first circulated in 1942, it was greeted with disbelief because the “von Neumann spike” seemed patently absurd.

Measurable Effects of the Reaction Zone

Figure 13 shows that a particle-velocity spike accompanies the pressure spike at the detonation front. We can measure particle velocity indirectly by placing a foil in the explosive and measuring the foil velocity induced by the passage of the detonation wave. The foil velocity is equal to the particle velocity of the explosive products. The
experiment is diagramed in Fig. 14, and the results are plotted in Fig. 15. The dashed line in Fig. 15 is the rarefaction behind the detonation front calculated with the simplest theory, that is, as if the reaction zone were negligibly thin. The solid line is the particle velocity measured in the experiment. Where the measured velocity slope is greater than the calculated slope, chemical reaction is still appreciable. The von Neumann spike is real.

The time during which the slope of the solid line differs from the slope of the dashed line is a measure of the chemical rate or reaction zone length. In Fig. 15, the time for passage of the reaction zone is about 0.5 µs, corresponding to a reaction zone length of 3 mm. These data determine a chemical reaction rate of the form

$$\frac{d\lambda}{dt} = k(1 - \lambda),$$  \hspace{1cm} (10)

where \(\lambda\) is the progress variable and the coefficient \(k\), with units of reciprocal time, measures how fast the reaction goes. The depletion term, in parentheses, makes the rate go to zero when all the explosive has reacted.

Obviously, one learns very little about chemistry from mechanical measurements. Any information about the real chemistry of the explosive reaction would be extremely valuable but, unfortunately, the pressures and temperatures in the reaction zone are far higher than laboratory measurements. Detonation data must be obtained from detonation measurements.

**Detonations in Cylindrical Sticks**

One way to obtain more information about the chemistry in the reaction zone and, in particular, about its dependence on pressure, is to change the boundary conditions so that they affect the chemistry. For example, we can study the detonation process in long cylindrical sticks, where the process has a chance to reach a steady state, but where surface effects, especially the decrease of pressure from the center of the stick to its edges, may change the chemistry.

Over the years, many experimenters have studied detonations in cylindrical sticks and have perfected measurements of the detonation velocity to achieve accuracies of a few parts in ten thousand. The most dramatic result of these experiments is the discovery of the failure radius. That is, for each explosive, there is a radius below which detonations fail to propagate.

Figure 16 shows a cylindrical stick
Fig. 16. Detonation velocity experiment ready for firing. Foils placed between segments of the long cylindrical stick of explosive are connected by coaxial cables to oscilloscopes. They measure the arrival time of the detonation wave.

Fig. 17. Plot of measured detonation velocity for solid and liquid explosives versus reciprocal charge radius. The curves end at the measured or estimated failure points. These data show that detonation propagates only for a very limited range of velocity for any particular explosive, the maximum decrement here being only about 15%.
The Two-Dimensional Reaction Zone

In the last 5 years, John Bdzil, of Los Alamos, has extended the theory of the detonation reaction zone to the case of a cylindrical stick of explosive in an inert tube, like the cylinder test described above. In his model, Bdzil assumes the detonation wave has run far enough in the tube that the flow is steady. Figure 18 shows a diagram of a steady detonation in a metal tube. Along the center line the reaction zone is much like the ZND detonation, but away from the line the difference becomes pronounced as the transverse flow transfers some of its energy to the metal tube. The shock wave is curved, and the shock pressure decreases with increasing distance from the center. Because the shock pressure is less, the explosive is heated less and the reaction takes longer. The dashed line shows where reaction is complete. The sonic surface, between the shock and the complete reaction line, is an important dividing surface in this flow. Only the portion of the chemical energy released above this surface contributes to driving the detonation. Even more important, energy used in the transverse expansion in the reaction zone is not available for driving the detonation. Thus, the detonation velocity is less than it would be in a plane wave detonation, or even in a stick with a larger radius.

The theory of this two-dimensional detonation reaction zone is complicated. The shape of the shock determines the initial conditions for the reaction zone, but is itself part of the solution. Bdzil obtained an ordinary differential equation for the shock shape, which can be solved analytically for some simple cases.

Fig. 18. Cross section of the detonation reaction zone in a metal tube. The curved shock wave is the leading front of the detonation. Explosive heated by the compression reacts behind the shock. Only material that reacts ahead of the sonic surface can contribute to driving the detonation wave.

Fig. 19. Comparison of measured detonation shock wave shapes with calculations of the shape for an assumed rate law. Getting agreement between measurement and calculation places restrictions on the form of the rate law.
Fig. 20. Plot of measured detonation velocity versus reciprocal radius for nitromethane, nitromethane with the catalyst DETA, and nitromethane with silica particles. The catalyst and the particles both decrease the failure radius by a factor of 2, but the silica particles change the shape of the curve. The graph on the left is a magnified view of the curves where they intersect the ordinate. The slopes of the curves in this region indicate the reaction zone lengths. The catalyst shortens the reaction zone, and the particles lengthen it.

chemical reaction rates and integrated numerically for others.

The theory must match the measured detonation velocity, the measured shape of the detonation front, and the measured velocity decrement at failure. Applying the theory to these data gives some insight into the chemical reaction mechanisms. If the chemical reaction rate is assumed to have a form

$$r = k(p/p^*)^{(1 - \lambda)}, \quad (11)$$

where $p^*$ is the limiting shock pressure for the large charges at the left edge of Fig. 17, the theory can be used to fit the observations. The coefficient $k$, with units of reciprocal time, measures the scale of the chemical reaction time and, therefore, the reaction zone length. It is determined principally by the slope of the velocity curves near their start at the left in Fig. 17. Larger slopes correspond to larger edge effects and, therefore, to longer reaction zones. The value of the exponent $n$ in Eq. (11) is determined principally by the amount the velocity decreases before the failure point is reached. For $n$ small, the effect on the chemical reaction rate of the pressure decrease at the edges of the stick is small, and the detonation can proceed at lower velocity. For $n$ large, the effect is greater, and the detonation fails with less decrease in velocity.

The measured shock wave shape at the front in a detonating stick is compared with the shape found from the theory, and the reaction rate is adjusted for the best match. Matching the shock shape for several different radii, but using the same chemical reaction rate for all, places functional requirements on the rate law. Figure 19 compares theoretical fits with data for cylindrical nitromethane sticks with two different radii.

New Reaction Zone Experiments

These advances in the theory have encouraged new experiments to explore the chemical reaction zone. The reaction rate and its dependence on pressure can be influenced by adding a catalyst or by suspending solid particles in a liquid explosive. In one series of experiments, nitromethane, a water-white, nonviscous liquid explosive, was chosen as the standard. The experiments compared the detonation velocity and failure radius of the standard with those of the standard plus small amounts of additional materials. Because the same explosive was used in all the experiments, any uncertainties in the equation of state or any other properties cancel out and the effects of the added materials on the reaction rate can be determined. The diameter-effect curve for nitromethane, in Fig. 20, appears to be a straight line, and its
velocity decreases only 0.5% at failure. Adding the catalyst DETA in a very small amount (0.03%—about 1 molecule of catalyst for each 5,000 molecules of explosive) decreases the failure radius by a factor of 2, but leaves both the detonation velocity and the velocity decrease unchanged. Adding silica particles and a little gelling agent to hold them in place also decreases the failure radius by a factor of 2, but changes the velocity decrease to about 13?40 at failure. The slopes of the curves at large radius, shown in the magnified view on the left, indicate [as discussed with Eq. (11)] that adding DETA shortens the reaction zone. On the other hand, adding silica particles lengthens the reaction zone appreciably.

Ray Engelke, of Los Alamos, who is doing these experiments, interprets the effect of the catalyst DETA as the expected one; it speeds up the reaction, thus shortening the reaction zone, decreasing the edge effects, and thereby decreasing the failure radius. The fact that the velocity decrease stays the same indicates that the catalyst doesn’t change the dependence of the chemical reaction rate on the pressure in this explosive. The silica particles lengthen the reaction zone but decrease the failure radius. Probably the particles create hot spots: that is, the shock wave develops irregularities as it passes over them, and the high temperature in these spots keeps the reaction going even when the average pressure and temperature fall near the edge of the cylinder. Another possibility is that real failure is not as simple as the model, and that strong transverse waves traveling from the edge into the reaction zone quench the reaction. If so, the silica particles may interfere with the action of the waves by diffusing their sharp fronts as they envelop the individual particles.

Perhaps experiments like these will develop enough understanding of the factors influencing the reaction rates in the detonation reaction zone that we can formulate new explosives with special useful properties. For example, the insensitive high explosives now in use are safe partly because of their slow reaction rates at low pressures. But their slow reaction rates at the high pressures in the detonation reaction zone cause unwelcome behavior. Understanding may lead to explosives with slow rates at low pressures and fast rates at high pressures.

Is the End of Reaction a CJ Point?

In the limit of large charge size and plane flow, we expect that chemical reaction ends at the CJ point, where the flow is exactly sonic. Direct comparison of theory and experiment to determine whether the end point of chemical reaction really is a CJ point is not possible for most solid and liquid explosives because the equations of state needed to do the calculation must be determined experimentally and the experiments incorporate the assumption that the end point is a CJ point.

To avoid this logical dilemma, we have developed a pressure-determination method that is independent of the exact equation of state of the final products. The method involves measuring how much the detonation velocity varies with initial energy and density of the explosive. The measurements are made for two explosives with the same atomic composition, and the data define a detonation velocity surface as described in Fig. 21. To determine the pressure of the explosive products from this surface, we apply the CJ theory. No knowledge of the exact equation of state is needed; we need only the assumption that for two explosives with the same atomic compositions, the equilibrium equation of...
Fig. 22. Outline of the theoretical results needed to use the detonation velocity data (see Fig. 21) for a test of the theory. The pressure obtained from this interpretation is compared with other pressure measurements.

state for the explosive products is the same for both.

The theory to determine the pressure is shown in Fig. 22. The expression for \( D \) at the top means that from experiment (Fig. 21) the detonation velocity is known as a function of initial density and energy over some small region. The sketch of the \( p-u \) plane shows the theoretical Hugoniot curve and Rayleigh line for a plane, steady, laminar detonation wave calculated with any of a class of simple reaction rate laws. The simple theory says that the straight line (the Rayleigh line) and the curved line (the Hugoniot curve) are tangent at the state point that occurs at the end of the reaction zone. The next two equations, derived from the CJ theory, determine the variation of CJ detonation velocity with initial energy and density in terms of certain thermodynamic derivatives \( (\alpha \) and \( \gamma \) evaluated at the tangent point. The derivatives of \( D \) on the left-hand side are determined from measurements shown in Fig. 21. The two equations can be solved to obtain the values of \( \alpha \) and \( \gamma \). Finally, the pressure at the tangent point can be obtained from the last equation. The pressure obtained from these detonation velocity measurements, interpreted using this theory, can be compared with the pressure from the free-surface measurements and cylinder tests described earlier. The best values I have for the pressures of nitromethane are \( 12.2 \pm 0.6 \) GPa, determined from the detonation velocity measurements, and \( 14.2 \pm 0.4 \) GPa, determined from the more conventional measurements. Disagreement between the values shows that the end point for the reaction zone in nitromethane (the final state) is not a CJ point.
Extended Theory for the Final State

Why is the final state not a CJ point? Some ideas about the final state can be garnered by looking at Fig. 23, which is like Fig. 13, but has a higher detonation velocity. The shock wave takes the material to state N, and as the reaction proceeds the pressure falls to state S (for strong point). In the case we discussed before, a rarefaction from behind can overtake state S and reduce the pressure until the CJ state is reached. Point W (the weak point) is a possible solution of the conservation equations, because it is an intersection of the Rayleigh line (conservation of momentum and mass) and the Hugoniot curve (conservation of energy). However, point W cannot be reached. The reaction starts at point N and is finished at point S; according to our simple theory there is no path from S to W.

The real world, however, is not so simple. Explosives are made from complicated molecules, and the chemical reactions take place in many steps, not just one. The Hugoniot curves for a partially reacted explosive cannot be described by a single progress variable \( \lambda \), because there are many possible pathways. The theory of detonation has been extended to consider all the added pathways for reaction. With some rates, the space between S and W is filled with possible Hugoniot curves, and point W becomes an attainable state.

The theory is discussed in detail in Detonation by W. Fickett and W. C. Davis, another book in the Los Alamos Series in Basic and Applied Sciences. To give an idea of the theory’s flavor, Fig. 24 shows the possible forms for a detonation reaction zone when there are two reversible reactions. The abscissa \( k \) is the ratio of the reaction rates, and the ordinate \( u \) is the particle velocity at the end of the reaction zone. The two forms to the right of \( k_c \), correspond to Figs. 13 and 23. All the other forms are new from the extended theory. Detonation physics is richer than was once thought.

These arguments show that the final state of the reaction zone need not be the CJ state, but they fail to show why the detonation in nitromethane is not a CJ detonation. Perhaps the many reactions lead to a weak state like some of those in Fig. 24, but I don’t think that is very likely. The ratio of the reaction rates must be extreme, say about 1,000 to 1, to reach a weak state. With many reactions, I think there must be a route to the completion of reaction without such extreme ratios.

Although this part of the extended theory does not seem to furnish an explanation directly, it does show what is needed to reach a weak point instead of the CJ point. What happens in a detonation with two rates, one much faster than the other, is that the fast rate goes too far
Fig. 24. Diagram of the $u$ versus $k$ plane, showing how it separates into regions where different kinds of strong and weak detonations occur. The particle velocity $u$ through the reaction zone is plotted versus ratio of the two reversible reaction rates assumed for this example. The CJ detonation of Fig. 13 is the pressure-distance plot at lower right, and the strong detonation of Fig. 23 is the plot at upper right. All the others, many of them weak detonations, appear when there are two reactions instead of only one.

and gets beyond its equilibrium composition. Then the slow rate keeps going, using material to get to its equilibrium state, and the composition controlled by the fast rate must shift back from its early state. When this happens, other things being proper, energy is returned from the flow to the internal energy of the chemicals. The return of energy from the flow to internal states is the process needed to make a detonation reach a weak point instead of the CJ state.

Hot Spots and Transverse Waves

The most likely reason that the final state is not a CJ state seems to me to be that energy from the flow is returned to local regions as kinetic energy of fast, small-scale, random flow, like turbulence. The flow contains spatial inhomogeneities, and the pressure and temperature vary from point to point. Thus the rate, dependent on pressure and temperature, varies, and energy is coupled selectively to the small-scale motions in the flow. Although this energy appears as kinetic energy, it is not available to drive the detonation, and it is equivalent to energy in an internal state. The inhomogeneities in explosives and their reaction zones seem to be important for determining the final state of the reaction zone, and they have a large effect on the apparent chemical rate.

Most practical explosives are polycrystalline materials, with small crystals and boundaries between the crystals. Also, they contain defects, such as voids and low-density regions. As the shock wave interacts with the polycrystalline material, it compresses and heats the explosive, but the tem-
Fig. 25. Six ways to concentrate energy in explosives as hot spots. Hot spots may be formed by material jetting from between explosive grains, by collapse of voids, by viscous heating in material around a void, by interaction of shocks around a high-impedance region, by friction between crystallites, and by internal shear of crystallites.
temperature is not uniform throughout the material. Figure 25 shows some of the processes that have been suggested for producing local high temperatures, or hot spots. Hot spots may come from jets of material ejected from little wedge-shaped intersections of crystallite, from impact of material thrown across a void, from viscous heating in material near the surface of a collapsing void, from shock collision around a high-impedance inclusion, from friction between two crystallite, or from internal slippage in a single crystallite. All these processes are important in one special case or another. Figure 26 shows average shock-wave temperature as a function of shock-wave pressure in an explosive called PETN. The two points are the shock points required to initiate detonation in 1 µs in this explosive when it is in two states. The high-pressure point is for a single crystal of PETN, and the low-pressure point is for the same chemical in powder form pressed to almost crystal density. In the single crystal, the temperature is the same everywhere and must be high to start detonation in 1 µm. In the pressed PETN, the average temperature is too low to start any reaction in a short time; if the pressed explosive is put in an oven at this temperature, it decomposes only slowly. At the hot spots the temperature is high, perhaps between 2,000 and 3,000 K; fast reaction takes place at these spots and initiates the explosive. The effect of hot spots is large and exists in most practical explosives.

In single crystals and liquids, heating in a shock-initiation experiment seems to be homogeneous. However, as if nature deliberately attempted to make our study difficult, even these materials develop hot spots in their detonation reaction.

Fig. 26. Plot of shock temperature versus shock pressure for the explosive PETN. A single crystal of PETN is initiated in 1 µs when it is shocked to 11 GPa; the bulk temperature, 570°C, causes rapid reaction. A pressed charge of PETN, made from fine particles of PETN pressed to almost the same bulk density, is initiated in 1 µs when shocked to 2.5 GPa; the bulk temperature, only 145°C, is far too low to cause rapid reaction. In this case the reaction takes place at hot spots and spreads from there.
Fig. 27. Image intensifier photograph of detonation light from an 85 vol% nitromethane 15 vol% acetone mixture. The photograph was taken looking straight down at a detonation in a 19-mm-i.d. brass tube. The exposure time was 20 ns. The explosive is water white, and the light can be seen through the unreacted explosive. The transverse wave structure is clearly visible. The apparent brightness temperature is certainly nonuniform, and probably the reaction zone temperature also is nonuniform. Thus, even a completely homogeneous explosive, a liquid in this case, makes its own hot spots.

zones. Figure 27 shows the luminous reaction zone in a transparent liquid detonated in a brass tube. The reaction zone was photographed through the unreacted explosive as the wave moved toward the camera. If the reaction zone were locally smooth and uniform, we would expect the light to be slightly brighter at the center and a little dimmer at the edge, but nearly uniform. The pronounced transverse structure, clearly visible in the figure, is evidence that even in this homogeneous liquid hot spots are generated by the instability of the reaction zone. Sequential photographs of the detonation show that the edges move and the spots transform. Similar structures have been photographed in various liquid and solid explosives, and they probably exist in most explosives.

About 20 years ago, Donald R. White, of the General Electric Research Laboratory in Schenectady, studied detonation structure in gases. He found that the final state of the reaction zone was not a CJ point, but was more like the weak point W in Fig. 23. He analyzed his results to show that the transverse structure in gases, known for many years, could lead to weak detonations. Bdzil also has studied the problem, and his results lead to the same conclusion.

Obviously, we need a theory of detonations with transverse structure or with turbulent reaction zones before we can make any real advance. In the meantime, not only do we have no theory, but we are unable to estimate the size of the effects to be expected. The trouble is that the details of the reaction process (its effective reaction rates) determine the position of the reaction zone end point on the complete reaction Hugoniot curve in Fig. 23. All the conservation condi-
Fig. 28. Summary of detonation physics.

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to ways to fill in the chemical reaction rate box, and new work in statistical mechanics and new capabilities for static high-pressure experiments should tell us more about the equations of state.

Another subject that must be treated is the averaging needed to take account of the inhomogeneities in the reaction zone. The hot spots present in most of the solid materials we use in shock-wave physics usually can be neglected because they cause only small effects compensated for by slight adjustment of the constitutive relations. In detonation, hot spots cannot be neglected because they are the main effect; reaction begins in their neighborhood, and large composition changes take place there. Until we can take account of the inhomogeneities, we cannot use real equations of state and real chemical rates. However, a relatively new mathematical technique called “homogenization” may yield insight into this problem. Homogenization has been applied to systems with great internal complexity to derive rigorous equations that describe the average behavior of the system. For example, a nuclear reactor has many fuel elements and many control rods, and a detailed description of the action of each element and rod combines to give a very complex set of equations that describe the whole system. Homogenization gives a single equation that describes the large-scale behavior of the system, simple enough to be useful, but still reflecting the detailed small-scale variations of its many parts. Perhaps using similar techniques for explosives will allow us to describe the average behavior of an inhomogeneous reaction zone with the real properties rigorously included in the description. Bdzil is studying homogenization of the equations that describe detonation.

For the most part, I have described attempts to develop scientific understanding. Another topic is practical application. Does detonation research have value for engineering? It is always hard to guess what new things might come from research, but we can try to extrapolate. A safe explosive system has all its explosive parts near failure size, so that they operate well when they are initiated intentionally, but will always fail if they should be initiated accidentally. In such a system, the reaction zone is important, and we must understand it before we can make one. We are already a long way in that direction with the insensitive explosives now in use. Further, inhomogeneities control the failure radius and the reaction zone, and we must understand them if the manufacture of explosives is to be controlled satisfactorily. Any systems designed for safety will need knowledge of transients, edge effects, and failure.

The next step beyond good engineering of systems using explosives is designing the explosive itself. If we could fill out the boxes of Fig. 28 in detail, we wouldn’t even have to make samples of the explosive molecules for testing or experiment to find the best particle-size distribution. Certainly we can’t go that far very soon, but every step toward explosive design is important.

To close, I would like to address any newcomer to the business who feels diffident about speaking up in disagreement with the majority when so many of us have been working so long with explosives. Let me quote from E. Bright Wilson, Jr., who says, “No one can be so obstructive of progress as the ‘expert’ who has worked all his life on a single subject.”
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**Further Reading**


