# Two Faces of Explosion: Deflagration and Detonation

## 3.1 Explosion

Explosion is one of the most common words used in our day-to-day life. "Bursting" and "detonation" are the words that appear to be synonymous with the word "explosion." In a way, "explosion" is a loosely used word implying different meanings under different situations. We say, "a balloon explodes," "a warhead or a bomb explodes," "a nuclear weapon explodes," "a gas cylinder explodes," "a reaction vessel explodes," and so on (not to mention its figurative usage such as "a boss explodes" or "a wife explodes"). although all of these situations vary greatly in terms of

- The type of energy release (physical/chemical/nuclear)
- The quantum of energy released, and
- The rate at which the energy is released.

Before we try to get the correct definition of the word "explosion," let us see how an explosion can be classified. There are three types of explosions: (1) physical explosions, (2) chemical explosions, and (3) nuclear explosions.

Physical explosions involve very fast physical transformation of a system or material that results in an explosion. An example is the explosion of an overheated water boiler. No chemical change takes place in this process. Only water in the liquid state gets converted into its vapor state. Because the water vapor occupies a much larger volume than liquid (water) at its boiling point, the pressure developed by the water vapor in a confined volume of the boiler is so high that it overcomes the strength of the container material, leading to sudden energy release.

On the other hand, nuclear explosions are disastrous because of the enormous amount of thermal energy and radioactivity released due to the conversion of mass into energy obeying the well-known equation of Einstein, $E = mc^2$.

This chapter excludes the above two types of explosions (physical and nuclear) and deals only with chemical explosions, in which a large amount of thermal energy, often accompanied by the evolution of a large amount of high-pressure, high-temperature gaseous products, is suddenly released because of a chemical reaction. Coming back to the

definition of the term "explosion," unfortunately, no definition is perfect in revealing all of the characteristics of an explosion. The most acceptable one can probably be stated as follows: "Explosion is a process of rapid physical or chemical transformation of a substance, accompanied by *an extremely rapid transition of its potential energy into mechanical work*." A chemical explosion can be subclassified as follows:
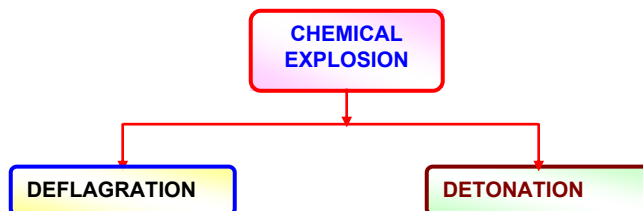


Most of the chemical explosions involve rapid chemical reactions, as a result of which large volumes of high-pressure and high-temperature gases are formed in a short time with the evolution of an enormous quantity of heat. For example, explosion of RDX (cyclotrimethylene trinitramine) is accompanied by the evolution of 9 mole of gaseous products in a few microseconds.

$$C_3H_6N_6O_6 \rightarrow 3CO_{(g)} + 3H_2O_{(g)} + 3N_{2(g)} + \text{Heat}$$
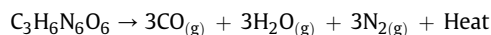
In rare cases, no or very little gaseous products are evolved during a chemical explosion. For example, the explosion of copper acetylide is as follows:

$$Cu_2C_2 \rightarrow 2Cu + 2C + \text{Heat}$$
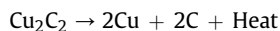
Here, the reactant and the products are solids. There are no gases.

In addition, when a mixture of hydrogen and oxygen explodes to produce water, there is actually a reduction in volume:

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)} + \text{Heat}$$
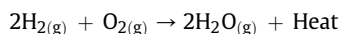
These can be explained by the fact that both of these reactions are highly exothermic and a large amount of heat is released in a very short time, thereby suddenly heating up the adjacent gases or air and creating high-pressure waves or shock waves.

## 3.2 Deflagration and Detonation

Explosives are those substances that have their own supply of oxygen in their molecules. When they are initiated, they may either burn violently (deflagrate) or explode disastrously generating shock waves (detonate). What are the differences between deflagration and detonation?
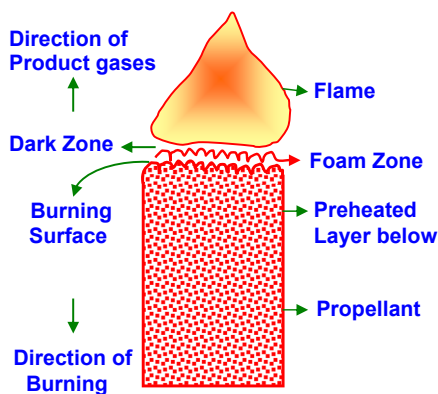
**Figure 3.1**
Deflagration of a Propellant Stick.

Let us take a stick of a rocket propellant, say, made of nitrocellulose (NC) and nitroglycerine (NG; i.e., a "double-base" propellant). When it is ignited at one of its ends, it burns rather vigorously, layer by layer. The salient points of a deflagration process are indicated in Figure 3.1.

Deflagration has the following characteristics:

1. The propellant burns layer by layer.
2. There are different zones existing above the burning surface as shown, varying in temperature, pressure, concentration, and composition of gaseous products.
3. The hot gaseous products emerge away from the regressing surface.
4. The most important characteristic of deflagration is that the rate of deflagration (or the rate of recession of a burning surface, often expressed in millimeters per second at a given pressure) is much below the sonic velocity of the material (i.e., the velocity of sound through the propellant material).
5. The process of deflagration is sustained by thermal feedback from the flame to the surface temperature by means of conduction, convection, and radiation.
6. The rate of regression (or burning rate, r) heavily depends on the pressure of the surrounding gases (P), and, according to Vielle's law, a double-base propellant nearly obeys the equation

$$r = bP^n$$

where *n* is the pressure exponent and b is a constant. The value of n depends on the propellant composition, the pressure, etc., the details of which will be seen in subsequent chapters on propellants.

Let us see what happens when the process of detonation occurs in an explosive.
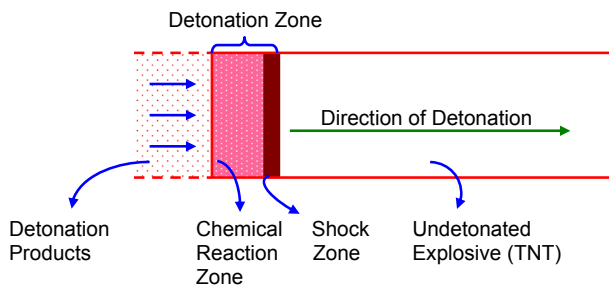
Detonation Zone

Direction of Detonation

Detonation
Products

Chemical
Reaction
Zone

Shock
Zone

Undetonated
Explosive (TNT)

**Figure 3.2**
Detonation of an Explosive.

When a cylindrical stick of trinitrotoluene (TNT) is detonated using a detonator, the following characteristics are noted during the process of detonation (see Figure 3.2):

1. The detonation is accompanied by the production of a shock wave.
2. The wave front of the shock wave has a high temperature and pressure gradient (shock zone), which instantaneously initiates chemical decomposition of the shocked explosive layer of the undetonated explosive. The chemical reaction of explosion is completed in the chemical reaction zone. The shock zone is very narrow ($\sim 10^{-5}$ cm) as compared with the chemical reaction zone (varies from 0.1 to 1.0 cm), and both of these zones together form the detonation zone.
3. The gaseous products flow in the same direction as that of the propagation of detonation.
4. The rate of propagation of the detonation front (velocity of detonation (VOD)) is more than the sonic velocity of the material (i.e., the velocity of sound in undetonated TNT). The VOD varies from 1500 to more than 9000 m/s for different explosives.

The important differences between deflagration and detonation are summed up in Table 3.1. The actual nature of a shock wave will be discussed in the subsequent section of this chapter.

## 3.3  Linear Burning and Mass Burning

In an earlier chapter, it was mentioned that when a chunk of coal burns in air, it takes its own time; however, when it is powdered to very fine dust, dispersed in air, and ignited, a violent detonation (that takes <1 ms) results. Has the basic characteristic of burning of this piece of coal changed after being reduced to fine dust? No. The chemistry of combustion of coal in air remains the same. If a given sample of coal burns at the rate of, say 1 mm/s under atmospheric pressure (what we call the "linear burning rate"), then this property does not change irrespective of how small you break it into pieces or grind to a fine dust. The finer it is, then the more surface area is exposed for burning. Let us assume

**Table 3.1: Comparison of deflagration vs detonation.**

| Sl. No. | Deflagration | Detonation |
|---|---|---|
| 1. | It is a **s**urface phenomenon (i.e., its propagation is by layer-to-layer burning). | It is a **s**hock-wave phenomenon (i.e., high-speed shock wave traveling through the explosive medium propagates detonation). |
| 2. | The rate of deflagration is lower than the sonic velocity in the medium. | The rate of detonation is higher than the sonic velocity in the medium. |
| 3. | The products of deflagration go away from (opposite to) the direction of propagation of deflagration. | The products of detonation travel in the same direction as that of the propagation of detonation. |

that, on average, after fine division, each coal particle (assuming to be a sphere) has 1 μm ($10^{-3}$ mm) as its radius. At the linear burning rate of 1 mm/s, each particle will take only $10^{-3}$ s (i.e., 1 ms) for burning. Because there are so many millions of such particles, a great amount of pressure is developed in 1 ms, when all of these particles undergo simultaneous ignition/burning. This results in a sudden increase in pressure (even before each particle is fully consumed), and the huge pressure converts the sound wave into a shock wave, resulting in detonation. Here, we talk about the "mass burning rate," which tells us how many grams of the material will be consumed per unit time. It depends on the linear burning rate of the material ($r$), the surface area exposed for burning (A), and the density of the material ($\rho$).

The mass burning rate, $\dot{m}$ is related to these parameters as follows:

$$\dot{m} = r A \rho$$

Please note that $r$ and $\dot{m}$ have units of millimeters per second (or cm/s) and grams per second (or kg/s), respectively. The purpose of introducing the concept of linear burning and mass burning at this stage is because it plays a key role in propellant ballistics and in phenomena such as deflagration-to-detonation transition (DDT), which will be separately discussed.

## 3.4 Shock Wave and Detonation Wave

A shock wave is a disturbance propagating at supersonic speed in a material, accompanied by an extremely rapid increase in pressure, density, and temperature. When a large amount of energy is suddenly released in a very limited space, it produces a shock wave. It may be mechanical energy (e.g., passage of a supersonic aircraft), electrical energy (e.g., discharge of lightning in a narrow channel), or chemical energy (e.g., detonation of an explosive). The shock wave caused by a detonation is called a "detonation wave." Therefore, a detonation wave is a shock wave, but all shock waves are not detonation

waves. When a shock wave is not sustained, say, by continuous feeding of energy (as in case of a detonation wave, in which continuous evolution of thermochemical energy and gaseous products behind the shock front keeps feeding the shock wave), it loses energy because of viscous dissipation by the surrounding medium and it degenerates into a sound wave (e.g., thunder).

The detonation process in an explosive requires a shock wave for initiation. This shock wave that initiates a detonation may originate from the detonation of an explosive nearby (sympathetic detonation) or from a process of deflagration (which is subsonic) that gets transformed into a supersonic disturbance because of reasons such as confinement. The shock wave in all of these cases should be supersonic. It compresses, heats, and ignites an explosive that gives out sufficient energy and expanding reaction products to sustain the shock wave.

### 3.4.1  The Concept of a Shock Wave

The formation of a one-dimensional planar shock wave can be visualized with the help of an accelerating piston in small increments from zero velocity to some final constant velocity (see Figure 3.3(a)−(d)).

Figure 3.3(a) shows that the first infinitesimal compression at the piston face results in the propagation of a sound wave (velocity = $C_o$). In Figure 3.3(b), the material that is in a compressed state has a higher density and the velocity of sound in this denser medium is more than $C_o$ (e.g., = $C_1$). This means that the wave front $C_1$ will catch up with the wave front $C_o$ after a particular time. Because the acceleration of the piston is continuous, it can be imagined that the medium facing the piston gets more and more compressed, resulting in a train of waves in which the first is at the speed of sound in the undisturbed material ($C_o$), followed by faster and faster moving wave fronts of higher and higher pressures.

From Figure 3.3(c), it can be visualized that after some time $C_1$ catches up with $C_o$, then $C_2$ catches up with $C_1$, and so on, so that eventually all of the waves coalesce into a single, steep, discontinuous wave front across which exists a sharp discontinuity in pressure, density, and temperature (Figure 3.3(d)). The width of this discontinuity is generally on the order of a few molecular mean-free-path lengths. Behind the piston, a reverse process of gas expansion creates a rarefaction wave that moves in a direction opposite to the shock wave and piston motion. There is a drastic change in the physical properties of the medium across the shock front (Figure 3.4). This change is described by the Rankine−Hugoniot (RH) equations, ensuring the following:

1.  Conservation of mass;
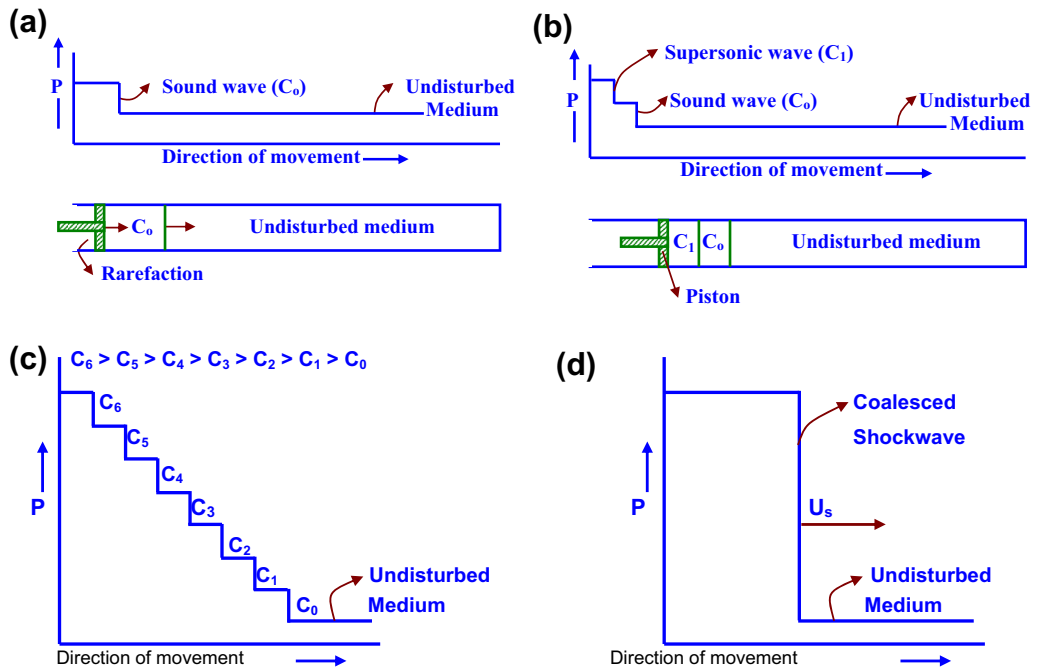
$$\frac{V_o - V}{V_o} = \frac{U_p - U_o}{U_s} \tag{3.1}$$

**Figure 3.3**

Formation of a Shock Wave at Time (a) $t_o$, (b) $t_1$, and (c) $t_6$. (d) Coalescence of Wavefronts to a Plane Shock Wave. (*Note*: The Velocity of Sound in a Medium is Given as $C = (\gamma RT_0)^{1/2}$, where $\gamma$ is the Ratio of the Specific Heat of the Medium, $T_o$ is its Absolute Temperature, and R is the Universal Gas Constant. During Compression, the Medium Gets Heated up and the Value of $T_o$ Increases, Thereby Increasing the Velocity of Sound in the Medium.)
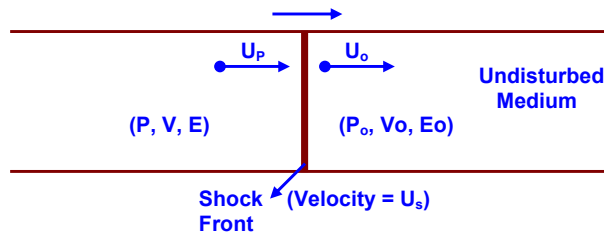


**Figure 3.4**
Movement of Shock Front.

2. Conservation of momentum; and

$$P - P_o = \frac{U_s(U_p - U_o)}{V_o} \tag{3.2}$$

3. Conservation of energy

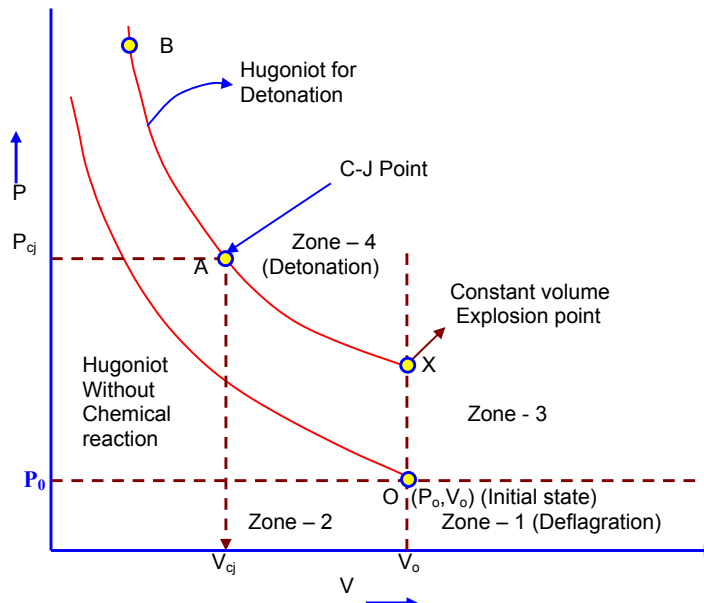$$E - E_o = \frac{(P + P_o)(V_o - V)}{2} \tag{3.3}$$

**Figure 3.5**
Hugoniot Curve for Detonation.

where $U_s$ is the shock velocity and E, V, P, and $U_p$ are, respectively, the energy, specific volume (i.e., volume occupied by 1 g of the substance), pressure, and material (or piston) velocity in the shocked states. The subscript zero indicates the initial state. The RH curve represents the locus of all final states that can be reached by shock-compressing a material from the same initial state. The resultant curve of pressure against volume is known as the Hugoniot curve (Figure 3.5). If the initial state is known, by measuring any two of the five final parameters, then the final state properties can be determined. The shock velocity ($U_s$) is usually measured.

The lower P—V curve in Figure 3.5 represents a simple Hugoniot curve for inert material that does not involve any chemical reaction, similar to the one formed by an accelerating piston in a closed cylinder as described above. This P—V curve is rather smooth. However, when we deal with a detonation wave, which is nothing but a shock wave sustained by an explosive reaction, it becomes more complex, as will be seen in the following subsection.

### 3.4.2 Detonation Wave

The study of detonation was first performed in the laboratory in 1881 by detonating an explosive mixture of gases by igniting it in a long uniform tube at one end. The initial combustion wave, which was subsonic, was found to accelerate rapidly to a high constant speed, which we now know as the detonation velocity, or VOD.

**Table 3.2: Detonation velocity of some common explosives.**

| Name of Explosive | Molecular Formula | Velocity of detonation (VOD) (km/s) | Name of Explosive | Molecular Formula | VOD (km/s) |
|---|---|---|---|---|---|
| TNT | $C_7H_5N_3O_6$ | 6.9 | CL-20 | $C_6H_6N_{12}O_{12}$ | 9.1 |
| RDX | $C_3H_6N_6O_6$ | 8.44 | PETN | $C_5H_8N_6O_{18}$ | 8.4 |
| HMX | $C_4H_8N_8O_8$ | 9.1 | TATB | $C_6H_6N_6O_6$ | 7.35 |
| NG | $C_3H_5N_3O_9$ | 7.6 | NC (dry) | $C_{12}H_{14}N_6O_{22}$ | 7.3 |
| Tetryl | $C_7H_5N_5O_8$ | 7.57 | HNS | $C_{14}H_6N_6O_{12}$ | 7.12 |

TNT: trinitrotoluene; RDX: research and development explosive; HMX: high melting explosive; NG: nitroglycerine; Tetryl: 2,4,6-trinitrophenyl-methyl-nitramine; CL-20: China Lake-20; TATB: triamino trinitro benzene; HNS: hexanitrostilbene; PETN (pentaerythritol tetranitrate); NC: nitrocellulose. For their molecular structure refer to fig 1.4, table 4.4 and table 11.1

The value of the VOD was found to depend mainly on the composition of the explosive mixture and not on the tube material, tube diameter (beyond certain minimum), and method of initiation. Typical detonation velocities, temperatures, and pressures in gas mixtures are in the range of 2000 m/s, 3000 K, and 2 MPa (20 bar), respectively. The detonation velocity of a few common explosives is given in Table 3.2.

As mentioned previously, for a shock wave without a chemical reaction, the Hugoniot curve passes smoothly from its initial state ($P_o$, $V_o$) (Figure 3.5). In case of detonation, it is not so. Detonation can be thought of as a two-step process in which a chemical reaction releases energy in a constant-volume explosion (point X) and the reaction products are then shock-compressed to some final state (point B). The velocity of the final state is proportional to the slope of the line passing through the initial and final states (Rayleigh line). This can be obtained by eliminating $U_o$ between Eqns (3.1) and (3.2) as follows:

$$U_s = V_o \left[ \frac{P - P_o^{1/2}}{V_o - V} \right] \tag{3.4}$$

The RH equations cannot by themselves predict which of the Rayleigh lines (OA or OB) corresponds to the unique detonation velocity. Chapman—Jouguet (C—J) theory makes an assumption that

$$D = C + U_p \tag{3.5}$$

where D = the velocity of the detonation front,

    C = the velocity of sound in the medium, and
    $U_p$ = the velocity of the detonation products

This is given by drawing a tangent from the initial state ($P_o$, $V_o$) to the Hugoniot curve (OA). Point A is called the "C—J point." The application of C—J theory to solid explosives is more complex. Here, the products form a very dense gas for which the P-V-E relationship is not well known; hence, the computed properties are less accurately predicted.

## 3.5  Detonation Theory

The development of a proper detonation theory was a complex task because the very process of detonation itself is complex. It has to deal with the chemistry of a very fast, exothermic reaction; changes of mass, momentum, and energy during the reaction from reactant to products; very high pressure, temperature, and density changes; the nonideal behavior of product gases at high pressures; and so on. In the later part of $19^{th}$ century and early part of $20^{th}$ century, Chapman, Hugoniot and Joguet studied the thermodynamics of shock waves and its extension to reactive systems. This led to the development of the so-called "hydrodynamic theory of detonation." The mathematical treatment of this theory is beyond the scope of this book, and those interested might refer to some of the books given in the Reference section of this chapter. The author aims to highlight only the salient points of this theory to help the reader understand the concepts and approach of the theory.

During a detonation, an explosive chemical reaction is initiated immediately in the wave front because of the drastic temperature and pressure conditions. Apart from these two parameters, there is a significant difference between the undetonated explosive and the molecules in the shock zone with respect to density ($\rho$), specific volume (V; i.e., volume occupied by 1 g of substance − inverse of density), internal energy (E), and the velocity of sound in the medium (c). Figure 3.6 shows that there is a sudden, discontinuous jump in all of these parameters at the interface between the shock zone (subscript 1) and undetonated explosive (subscript o).

The sudden discontinuity in such parameters was mathematically treated using the following laws and conditions:

1. Law of conservation of mass (before and after explosion),
2. Law of conservation of energy (internal energy),
3. Law of conservation of momentum,
4. The equation of state (for gases), and
5. It is also assumed that the velocity of the detonation wave is equal to the sum of the velocity of sound in the medium and velocity of the products.
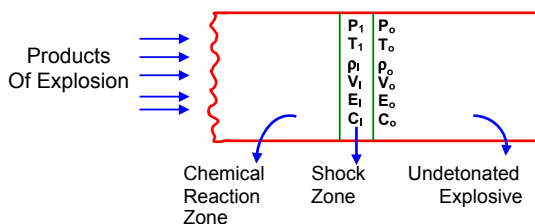


**Figure 3.6**
Discontinuity between Shock Zone and Undetonated Explosive.

The following are the salient points worth mentioning as the outcome of the hydrodynamic theory of detonation:

1.  The relationship between detonation velocity, detonation pressure, and density.

It can be shown (see Figure 3.6) that

$$P_1 = \rho_0 D U_p, \tag{3.6}$$

where $P_1$, $\rho_0$, D, and $U_p$ represent, respectively, the detonation pressure, the density of the undetonated explosive, the VOD, and the VOD products. Combining Eqns (3.4) and (3.5) and using the adiabatic condition ($PV^\gamma$ = constant) and equation of state, one finds that $U_p$ is related to D as

$$U_p = D/\gamma + 1 \tag{3.7}$$

where $\gamma$ is the ratio of specific heats of gaseous products. Substituting Eqn (3.7) in Eqn (3.6),

$$P_1 = \rho_0 D.(D/\gamma + 1) \tag{3.8}$$

Under the detonation conditions of high temperatures and pressures in the shock zone, the value of $\gamma$ of gases is approximately 3 and Eqn (3.8) becomes

$$P_1 = \frac{\rho_0 D^2}{4} \tag{3.9}$$

Hence, any increase in the density of an explosive exponentially boosts the detonation pressure, showing the importance of the density of high explosives.

2.  Hugoniot curve and C−J pressure.

We have seen in Figure 3.5 that the Hugoniot curve describes the locus of all P−V states attained by shock wave compression. Some of the interesting points that can be noted from this curve can be summarized as follows:

*   Zone 1 (bottom right quadrant with respect to initial state ($P_o$, $V_o$) is the deflagration zone, where $V > V_o$ and $P < P_o$ i.e., the deflagration products expand rapidly and there is no compression).
*   Zone 4 is the detonation zone, where $P > P_o$ and $V_o > V$ (see Eqn (3.4)).
*   As mentioned earlier, point A is called the C−J point. It is at this point where the detonation is stable. Above this point (e.g., at point B), the rarefaction wave catches up with the detonation wave; therefore, the detonation dies out. On the other hand, at point A, the detonation wave is constantly sustained by the chemical energy and products of explosion. At this steady state, the detonation has a constant intensity

and constant velocity. Under this condition, the VOD becomes equal to the sum of the velocity of sound through the medium and the velocity of the detonation products. This can be written as

$$D_{CJ} = C_{CJ} + U_{CJ}$$

as described earlier (Eqn (3.5))

- Zone 2 (where $V_o > V$ and $P_o > P$) and Zone 3 (where $V_o < V$ and $P_o < P$) do not have any physical significance because the substitution of these values results in imaginary values for shock wave velocity $U_s$ (in case of detonation, we call it D). The values of VOD and the detonation pressure ($P_d$) of explosives vary anywhere from 1500 to approximately 9500 m/s and from 2 to 50 GPa, respectively. (Note: 1 GPa = 1 gigapascal = $10^9$ Pa; $10^5$ Pa = 1 bar ≈ 1 atm pressure. From these relations, it is seen that 1 GPa = $10^4$ bar = 10 kilobar = 10 kbar. Both of the units of gigapascals and kilobars are used while quoting the values of $P_d$ of explosives. e.g., 40 GPa or 400 kbar).

## 3.6 Theoretical Estimation: VOD and $P_d$

Several attempts have been made over the last many decades to theoretically predict the VOD and $P_d$ of explosives. Four popular methods of VOD calculation are briefly mentioned in the following subsections.

### 3.6.1 Kamlet–Jacob Method

The Kamlet–Jacob (KJ method) method, developed by M. J. Kamlet and S. J. Jacobs of the Naval Ordnance Laboratory (United States) assumes that during detonation of a CHNO explosive, carbon dioxide ($CO_2$) and carbon (C) are preferentially formed rather than carbon monoxide (CO). The detonation equation was derived accordingly, and the same is given in Eqn (3.10):

$$D = A\left[NM^{1/2}(-\Delta H_d)^{1/2}\right]^{1/2}\left(1 + B\rho_o\right) \tag{3.10}$$

where D = VOD, A = a constant having a value of 1.01,

N = the number of moles of gases evolved per gram of the explosive,
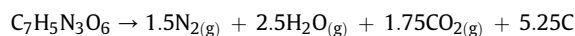M = the average molecular weight of the gases,
B = a constant having a value of approximately 1.30,
$\rho_o$ = the density of the unreacted explosive in grams per cubic centimeter, and
$\Delta H_d$ = the heat of detonation (explosion) in calories per gram.

Example: Let us calculate the VOD of TNT, having molecular formula $C_7H_5N_3O_6$, at its density of 1.64 g/cc. The heat of detonation is 1090 cal/g.

Step 1: Write the detonation equation.

$$C_7H_5N_3O_6 \rightarrow 1.5N_{2(g)} + 2.5H_2O_{(g)} + 1.75CO_{2(g)} + 5.25C$$

(Note: CO is not written as a product)

Step 2: Calculate the number of moles of gases formed per gram of TNT (molecular weight of TNT = 227).

$$N = \frac{1.5 + 2.5 + 1.75}{227} = 0.02532$$

Step 3: Calculate the average molecular weight of the gases formed.

$$M = \frac{(1.5 \times 28) + (2.5 \times 18) + (1.75 \times 44)}{5.75} = 28.51$$

Using the above formula of the KJ method.

$$D = 1.01\left[(0.02532)(28.51)^{1/2}(1090)^{1/2}\right]^{1/2}\left[1 + (1.30 \times 1.64)\right]$$
$$= \mathbf{6680\ m/s}\ \text{which fairly agrees with the experimental value of 6930 m/s.}$$

Detonation pressure ($P_1$):

From Eqn (3.9),

$$P_1 = \frac{\rho_0 D^2}{4}$$

Converting the values of $\rho_0$ (density of explosive) into SI units,

$$\rho = 1.64\ \text{g/cc} = 1.64 \times 10^3\ \text{Kg/m}^3$$
$$D = 6680\ \text{m/s} = 6.68 \times 10^3\ \text{m/s}$$

Substituting these values in Eqn (3.9),

$$P_d = 1.64 \times 10^3 \times \left(6.68 \times 10^3\right)^2$$
$$= 18.3 \times 10^9 \text{Pa}$$
$$= 18.3\ \text{GPa}$$

(Experimental value is $\sim$21.0 GPa).

### 3.6.1.1  CO first or $CO_2$ first?

While writing the chemical equation for detonation, the explosives chemist faces this quandary. In the case of underoxidized products resulting from low or highly negatively oxygen-balanced explosives, the CO-first approach gives higher values of n and lower values of M. It also appears from limited experimental data (cf., American Institute of Physics Handbook, 2nd ed., McGraw Hill Publishers, New York, 1963) that equilibrium shifts toward CO at a lower density of loading of explosives and toward $CO_2$ when the density of loading is higher.

As a sort of a thumb rule, we can write down the CO-first equation when the OB of the explosive is low or negative and/or when the loading density of the explosive is low. The converse is true for the $CO_2$-first equation.

### 3.6.2  Becker-Kistiakowsky-Wilson Method

We have learned that any gas that obeys the universal gas equation, $PV = RT$ (or $PV = nRT$ for n moles of a gas) is known as an ideal gas. However, all gases are nonideal and they deviate from the expected ideal behavior more and more at higher pressures and lower temperatures because of higher intermolecular attraction and the higher percentage of volume the molecules themselves occupy in a container. The well-known van der Waal's equation, $(P + a/V^2)(V - b) = RT$ (for 1 mol of a gas), overcame this problem but only to a limited extent.

The term $a/V^2$ compensates for the less pressure experienced by the walls of the container of the gases due to intermolecular attraction. The term b is the covolume that takes into account the volume occupied by the molecules themselves.

The situation becomes much worse during the process of detonation because in the detonation zone the pressure of the product gases is extremely high. The detonation pressure of explosives varies anywhere between 2 and 50 GPa (i.e., on the order of $10^5$ atm). During the last 50 years, different groups of authors have attempted to evolve different equations of state that take into account of the nonideal behavior of gases at such high pressures, but again with limited success. All of these methods use model equations that do not quite satisfactorily yield the condition of highly dense and heated detonation products. This includes the Becker-Kistiakowsky-Wilson (BKW) method, which needs five parameters: pressure (P), temperature (T), internal energy (E), density ($\rho$), and detonation velocity (D). It also needs two separate sets of data for calculations— one set for explosives with negative OB and the other set for those with positive OB.

### 3.6.2.1 BKW Method

This scheme utilizes thermodynamic and hydrodynamic properties to solve a set of equations. The BKW equation of state is given as

$$P = nRT\rho\left(1 + xe^{\beta x}\right)$$

where $\rho$ = density (inverse of specific volume),

$x = b\rho\kappa T^{-\alpha}$ (b is the covolume),
$\beta = 0.3$, $\alpha = 0.25$, and $\kappa \approx$ unity.

The above equation makes allowance for the compressibility of the molecules of the product gases at very high pressures in the detonation front. The values given for $\alpha$, $\beta$ above are found to be an optimal fit on the basis of experimental results. On the basis of this, several computer programs (RUBYCODE, STRETCH BKW, TIGERCODE, LOTUSES) have been worked out for the calculation of VOD, $P_d$, and the temperature of detonation.

Because of the iterative nature and arduous calculations involved, this scheme is performed by a computer program. The equation has four arbitrary constants—$\alpha$, $\beta$, $\theta$, and $\kappa$—that require calibration to suit any particular type of explosive. An attempt has been made to obtain a unique set to satisfy many explosive compositions.

### 3.6.3 Rothestein and Petersen Method

One method that relies only on the chemical structure of the explosive molecule is by Rothestein and Petersen (1979 and 1981). It yields values for VOD at the theoretical maximum density. A simple, empirical linear relationship between detonation velocity at theoretical maximum density and factor $F$, which is dependent solely on chemical composition and structure, is postulated for a gamut of ideal CHNO-type explosives by L. R. Rothstein and R. Petersen. The factor $F$ is expressed as

$$F = 100x\frac{nO + nN - \frac{nH}{2nO} + \frac{A}{3} - \frac{nB}{1.75} - \frac{nC}{2.5} - \frac{nD}{4} - \frac{nE}{5}}{MW} - G$$

$$D = \frac{F - 0.26}{0.55}$$

where $nH$, $nN$, and $nO$ are the number of hydrogen, nitrogen, and oxygen atoms in a molecule;

$nB$ is the number of oxygen atoms in excess of those already available to form $CO_2$ and $H_2O$;

$nC$ is the number of oxygen atoms doubly bonded to carbon as in a carbonyl group;

$nD$ is the number of oxygen atoms (other than those in $-O-NO_2$ group) singly bonded to carbon;

$nE$ is the number of nitro groups existing either as in a nitrate ester configuration or as a nitric acid salt such as hydrazine mononitrate;

$A = 1$ if the compound is aromatic, otherwise $A = 0$;

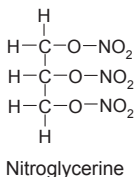$G = 0.4$ for a liquid explosive and $G = 0$ for a solid explosive;

$F = $ factor; and

$D = $ the detonation velocity in kilometers per second.

To achieve the maximum VOD for a homogeneous explosive, it is necessary to consolidate the explosive composition to its maximum density.

### 3.6.3.1  Illustration

Let us examine detonation velocity of NG as shown below.



Nitroglycerine

The empirical formula of NG is $C_3H_5N_3O_9$. The explosion reaction of NG is

$$C_3H_5N_3O_9 \rightarrow 3CO_2 + 2\tfrac{1}{2}H_2O + 1\tfrac{1}{2}N_2 + \tfrac{1}{4}O_2$$

$A = 0$ because NG is nonaromatic,

$G = 0.4$ because NG is a liquid,

$nO = 9$ because the number of oxygen atoms in the NG molecule is nine,

$nN = 3$ because the number of nitrogen atoms in NG is three,

$nH = 5$ because the number of hydrogen atoms in NG is five,

$nB = 0.5$ because nine oxygen atoms are available (2.5 of these are required to form 2.5 mol of $H_2O$ from the five hydrogen atoms and six of the oxygen atoms are needed to form 3 mol of $CO_2$ from the three carbon atoms, leaving 0.5 oxygen atom (or 0.25 oxygen molecule)),

$nC = 0$ because no oxygen atoms are double bonded to carbon in the NG molecule,

$nD = 0$ because all oxygen atoms in the molecule belong only to $-O-NO_2$ groups,

$nE = 3$ because there are three nitrate ester groups, and

$MW = 227.1$ (the molecular weight of NG).

Armed with these variables, we can calculate the value of detonation factor $F$:

$$F = 100 \left( \frac{9 + 3 + 0 - \frac{5-0}{2 \times 9} + \frac{0}{3} - \frac{0.5}{1.75} - \frac{0}{2.5} - \frac{0}{4} - \frac{3}{5}}{227.1} \right) - 0.4 = 4.372$$

$$D' = \frac{4.372 - 0.26}{0.55} = 7.48 \text{ km/s}$$

From the literature, the detonation velocity of NG is found to be 7.60 m/s. The error of the estimation in this example is 100 (7.48−7.60)/7.60 = −1.6%.

### 3.6.4 Stine Method

A relatively accurate method of estimating detonation velocities for CHNO explosives (Stine, 1990) is based on using the atomic composition of either a pure or mixed explosive, along with the explosive's density and heat of formation. In this method, the explosive composition is defined as $C_aH_bN_cO_d$, where $a$, $b$, $c$, and $d$ are atomic fractions (i.e., $a$ is the number of carbon atoms in the molecular formula divided by the total number of all atoms in the molecular formula, etc.). The equation is given by

$$D = 3.69 + (-13.85a + 3.95b + 37.74c + 68.11d + 0.6917\Delta H_f)\left(\frac{\rho}{M}\right)$$

where $\rho$ is the initial explosive density (g/cm$^3$), $\Delta H_f$ is the heat of formation of the explosive (kcal/mol), and M is the molecular weight of the explosive.

## 3.7 Deflagration-to-Detonation Transition

Let us consider the deflagration of a propellant stick. For a given composition, at a given ambient pressure, the propellant burns at a fixed rate (linear burn rate, $r$). We mentioned two important equations in Sections 3.2 and 3.3: $r = bP^n$ (exponential dependence of $r$ on P) and $\dot{m} = rA\rho$ (relationship between the linear burn rate ($r$) and $\dot{m}$ the mass burn rate ($\dot{m}$)).

As long as the rate at which the deflagration products evolved (i.e., $\dot{m}$) is equal to or less than the rate at which they are removed from the scene (e.g., $m_r$), one does not expect any accumulation of product gases around the burning propellant resulting in increased pressure around it. However, if $\dot{m} > m_r$, it results in an increase in pressure around the burning propellant. Higher pressure leads to a higher value of $r$. Higher $r$ means still a higher rate of buildup of pressure. It becomes a superfast, vicious cycle between pressure increase and $\dot{m}$ increase until at one stage the value of $r$ exceeds the sonic velocity of the medium (burning propellant). Once $r$ exceeds the sonic velocity, as we have seen in Section 3.5, it leads to the formation of the vertical fronted (shock) detonation wave. This is known as the DDT, a very important phenomenon in the field of explosives.

### 3.7.1 When Can DDT Occur?

1. When there is a high degree of confinement experienced by the deflagrating material.
2. If the deflagrating explosive is initiated by a high-intensity shock wave.

3. In the presence of a large degree of porosity in deflagrating material (which means a very large surface area of exposure—remember, $\dot{m} = rA\rho$, where A is the area exposed for burning).

4. In large explosive charges in which the bulk of the explosive itself provides necessary confinement—particularly when they are in the form of finely divided material. (Granular TNT initiated with black powder burns quickly if the TNT is spread in thin layers on the ground ($\dot{m} < m_r$). It is bound to detonate if piled up in a large mound ($\dot{m} > m_r$)).

Therefore, during disposal of waste explosives or propellants, one has to ensure that the material is spread into thin layers to avoid the DDT phenomenon. Some of the disastrous explosions involving some seemingly innocuous materials are known to have been caused by DDT. DDT studies are essential to avoid unwanted and catastrophic detonations. During the development of new propellant compositions and scaling up of the processing of explosives, DDT studies should be performed. For example, one cannot afford the loss of a costly gun barrel if the newly developed gun propellant undergoes DDT. Likewise, scaling up the production of explosives without DDT trials may destroy the production plant because there exists a possibility of detonation because of the mass effect.

## *Suggested Reading*

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## Questions

1.  How do you define explosion and how can it be classified?
2.  All explosions result in gaseous products with increased volume. Is this statement always true? If not, then give some examples that are contrary to the above statement.
3.  What are the differences between deflagration and detonation?
4.  Why does an ordinary, innocuous fuel become dangerous when it is finely dispersed in air?
5.  Ten kilograms of a propellant are to be disposed of by open burning after breaking into cubical pieces, each piece having a length of 1 cm. If the density of the propellant is 1.5 g/cc and its linear burning rate is 2 mm/s at atmospheric pressure, then what will be the initial mass burning rate when the entire lot of propellant is simultaneously ignited? (Answer: 12,000 $gs^{-1}$).
6.  Why does a shock wave assume a plane wave front?
7.  What are the different zones identifiable when a column of solid explosive undergoes detonation?
8.  Why do detonation products move along the direction of the propagation of detonation?
9.  β-HMX has a detonation velocity of 9100 m/s and density of 1.96 g/cc. What is the expected detonation pressure (in GPa) when β-HMX detonates? (Answer: 40.58 GPa).
10. What conditions can favor DDT?
11. Name some computer programs developed for the calculation of VOD and detonation pressure.
12. Name some methods for the theoretical estimation of VOD.
13. What is the difference between linear burning and mass burning?
14. Give the relationship among the detonation velocity, detonation pressure, and density of an explosive.
15. What is the significance of the Hugoniot curve?