

Explosions and Explosives: Fundamental Aspects

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An explosion may be broadly defined as the sudden and rapid escape of gases from a confined space accompanied by high temperatures, violent shock and loud noise. The explosion is essentially a physical process which involves rapid dissipation of power with the equalization of pressure and should never be treated as a chemical phenomenon. The generation and violent escape of gases is the primary criterion of an explosion and occurs in all three basic types of explosion, viz. mechanical, chemical and atomic explosions.

Mechanical Explosion

It is illustrated by the gradual build-up of pressure in a steam boiler or a pressure cooker. As heat is applied to the water inside the boiler, steam is generated and the steam pressure eventually reaches a point when it overcomes the structural or material resistance of its container and an explosion occurs. Such a mechanical explosion should be accompanied by high temperature, rapid escape of gases or steam and a loud noise. An example of a mechanical explosion is the steam explosion, such as might be caused by accidental dumping of a molten slag car into water. The greatest steam explosion of the history¹ was the famous Krakatao Volcanic explosion of 27 August 1883. It was caused by the sudden vaporization of an estimated cubic mile of ocean water, when a volcano erupted and spilled a great mass of molten lava into the ocean. This explosion involved an energy possibly equivalent to more than five million kilotons of TNT. It illustrates dramatically the potential of the mechanical explosion.

Chemical Explosion

A chemical explosion is caused by the extremely rapid conversion of a solid or liquid explosive compound into gases having a much greater volume than the substances from which they are generated. When a block of explosive is made to detonate, the

gases produced may have 10,000 - 15,000 times greater volume than the original volume of the explosive. The expansion of the gases generated is very rapid, reaching velocities of 7000-8000 m/sec. The temperature generated may reach 3000°-4000°C. The entire conversion process takes only a fraction of a second and is accompanied by shock and loud noise. All explosives manufactured by man with the exception of atomic explosives are chemical explosives.

Atomic Explosion

An atomic explosion may be induced by fission, the splitting of the nucleus of atoms or fusion, the joining together under greater force of nuclei of atoms. Nuclear fission or fusion occurs only in extremely heavy elements which are atomically unstable or radioactive. When fission or fusion occurs, a tremendous release of energy, heat, gas and shock takes place.

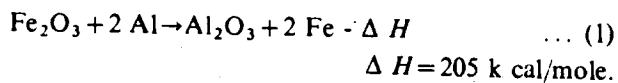
The explosives normally used by ordnance and mining personnel are chemical in nature and result in chemical explosions. Therefore, the present discussion is restricted to chemical explosions.

Chemical Explosion and Its Characteristics

A chemical explosion is characterized by the following features: high rate of reaction, exothermicity, large volume of gases evolved, and initiation by (a) mechanical action which also includes action of shock wave from another detonation, (b) high temperature and (c) direct flame.

Most of the explosion reactions fit into the above scheme. The evolution of heat when crystallization of a supercooled liquid takes place cannot be regarded as an explosion, since only one of the above conditions is satisfied. Moreover, no chemical change is involved.

The thermite reaction represented by Eq. (1) is not an explosion, since no gases are evolved.



The rate of an explosive reaction may be represented as shown in Fig. 1.

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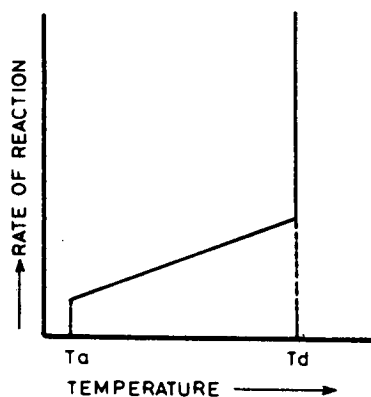
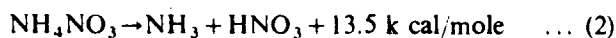


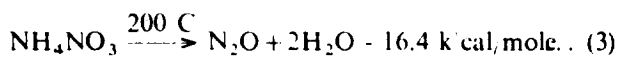
Fig. 1—Reaction rate vs temperature for an explosion reaction

In an explosion reaction, the reaction rate increases instantaneously at a particular temperature, say t_d . At room temperature, no decomposition takes place. At temperature t_a , the decomposition starts slowly, but there is no explosion. The temperature t_d , at which there is a sudden change in the rate of reaction, is called explosion temperature.

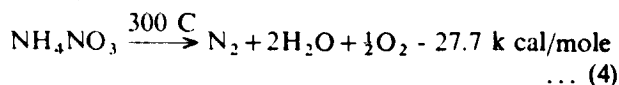
The decomposition of the cheapest explosive known, ammonium nitrate, is interesting. Ammonium nitrate was not considered an explosive by itself, but some disasters occurred during the accidental breaking of caked ammonium nitrate and proved beyond doubt that it is an explosive. At room temperature, ammonium nitrate decomposes endothermally according to Eq. (2).



The heat which should be introduced into the system is the reverse of heat of neutralization of ammonia with nitric acid. As the temperature increases to 200°C, the following reaction takes place:



Even though this is an exothermic reaction, the rate of reaction is so low that it cannot be considered as being an explosion. At about 300°C, the following reaction takes place:



The steep nature of the curve in Fig. 2 confirms that this reaction can be considered as an explosion.

Theory of Chemical Explosion

The most widely accepted theory of chemical explosion is the chain reaction theory². To explain a chain reaction let us consider the simple reaction between hydrogen and chlorine represented as follows:

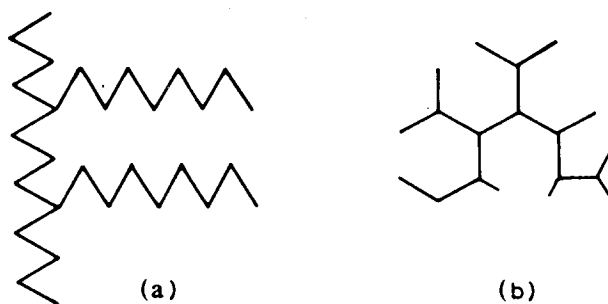
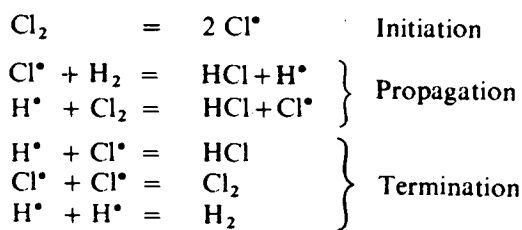


Fig. 2—Schematic representation of (a) a chain reaction with rare branches, and (b) a continuously branched chain reaction

At ordinary temperature, the reaction does not take place. But when a mixture of hydrogen and chlorine is exposed to sunlight or ultraviolet radiation, the reaction starts. The steps involved in this reaction are:



In the case of an explosion, the reaction can be initiated by mechanical impact, flame or another explosion and there is a branched chain reaction instead of a simple one. It means that a radical initially formed reacts with several molecules to give several radicals and so on. Finally, there are an increasing number of radicals which can propagate the chain. Branched chain reaction may be of two types: (i) Long chains with rare branching (Fig. 2a), and (ii) continuously branched chain when branching occurs at every cycle (Fig. 2b).

If the rate of chain branching is much greater than that of the chain terminating reaction, the rate of reaction will become indefinitely large and an explosion will occur. Such a branched chain reaction may be represented diagrammatically as in Fig. 2b.

Such an outburst in reaction rate is sometimes referred to as avalanche by analogy with such a phenomenon in mountaineering.

Explosive System

According to some workers in the field of thermodynamics, every system capable of transferring itself with the release of heat must be considered in a state of inequilibrium. Probably these workers linked an explosive composition with an unstable composition. Duhem³ suggested that an explosive system can be compared with a ball placed on a well polished inclined plane and held in position by a certain minimum force; on application of a certain minimum

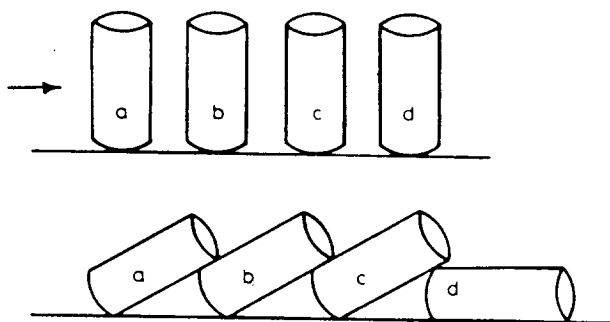


Fig. 3—Diagrammatic representation of the propagation of decomposition in a mass of explosives

shock, it gets displaced. But this analogy was not correct, since explosive molecules, with the exception of nitrogen halogenides, are not unstable.

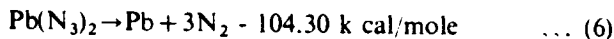
Muraour⁴ suggested a model to show that the propagation of decomposition in a mass of explosives is not related to instability of the explosive molecules in itself. This viewpoint is illustrated in Fig. 3. Cylinders a, b, c and d are placed in a line not far from each other. Let us assume that when we push the cylinder a, its falling makes the other cylinders, b, c and d, to fall successively. In this case, the propagation of falling does not prove at all that cylinder a is unstable, because a lot of energy may be required to make cylinder a fall and we can conclude that propagation means the work necessary to be performed to make one cylinder fall. It is the same for the explosive molecules. The energy needed for the molecules to enter into the reaction corresponds in this case to the work necessary to make the cylinder a to fall; in terms of physical chemistry this is activation energy.

It is possible that the activation energy of an explosive molecule may be more than that of another non-explosive molecule; the latter in that case will seem to be more unstable than the first molecule. But as such, the decomposition of the non-explosive molecule does not lead, in general, to any release of heat. Decomposition of the explosive molecule and explosive reactions are accompanied by the liberation of heat sufficient to provoke the decomposition of neighbouring molecules. Therefore, explosive compounds can be looked upon as a chemical combination of atoms in a metastable state, which spontaneously on passage of detonating wave rearrange themselves to give simple products with concurrent liberation of large volumes of gases and considerable energy mainly in the form of heat. Explosive molecules are neither particularly unstable, nor are they characterized by a low value of activation energy. But in these molecules, there is rapid transfer of activation energy between the decomposition products and the molecules which are still unreacted.

Classification of Explosives

The rate of release of calorific or heat energy liberated by the explosive reaction permits classification of the explosives into two groups.

Endothermic explosives—These explosives are formed from their elements with absorption of heat. In this case, the release of heat is only due to the decomposition of explosive substances into the constituent elements, as illustrated by the decomposition of lead azide,



Nitrogen tri-iodide also belongs to this group.

It is not enough that a molecule to be an explosive should be endothermic. There are numerous compositions which are endothermic in nature but do not possess explosive properties. Some typical cases are listed in Table 1.

Table 1—Typical Non-explosive and Explosive Compounds

	Compound	Heat of formation k cal/mole
Non-explosive compound	Carbon disulphide	+ 19.0
	Ethylene	+ 12.5
	Prussian blue	+ 338.60
Explosive compound	Ozone	+ 34.0
	Acetylene	+ 54.2

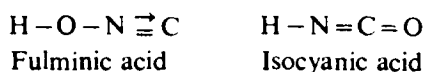
The release of heat does not give an idea of the "explosivity" of a substance. Ozone and acetylene are explosive in nature, whereas carbon disulphide, ethylene and prussian blue are not explosive. This is explained by the fact that the energy released by decomposition of the molecule is insufficient to cause decomposition of the neighbouring molecule, the intramolecular bonding being too strong or the bonds too many in numbers. Moreover, in these cases the energy released is less than the activation energy and hence there is no propagation of reaction.

Exothermic explosives—The molecules of these explosives are formed from the constituent elements with the release of heat. In this case, the origin of energy released by the explosive cannot be the decomposition of the molecule into its elements (because decomposition absorbs heat), but destruction of molecular structure with reaction between certain groups or certain elements or molecule, which release the heat. Most of the time it is the phenomenon of internal combustion between groups carrying oxygen and easily oxidizable elements like carbon and hydrogen. In such explosives, elements like carbon and hydrogen are separated from oxygen by providing a buffer like nitrogen*.



subjected to an energetic external action, the buffer is knocked out and the combination of C and H with oxygen with the formation of CO₂ and H₂O evolves a large amount of heat. It is thus essential that for such intramolecular combustion, the oxygen should not be bonded directly to carbon.

An interesting example of the situation arising from the difference in structure is the salt of two isomers of fulminic acid and isocyanic acid.



The fulminates are explosive in nature, whereas in the isocyanates, the oxygen is bonded directly to the carbon which that way is partly burnt prior to combustion. In the fulminate, on the contrary, the oxygen is separated from the carbon. Then the heat of formation of fulminate is negative and that of isocyanate, positive (e.g. the heat of formation of silver fulminate is -43.3 k cal/mole and that of silver isocyanate, +23.1 k cal/mole) and no exothermic reaction can occur at the moment of their decomposition.

Chemical Structure of Explosives

Most of the organic explosives have nitro groups in them and mainly these groups are responsible for the explosive characteristics. Pletz⁵ examined the various other functional groups responsible for explosive characteristics. These groups are:

-NO₂ and -ONO₂ in both inorganic and organic substances

-N=N= and -N=N=N- in inorganic and organic azides

-NX₂, for example, in NCl₃ (X, a halogen)

-N=C in fulminates

-OClO₂ and OClO₃ in inorganic and organic chlorates and perchlorates respectively.

-C≡C= in acetylene and metal acetylide

M-C metal bonded with carbon

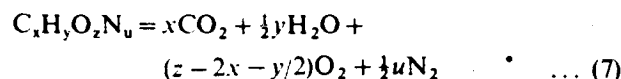
The compounds with these functional groups undergo explosive decomposition and the branched chain mechanism is responsible for the exothermicity. As discussed earlier, organic high explosives in the main are composed of combinations of only four elements: carbon, hydrogen, oxygen and nitrogen. Since combustion is the process taking place, a simple computable term should be of value in stating the degree to which oxidation is possible. For this purpose, the expression known as oxygen balance is useful. It is the percentage of oxygen required for complete conversion of the carbon and hydrogen present to

carbon dioxide and water. For any compound containing 'x' atoms of carbon, 'y' atoms of hydrogen and 'z' atoms of oxygen, the oxygen balance will be:

$$\% \text{ oxygen balance} = \frac{-1600(2x + y/2 - z)}{\text{Mol. wt}}$$

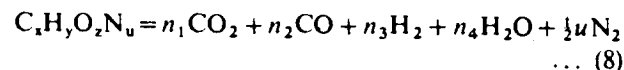
Thus, an explosive having perfect oxygen balance to yield carbon dioxide and water has zero balance; the one lacking sufficient oxygen has a negative balance and that containing excess oxygen balance has a positive balance.

For an explosive of the type C_xH_yO_zN_u having positive oxygen, the equation of decomposition is:

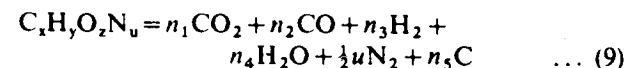


Ammonium nitrate, ammonium perchlorate, nitroglycerine and dinitroethylene glycol belong to this class.

If the explosive substance is oxygen-deficient, but entirely gasifiable under the conditions of decomposition, the decomposition takes place according to Eq. (8):



If the substance is oxygen-deficient, but there is liberation of free carbon, the decomposition follows the following course:



where

$$\begin{array}{l} n_1 + n_2 + n_5 = x \\ 2(n_3 + n_4) = y \\ 2(n_1 + n_2 + n_4) = z \end{array}$$

A majority of the organic explosives are oxygen-deficient. A few typical ones are listed in Table 2. The respective oxygen deficiencies are also given.

Table 2—Some Typical Oxygen-deficient Explosives

SI No	Explosive	Mol wt	kg of oxygen needed by 1 kg of substance
1	1,3-Dinitrobenzene(DNB)	168	-0.953
2	2,4-Dinitrotoluene(DNT)	182	-1.144
3	2,4,6-Trinitrobenzene(TNB)	213	-0.563
4	2,4,6-Trinitrotoluene(TNT)	227.1	-0.740
5	Picric acid	229	-0.454
6	Pentaerythritol tetranitrate (PETN)	316	-0.101
7	Cyclotrimethylene trinitramine (RDX)	222	-0.216
8	Nitroguanidine	104	-0.308
9	Tetryl	287	-0.474

Table 3—Some Typical Oxygen-carriers for Oxygen Deficient Explosives

Sl No.	Oxygen carrier	mol wt	kg oxygen supplied by 1 kg of the substance
1	NH ₄ NO ₃	80	+ 0.200
2	Ba(NO ₃) ₂	261	+ 0.306
3	KNO ₃	101	+ 0.475
4	NaNO ₃	85	+ 0.567
5	KClO ₄	138.5	+ 0.465

To fulfil the oxygen deficiency, oxygen carriers (Table 3) like ammonium nitrate, barium nitrate, potassium nitrate, etc. are added to the oxygen-deficient explosives mentioned in Table 2.

All compounds which have got an excess oxygen balance or the same oxygen balance as an explosive need not be explosive. Mellitic acid and 2,4,6-trinitrobenzene (TNB) are typical cases; the former is not an explosive. TNB is an explosive, because heat is evolved on decomposition and it is capable of forming free radicals for chain reaction. Mellitic acid has got a low heat of formation and is unable to form free radicals on heating and so the compound is not an explosive.

It is clear that oxygen balance is not the only criterion for a compound to be an explosive. Hexamethylene triperoxodiamine (HMTD) is a strong initiator explosive because of the peroxide linkages, which can give rise to free radicals easily. This compound is too sensitive to be of any commercial use. The number of oxygen atoms in a particular compound is not a proper indication of the heat of explosion. Compared to TNB, we may expect picric acid or styphnic acid to have a higher heat of explosion, but actually it is not so. The contribution from hydroxyl oxygen to heat of explosion is not as great as that from nitro group. So, TNB has approximately the same strength as that of picric acid or styphnic acid. Some of the popularly used explosives are depicted in Fig. 4.

Different Modes of Decomposition of Explosives

The different modes of decomposition of the explosives are thermal decomposition, combustion, deflagration and detonation. These modes of decomposition are characterized by the process by which the activation energy is transferred to the explosive molecule. Here, only secondary explosives are dealt with. The secondary explosives are those which in contact with flame burn without detonation and without producing mechanical effect. This is the case with a majority of explosives.

Thermal Decomposition

As a typical example of secondary explosives, the case of picric acid contained in a test tube placed in a hot oil bath may be considered. Slow decomposition of the explosive starts and at moderate temperature, the entire mass of the explosive decomposes. It is important to note that in majority of the cases the decomposition occurring does not follow the same equation under high pressure or under detonation. The reaction, in general, is incomplete. Usually, on decomposing, the molecules of the explosive release heat. This heat is dissipated by conduction and radiation. But if the temperature of the oil bath is increased rapidly, the heat released by the decomposition becomes more than that of the bath and the temperature rises progressively. Finally, the reaction becomes progressive and there is deflagration of the explosive. It is not the real detonation and the mechanical effect registered is of relatively low magnitude.

The energy given by the heat source is distributed into different molecules. This distribution is statistical. A large number of molecules receive moderate amounts of energy. Very few molecules have more than moderate energy. Naturally, the latter are the first to decompose.

For a molecule, the various energies are: the energy of translation, vibrational energy, energy of rotation and ionization energy.

If the energy of vibration or rotation becomes too large, the molecule breaks. When two molecules

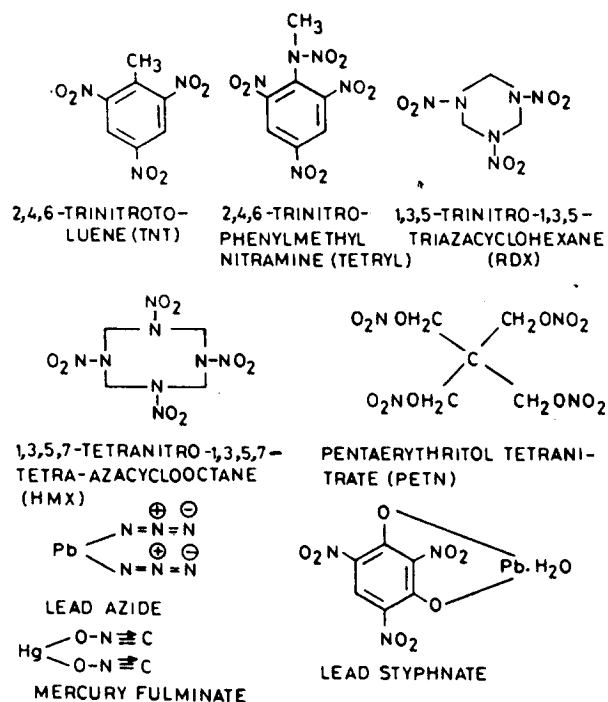


Fig. 4—Some commonly used explosives

collide, the energy of translation is transferred partially into energy of vibration or rotation. The fraction of energy of translation thus transferred may vary with the nature of the molecule involved. This fraction seems to be important in the case when frequencies of vibration of the excited molecules and of the exciting molecules become almost equal. Then it may result in resonance which can facilitate transfer of energy.

At normal temperature, the intramolecular links are already in vibration and the vibration can be completely absent at absolute zero (-273°C). It may be assumed that even at normal temperature and by the statistical distribution of the energy in molecules, a very small number of molecules can get the energy to be decomposed. In reality, this decomposition at the normal temperature has been proved in explosive molecules of very few compounds. It may be concluded that the explosives produced at the normal temperature can stay indefinitely, provided they are in purified form.

Explosive Combustion

Secondary explosives burn without detonation at the contact of flame. In the phenomenon of combustion, the energy necessary for decomposition of the explosive molecules (activation energy) is given in two ways: (i) by conduction, and (ii) by collision of gas molecules (released by combustion reaction) on the surface of the explosive which is still undecomposed.

The energy given by conduction is independent of the pressure, while that given by collision of gas molecules is proportional to the pressure. At very low pressures, it is the first mechanism which predominates, while at high pressure, the second one predominates. The velocity with which the combustion is propagated depends on (i) the number of calories (heat) which are needed by the explosive molecule to undergo decomposition, (ii) the energy given by the collision of gas molecules; this energy depends on the temperature of the given gas and the pressure,

and (iii) the available surface of the explosive.

On coming in contact with a flame, a secondary explosive can burn slowly without producing mechanical effect. But the combustion stops in vacuum. It is not the same for initiating explosives. They detonate in the open air producing spot effect. This is remarkable, because the damage occurs even when the explosive is burnt in vacuum. If 25 mg of lead azide is detonated in vacuum on a sheet of iron of 13 mm thickness, a hole of 10 mm diameter results. With 80 mg of explosive, the iron sheet is broken into many pieces. It is really surprising that even in vacuum, combustion can proceed quickly enough to make a hole in the iron sheet. It is not a case of simple combustion of explosives, nor is it a case of transition from deflagration to detonation. In this case, the explosive is decomposed into Pb and N_2 with the release of energy. The atoms of lead and the molecules of nitrogen take with them the liberated energy and the activation energy. The energy in this case is transmitted mainly by molecular induction.

Detonation, Deflagration and Thermal Explosion

The term 'detonation' is rather widely misused by many people, but until a few years ago, detonation seemed capable of rigorous definition. In the classical sense, 'detonation' is a steady state combustion reaction that propagates through the reacting medium at greater than the local sound velocity, i.e. the sound velocity in the unreacted material. In detonation, the principal energy transfer process to cause propagation of the wave is hydrodynamic, in contrast to the usual conductive, convective and radiative processes associated with 'deflagration', the more familiar flaming reaction. Deflagrations are ordinary combustion reactions characterized by subsonic propagation rates, with heat transfer occurring by conduction, convection and radiation and with the products streaming in a direction opposite to the direction of propagation. The differences in these two process are given in Table 4.

Table 4—Values of Different Parameters for the Deflagration and Detonation Processes

Mode of decomposition	Ma'_u	Ma_x	p_x/p_u	v_x/v_u	s_x/s_u	t_x/t_u	Front of the reaction product	velocity of propagation cm/s	Power W/cm^3
Deflagration	<1	≥ 1	<1	>1	<1	>1	Anti-parallel	$1 \cdot 10^3$	5×10^3 (solid) $5 \cdot 10^3$ (gas)
Detonation	>1	≥ 1	>1	<1	>1	>1	Parallel	$0.5 \times 10^5 \cdot 10^6$	-10^{10} (gas)

Ma , Mach No; p , pressure; v , volume; s , density; t , temperature ($^{\circ}\text{K}$); x , products after reaction; and u , reactants.

More precisely, detonation may be defined as a supersonic chemical reaction initiated by a shock wave, which, in turn, is supported by the chemical energy released in the reaction. Of course, a shock wave is a compression wave moving at supersonic velocity through a compressible medium. Compression heats the medium, causing reaction to occur, the extent of reaction depending upon the degree of compression, physical state of the material, thermochemistry and chemical kinetics.

The initiation of combustion, deflagration and detonation by various physical processes is depicted in Fig. 5.

Thermal explosion can occur in unstable materials that decompose throughout the mass, with the result that the chemical reaction is accelerated because of increase in temperature due to self-heating. Obviously, thermal explosions hold interest in themselves, but have greater importance, because the basic processes involved in thermal explosion have close analogies in certain types of initiation of deflagration or initiation of detonation. The relative rates and modes of heat transfer involved in the propagation of the above processes are given in Table 5.

Deflagration can, under certain circumstances, change into detonation and this transition has major importance in understanding some initiation processes. The experimentally demonstrable transition from thermal reaction to deflagration, from deflagration to detonation, etc. may be taken to indicate the existence of qualitative shifts in the reaction mechanisms. By focusing attention on these shifts, a qualitative model encompassing thermal explosion, burning and detonations immediately suggests itself⁸. The schematic diagram in Fig. 6 is based on this simple model.

Detonations in condensed phase systems produce exceedingly high pressures, depending upon density, energy and other factors. Pressure ranges from tens of kilobars to 200-300 kilobars for most systems. Clearly, it is impossible under normal circumstances to contain such pressures; so the consequence is a blast wave and fragments from containers or surrounding objects. Air blast effects at a distance from a condensed phase

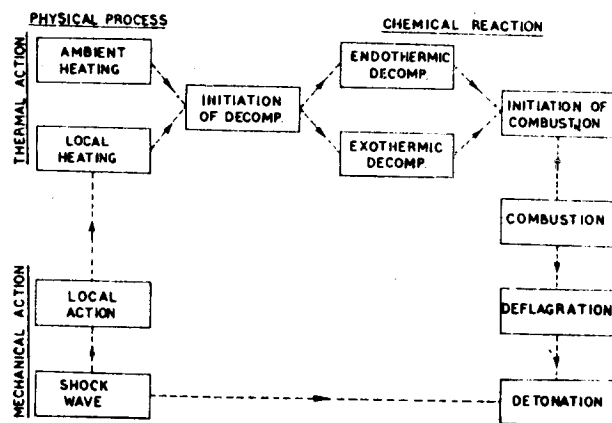


Fig. 5—Initiation of combustion, deflagration and detonation by different physical processes (according to Simchen⁶)

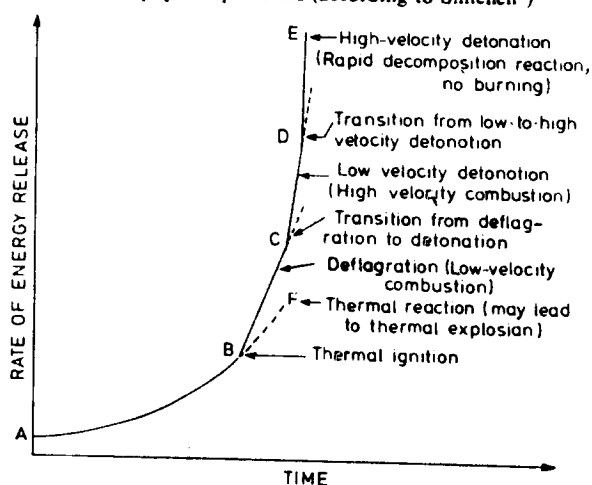


Fig. 6—Model depicting the processes of explosion, burning and detonation

detonation can be predicted with some certainty based upon Sachs scaling law⁹.

Formation of a Super-explosive

Explosives like NG, TNT, and RDX, etc. are very powerful. For example, NG liberates about 1500 cal energy per kg. Does chemistry permit us to prepare explosive which can release more energy? Theoretically, this is possible, in particular, if we are dealing with mixing of combustibles and fuel prepared with endothermic components like acetylene and liquid ozone, which by themselves are already explosive. The energy liberated by the decomposition of these components adds itself to the energy released by the combustion of carbon and hydrogen. For example, the heat released by the combustion of 1 kg of different mixtures on the basis of the equations is as follows:

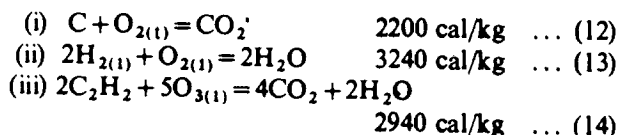
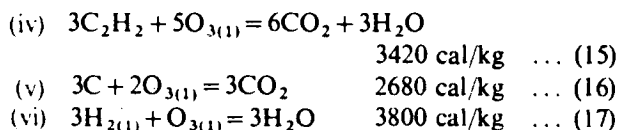


Table 5—Rates and Mechanisms of Heat Transfer for Different Processes

Process	Rate	Heat transfer mechanism
Thermal explosion	Very slow (normally)	Conduction, convection
Deflagration	Slow to fast	Conduction, convection and radiation
Detonation	Very fast	Hydrodynamic



Mixture (iv) would be theoretically very powerful. But it will detonate by itself when the constituents are brought together. Mixtures (v) and (vi) would also be dangerous to manipulate. It is the same for mixture (iii). The accidental formation of these mixtures can cause tremendous explosions. Mixture (ii) will also be a powerful explosive, but not stable when it is made. In fact, mixture (i) is stable and can release a good amount of energy. The decomposition of 1 kg of this mixture releases a quantity of energy equal to 1.5 times that released by 1 kg of NG. But the practical effect is not 1.5 times that of NG. This is attributed to density and VOD of liquid air explosives.

Recently, it has been reported that United States of America and Soviet Union^{10,11} have developed fuel-air explosives which are likely to create a revolution in the conventional warfare. This type of explosives are based on volatile hydrocarbons which (i) do not require oxygen for spontaneous combustion, e.g. ethylene oxide, (ii) continue to burn without oxygen or air (e.g. propyl nitrate), (iii) contain a high proportion of oxygen and cause a violent reaction on coming in contact with the combustible material (e.g. acetic peroxide), and (iv) explode on coming in contact with moist air at ambient temperature (e.g. anhydrous unsymmetrical dimethyl hydrazine).

Out of the above mentioned systems, ethylene oxide has been employed widely in fuel-air explosive devices. On the basis of typical blast wave geometries, ethylene oxide has a TNT equivalent of 2.7 - 5.0. In

other words, the blast wave effect of detonation of 1 kg of ethylene oxide is equivalent to the detonation effect of 2.7 - 5.0 kg of TNT¹².

Summary

The fundamentals of the chemical processes involved in an explosion are outlined. The importance of deflagration to detonation transition has been emphasized in the light of its importance in assessing the potential hazards of reactive systems.

Acknowledgement

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