Energetics of Energetic Materials

2.1 Are Explosives and Propellants High-Energy Materials?

Explosives are storehouses of energy. The potential energy lying dormant in the molecules of these materials is released when they are properly triggered or initiated and the release of this energy originates at the breaking of the energetic chemical bonds in the molecule of the explosive compound. The explosives (and propellants, which are categorized as low explosives) are sometimes referred to as "high-energy materials" (HEMs) or "energetic materials." Is one justified in using these terms for explosives? Let us compare the most powerful high explosive in use today—HMX (an abbreviation for High Melting Explosive; chemical name being cyclic tetramethylene tetranitramine)—with a well-known fuel—coal—in terms of their energetics.

From Table 2.1, it is seen that for every gram, coal produces more than 5 times the heat produced by HMX. The heat evolved by 1 g of coal and HMX is illustrated as a chart in Figure 2.1. A similar comparison will show us that all fuels of day-to-day use release far more heat than any known explosive. Therefore, in a thermochemical sense, explosives and propellants are not really HEMs. However, we also observe that HMX detonates in much less time than a piece of coal takes to burn. The former undergoes the process of detonation accompanied by shock waves whereas the latter takes its own time for combustion with the help of oxygen available in air. If we take the rate at which the heat is released, then the power of HMX is approximately 5.6×10^9 W in comparison to 488 W of coal in the above example. This power generation by HMX is far more than the capacity of all of the power generators in the country put together. The better term for explosives may not be HEMs but "power-packed materials."

In the above example, an arbitrary figure of 60 s has been given for the burning of coal. Under static wind conditions, the time taken for 1 g of coal to burn depends on its surface area exposed to air. As we go on breaking it into pieces, the burning time of coal comes

Table 2.1: Heat generated by coal and HMX.

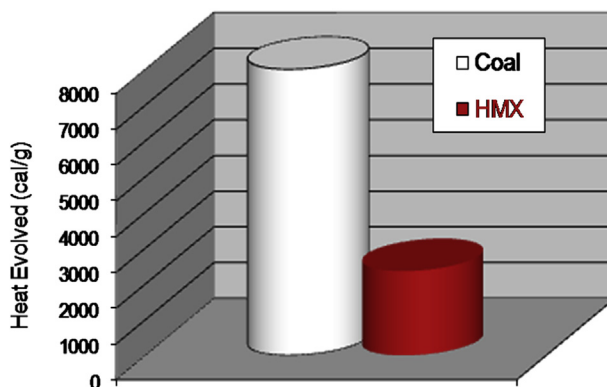| Sl. No.	Property	Coal (1 g)	HMX (1 g)
1.	Heat evolved	7000 cal (heat of combustion)	1355 cal (heat of explosion)
2.	Time (burning/detonation)	60 s	10^{-6} s
3.	Power	488 W	5.6×10^9 W

Figure 2.1
Comparison of Heat Evolved by 1 g of Coal and HMX.

down drastically. At its extreme, when the same 1 g of coal is finely powdered and dispersed as coal dust in air, facilitating the exposure of the maximum surface area to air, each such dust particle is in intimate contact with the oxygen molecules of air. When initiated, the combustion reaction takes place so fast that it is virtually converted into a violent detonation. Disastrous coal-dust explosions in coal mines are a result of this phenomenon. Such dust explosions are not uncommon in many other industries.

2.2 Explosive: The Wonderful Lamp

An explosive is similar to the genie that we come across in the ever-fascinating tale of Aladdin and the Wonderful Lamp. It has great potential, but then it has to be kept under check or "bottled-up." Only when its services are needed do we open the bottle, and, in the case of explosives, we give the necessary trigger energy. An explosive is a substance in a metastable equilibrium, in a "ready-to-go-off" stage with huge potential energy. The relation between the energy needed to make an explosive and the energy released by it on explosion can be qualitatively understood by comparing it with a huge boulder brought to the apex of a cliff.

Figure 2.2(a) and (b), respectively give an analogy between a boulder kept on the brink of a cliff and an explosive synthesized and "kept" in a metastable state. One has to make great efforts (or spend much energy) to place the boulder on the cliff (A) in Figure 2.2(a). The boulder continues to remain there until someone decides to push it (giving an energy equal to B) so that it falls off from a great height, converting the potential energy into kinetic energy, which is dissipated as heat and sound when it strikes the ground. Release of energy is equal to C. Likewise, the synthesis of an explosive molecule is done by packing in it a great amount of potential energy such as high bond energy, structural strain, etc., and it is kept in the metastable state as shown in Figure 2.2(b). (D−E) is the
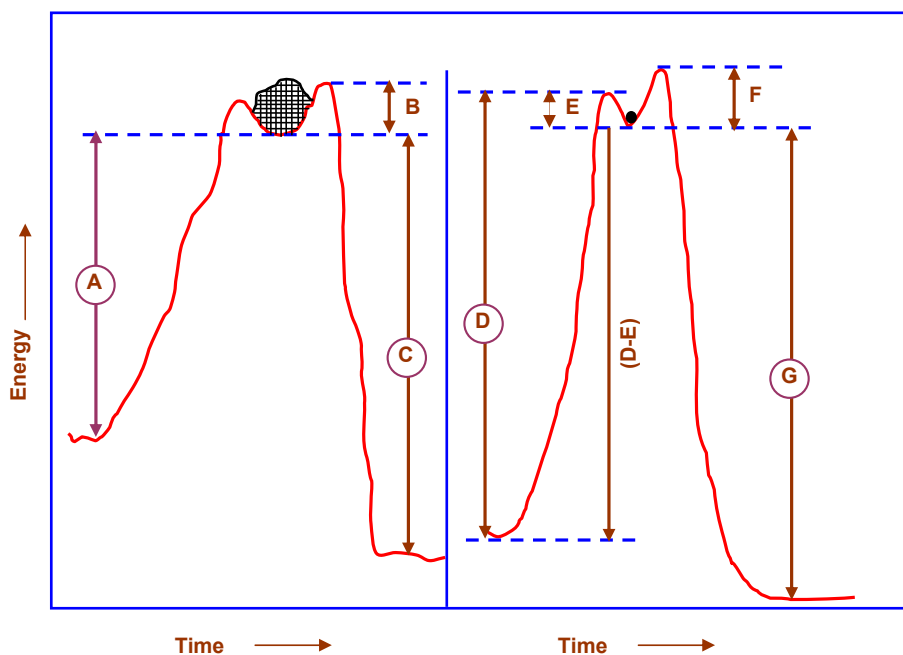
Figure 2.2
A Boulder on a Cliff and an Explosive Molecule.

effective energy spent in such a synthesis. If the reactants are assumed as elements such as carbon, hydrogen, and oxygen, (D−E) is referred to as the heat of formation of the explosive. The explosive now needs only a trigger energy (generally called activation energy) equal to F, so that a net energy equal to G is liberated during the explosive process and the formation of stable products.

The chemist who wants to synthesize an explosive ensures that (1) as far as possible the product has a high positive heat of formation (i.e., the energy level of the explosive molecule is higher than that of the elements from which it is made), (2) it has its own supply of oxygen in the molecule to be independent of external or atmospheric oxygen to affect the process of explosion, and (3) the explosive reaction results in a large amount of gases.

Factors 1 and 2 will ensure that the explosion process releases a large amount of heat (heat of explosion), thereby enormously increasing the temperature of the products, normally more than 2000 °C. Factor 3 will ensure that, with so many gases at a high temperature, there will be development of very high pressures. The gases expand rapidly from very high pressures to the atmospheric pressure, thereby performing a large amount of work in a short time; that is, the produced gases will work as a powerful working fluid to perform certain assigned tasks such as the blast effect produced by high explosives in microseconds, the work of throwing a projectile through a gun barrel in a few

milliseconds, or the self-propulsion by a rocket in a time period varying from a few seconds to even a few minutes.

Is an oxidation reaction always necessary in a chemical explosion? Although most of the chemical explosions involve fast oxidation of fuel elements, it need not be so in some cases. For example, lead azide ($Pb(N_3)_2$), a well-known primary explosive, does not contain any oxygen atoms in its molecule. However, it has a positive heat of formation. The azide ($-N-N\equiv N$) groups attached to the lead atom have weak linkages and are themselves at a higher energy level. Only a small trigger energy is necessary to rupture these linkages to produce more stable products with the evolution of energy.

$$Pb\left(-\overset{(-)}{N} - \overset{(+)}{N} \equiv N\right)_2 \rightarrow Pb + 3N_2 + 110.8 \text{ kcal}$$
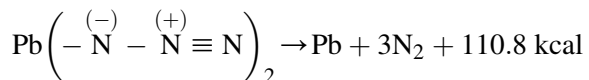
2.3 Thermochemistry and Explosive Energy

Chemical reactions are accompanied by energy changes, mainly in the form of heat. The branch of science that deals with the heat changes during chemical reactions is called "thermochemistry." It is essential to remember certain basic concepts in thermochemistry to obtain better insight into the heat transactions during the formation and explosion of explosives. The concepts about the three important parameters—internal energy (E), heat content or enthalpy (H), and work (W)—should also be clear. The internal energy of a substance is the total quantity of energy it possesses by virtue of its kinetic portion of energy (due to translational, vibrational, and rotational motions associated with the molecules) and the potential portion of energy (due to various interatomic, intermolecular, and submolecular forces of attraction and repulsion). In a chemical reaction in which certain bonds of the reactant molecules are broken and certain bonds of the product molecules are formed, it is mostly the kinetic portion of the internal energy that undergoes a change and may be positive or negative. E is a measure of the absolute temperature of the given substance. When the temperature increases, all of these kinetic aspects of energy obviously increase in the molecule.

Heat content, or enthalpy (H), which is defined as $H = E + PV$, where P and V are pressure and volume, respectively, comes in picture when the system undergoes a change in its E and, at the same time, a certain amount of work is also performed. The work, W, is taken as $W = P(\Delta V)$, where ΔV is the change in volume due to the work of expansion. The absolute values of E and H have no significance. We are interested only in the changes in the values of E and H (i.e., ΔE and ΔH, respectively) of a system when changes such as a chemical reaction take place.

2.3.1 Heat of Reaction

The net heat absorbed or evolved during a chemical reaction is known as the heat of reaction (ΔH_r). The reaction involves the expenditure of heat energy to break certain bonds in reactant molecules and the evolution of heat energy when certain bonds are made in the product molecules. If the expenditure is more than the evolution, then it is an endothermic reaction and the converse is true for an exothermic reaction. In an endothermic reaction, ΔH of the products is more than that of the reactants and the converse is true for an exothermic reaction.

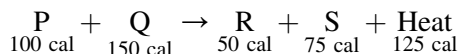#### 2.3.1.1 An Endothermic Reaction (Net Heat Absorption)

Heat content	A	+	B	$\rightarrow$	C	+	D	—	Heat
(arbitrary values)	80		100		120		100		40
	cal		cal		cal		cal		cal

$$\Delta H = H_{(products)} - H_{(reactants)}$$
$$= (120 + 100) - (100 + 80) = 40 \ \text{cal}, \quad \Delta H = +40 \ \text{cal} \tag{2.1}$$

In its general form, an endothermic reaction can be represented as

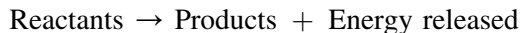$$\text{Reactants} + (\text{Energy absorbed by reactants}) \rightarrow \text{Products}$$

2.3.1.2 An Exothermic Reaction (Net Heat Evolution)

$$\underset{100 \ \text{cal}}{P} + \underset{150 \ \text{cal}}{Q} \rightarrow \underset{50 \ \text{cal}}{R} + \underset{75 \ \text{cal}}{S} + \underset{125 \ \text{cal}}{\text{Heat}}$$

$$\Delta H = H_{(products)} - H_{(reactants)}$$
$$= (50 + 75) - (100 + 150) = -125 \ \text{cal} \quad \Delta H = -125 \ \text{cal}$$

In its general form, an exothermic reaction can be represented as

$$\text{Reactants} \rightarrow \text{Products} + \text{Energy released}$$

It should be remembered that ΔH is negative for exothermic reactions and positive for endothermic reactions. All explosive chemical reactions are exothermic, and the ΔH values of these reactions are negative.

All heats of reactions are compared at a standard state, which is normally defined as 25 °C (298 K) and 1 atm pressure.
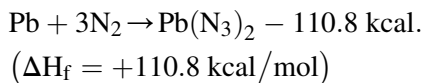
2.3.2 Heat of Formation

The heat of formation (ΔH_f) of a compound is defined as "the heat evolved or absorbed when 1 mole of the compound is formed from its elements in the standard state."

It is assumed that the heat of formation of elements (e.g., H, O, C, etc.) is taken as zero. The heats of formation of explosives can be either exothermic or endothermic; for nitroglycerine (NG), its heat of formation reaction is written as

$$3C + 5/2H_2 + 3/2N_2 + 9/2O_2 \rightarrow C_3H_5(NO_3)_3 + 84\,\text{kcal}(\Delta H_f = -84\,\text{kcal/mol})$$
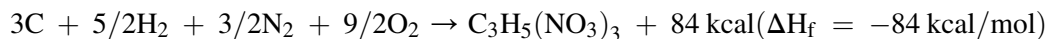
$Pb(N_3)_2$, a primary explosive, is formed endothermically.

$$Pb + 3N_2 \rightarrow Pb(N_3)_2 - 110.8\,\text{kcal.}$$
$$\left(\Delta H_f = +110.8\,\text{kcal/mol}\right)$$

As we will see shortly, ΔH_f is a very important thermochemical parameter for an explosive because it plays a vital role in the heat of explosion or heat of detonation and other related parameters. An explosive that has a positive heat of formation or a low negative value of heat of formation is preferred for release of maximum heat during its explosion.

2.3.2.1 Experimental Estimation of ΔH_f

In most cases, it is not possible to experimentally form a compound from its elements. For example, we cannot synthesize NG from its elements of C, H, N, and O as shown above. It is not that simple to produce NG. We use Hess's law of constant heat summation to solve this problem. It states: "If a chemical reaction is carried out in stages, the algebraic sum of the amounts of heat evolved in separate stages is equal to the total amount of heat evolved when the reaction occurs directly." That is, the resultant heat change in a chemical reaction performed either at constant pressure or constant volume is the same whether it takes place in one or several stages. Thus, according to this law, ΔE and ΔH are dependent only on the initial and final states and not on the path connecting them. It is pictorially represented in Figure 2.3. This law is a corollary of the Law of Conservation of Energy.
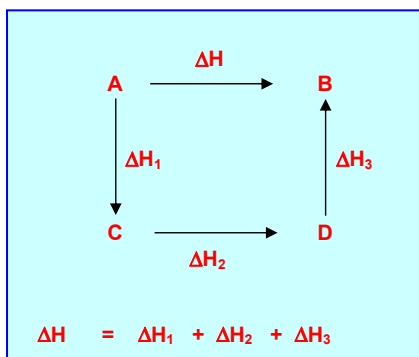

**Figure 2.3**
Hess's Law.

Another way of stating Hess's law is

Heat of the reaction $(x) = \sum(\Delta H_f)$ products $- \sum(\Delta H_f)$ reactants, or

$$\text{i.e.,} \quad x = \left(\Delta H_f\right)_C + \left(\Delta H_f\right)_D - \left(\Delta H_f\right)_A + \left(\Delta H_f\right)_B \tag{2.2}$$

where A and B are the reactants and C and D are the products of a reaction.

Coming back to the example of NG, how can we calculate its ΔH_f? (Data given are heat of explosion of NG, $\Delta H_e = -367$ kcal/mol; $\Delta H_{f(CO_2)} = -94$ kcal/mol; and $\Delta H_{f(H_2O)} = -67.4$ kcal/mol.)

The explosive reaction of NG can be written as

$$C_3H_5(NO_3)_3 \rightarrow 3CO_2 + 5/2H_2O + 3/2N_2 + 1/4O_2 + 367 \text{ kcal}$$
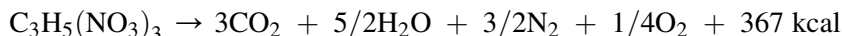
(Note: The heat of explosion can be experimentally determined.)

Using Hess Law, $\Delta H_{reaction} = \sum(\Delta H_f)_{prod} - \sum(\Delta H_f)_{react}$

$$-367 = [(3 \times -94) + (5/2 \times -67.4)] - [(\Delta H_f)_{NG}]$$

(Note: ΔH_f of the elements is taken as zero.)

$$\Delta H_f \text{ of NG} = -83.5 \text{ kcal/mol}$$

Therefore, NG is an exothermic compound. Alternatively, if the ΔH_f value of an explosive is available, then we can calculate its heat of explosion.

2.3.2.2 Theoretical Prediction of ΔHf

There are many computer codes to theoretically evaluate or predict the performance of high explosives (e.g., TIGER, BKW Code), rocket propellants (e.g., NASA-LEWIS), and gun propellants (e.g., BLAKE). However, none of these can operate without having the data on ΔH_f of the concerned energetic materials and their products of explosion. There are several potential candidate molecules of explosives that are yet to be synthesized. In addition, if we want to theoretically predict their performance as high explosives or propellant ingredients (and decide whether it is worth synthesizing them), then we need to know their ΔH_f values. Naturally, we cannot resort to the experimental method (as in the case of NG) because the compound is still not available. This section briefly mentions a few theoretical methods available for the purpose of predicting the ΔH_f values.

1. Group additivity method:
   In this method, the explosive molecule is divided into different groups and each group is assigned an enthalpy value. The individual group enthalpies are added to give the ΔH_f of the molecule. This method neglects the effect of intergroup interactive forces. It
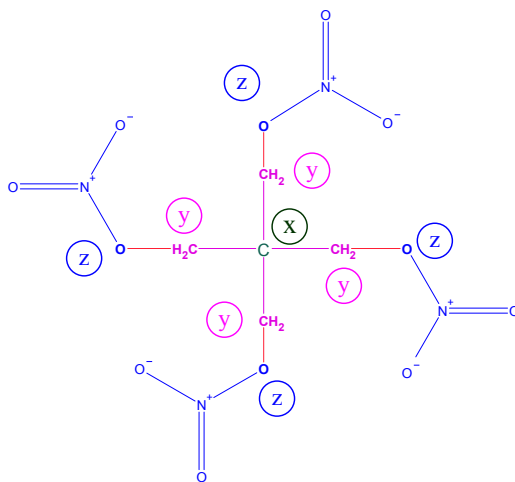
Figure 2.4
Pentaerythritol Tetranitrate Molecule.

is mainly applicable to gases, and for solids a correction by approximately 25 kcal/mol is applied as heat of sublimation. Taking the example of the explosive pentaerythritol tetranitrate (PETN; Figures 2.4 and 2.5), we see that in a PETN molecule the following groups are available:

a.   One $C-(C)_4$ group marked by $\Delta H_f = +0.50$ kcal/mol (i.e., central carbon atom)
b.   Four $C-(CH_2)-(O)$ groups marked by $\Delta H_f = -8.1$ kcal/mol
c.   Four $C-(O-NO_2)$ groups marked by $\Delta H_f = -19.4$ kcal/mol

$$\Delta H_f \text{ (PETN)} = (1 \times 0.5) + (4 \times -8.1) + (4 \times -19.4)$$
$$= -109.5 \text{ kcal/mol}$$

Subtracting the assumed heat of sublimation,

$$\Delta H_f(\text{PETN}) = -109.5 \text{ kcal/mol} - 25 \text{ kcal/mol}$$
$$= -134.5 \text{ kcal/mol} \quad (\text{Experimental value} = -128.7 \text{ kcal/mol})$$

S. W. Benson has determined the ΔH_f values for many groups in aliphatic, aromatic, and heterocyclic compounds. These data are of great help in calculating, at least approximately, the ΔH_f values of many compounds.

2.   Other methods:

The Russian scientist Dmitrii V. Sukhachev and colleagues have recently evolved a method based on Quantitative Structure–Property Relationship and Efficient Modelling of Molecular Activity software to estimate and predict the ΔH_f values of nonaromatic polynitro compounds. This approach is based on the construction of regression equations that relate the structure of known compounds to their physical, chemical, and
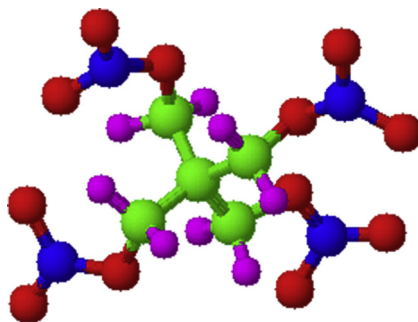
Figure 2.5
Ball and Stick Model of Pentaerythritol Tetranitrate Molecule.

topological properties. The best model equation is chosen and is used to predict the properties of novel structures and select potentially active structures for further synthesis.

Software packages that are based on a quantum mechanical approach have been developed to predict the ΔH_f values with better accuracy.

2.3.3 Heat of Explosion (ΔH_e) and Heat of Combustion (ΔH_c)

Most of the explosives contain C, H, N, and O atoms. During an explosive reaction, the molecule uses the oxygen atoms available within it and does not depend on the external, atmospheric oxygen; it probably has no time for that because of the fast nature of the explosive process. It must be noted that all oxidation reactions (C $\rightarrow$ CO, CO $\rightarrow$ CO$_2$, H $\rightarrow$ H$_2$O) and all explosive reactions are exothermic. Let us now distinguish between two types of oxidation reactions—combustion and explosion.

1. Heat of combustion (ΔH_c): This is defined as the heat evolved when 1 mole of a compound is completely burnt in excess of oxygen. It means that all C atoms and H atoms in the molecule are converted into carbon dioxide (CO_2) and water (H_2O), respectively. A fuel burning in air gives out heat of combustion. Heat of combustion is often referred to as the "calorific value." The amount of heat produced in our body when certain components of food such as fat undergo combustion during metabolism is referred to by this term or simply "calories," a term of which we are so conscious about today.

2. Heat of explosion (ΔH_e): If we take explosives, barring a few examples such as NG, we find that the amount of oxygen available in their molecules is not sufficient to convert C and H atoms completely to CO_2 and H_2O, respectively. Then it becomes a competition between the C and H atoms to get themselves oxidized. However, the end result is that the products of explosion are underoxidized, containing carbon monoxide (CO) and

sometimes H_2 and C also. It is evident that the heat of explosion is always less than the heat of combustion. The underoxidized products of explosion are themselves fuels, and, in cases of explosion, one finds the secondary fire balls formed due to the further oxidation of these underoxidized products by atmospheric oxygen.

Conventionally, the term heat of explosion is applied to propellants (which are deflagrating "explosives") and heat of detonation is used for high explosives. Dunkel defines the heat of detonation as the heat evolved when an explosive detonates and the products are still at the Chapman−Jouguet condition (see Chapter 3), in which the gases are at approximately 5000 K and 10^5 atm in the detonation zone. The composition of the products at the detonation zone is slightly different from what we may find in a calorimeter; therefore, the heat of detonation as defined by Dunkel will be slightly different from the heat of explosion. For all practical purposes, we can take that the heat of detonation is almost synonymous with the heat of explosion. We will use the term heat of explosion for all purposes of calculation. Heat of explosion (ΔH_e) is also referred to as the calorimetric value (shortly "cal.val"). The explosives and propellants depend only on the oxygen available in their molecules; therefore, they can function even in vacuum. Moreover, the explosive reactions are too fast to rope in the atmospheric oxygen even if it is available. In view of this, cal.val (ΔH_e) plays a very important role in the field of explosives and we rarely talk about calorific value (ΔH_c).

2.3.3.1 Need to Standardize Calorimetric Value

ΔH_e and ΔH_c are experimentally determined using a bomb calorimeter, the experimental details of which can be had from any standard book on explosives and propellants. In the case of determination of cal.val, a fixed weight of the explosive (or propellant), usually approximately 2.5 g, is ignited and exploded after purging the bomb calorimeter with nitrogen or helium to ensure that no oxygen due to residual air is present at the time of explosion. The heat evolved is calculated by measuring the increase in temperature of water in the calorimeter. The cal.val obtained is for the reaction in which water is obtained in the liquid form. In the case of ΔH_c (calorific value) determination, to ensure complete combustion, the calorimeter is flushed with an excess of oxygen before the ignition of the explosive.

For a given explosive compound, ΔH_c is a standard value whereas ΔH_e is not. There is a need to standardize the conditions under which ΔH_e is to be measured. Let us assume that in the first experiment we take 2.5 g of an explosive and perform its ΔH_e determination in a bomb calorimeter, the volume of which is 700 cc (i.e., loading density of the explosive = 2.5/700 g/cc) and let the cal.val obtained be Q_1 cal/g. If the experiment is repeated with, say, 5 g of the same explosive in the same calorimeter (loading density = 5/700 g/cc, i.e., twice as in the case of first experiment), then the cal.val obtained will be different, say Q_2 cal/g. In the second experiment, after the explosion, the

pressure of the product gases will be higher in comparison to the first experiment because of increased loading density. At higher pressures, the product gases (a mixture of CO, CO_2, H_2O, probably some H_2 and C also in the case of explosives with low oxygen balance (OB)) undergo a shift in the equilibrium and the resultant heat output will be different. Therefore, cal.val experiments should be conducted under standardized conditions, particularly with respect to loading density. (In the case of ΔH_c determination, this problem does not arise because all of the products are already in a completely oxidized condition).

2.3.3.2 Partial Heat of Explosion

Schmidt proposed a simplified way of estimating the probable heat of explosion of a propellant containing explosive and nonexplosive ingredients. In this method, a partial heat of explosion is assigned to each component and materials with high negative OB (e.g., stabilizers, gelatinizers) are assigned negative values. The heat of explosion of the propellant is calculated by the addition of the partial values weighted in proportion to the respective percentage of the individual components.

It is interesting to note that in the case of compositions containing NG (which has a positive OB), the heat of explosion value is more than the calculated value because the excess oxygen from NG reacts with the carbon of other components to produce more heat.

2.3.4 Oxygen Balance

The percentage excess or deficit of oxygen present in a compound required for its complete oxidation to CO_2, H_2O, etc., is known as the OB of that compound.

If the compound has less oxygen in its molecule than that required for complete oxidation, then it is said to have a negative OB and vice versa.

Example 1: NG (Figure 2.6) has a positive OB. Its explosive reaction can be written as
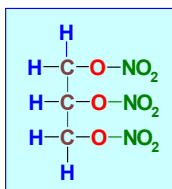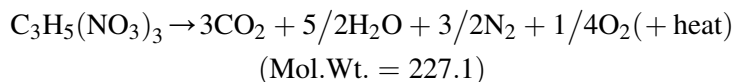
$$C_3H_5(NO_3)_3 \rightarrow 3CO_2 + 5/2H_2O + 3/2N_2 + 1/4O_2(+\text{heat})$$
$$(\text{Mol.Wt.} = 227.1)$$

Figure 2.6
Nitroglycerine.

We find that 227.1 g of NG (1 mole weight of NG) has enough oxygen in its molecule so as to evolve an excess of oxygen ($1/4 O_2 = 8$ g of oxygen) even after completely oxidizing C and H to CO_2 and H_2O, respectively.

$$227.1 \text{ g of NG evolves} \qquad 8 \text{ g of } O_2$$
$$\text{Therefore } 100 \text{ g of NG evolves} \quad 8/227.1 \times 100 \text{ g of } O_2$$
$$= 3.5\%$$
$$\text{OB of NG} \quad = +3.5\%$$

Example 2: Trinitrotoluene (TNT; Figure 2.7) has a negative OB. In the TNT molecule ($C_7H_5N_3O_6$), we can see that the number of oxygen atoms (6) is very insufficient to completely oxidize 7 carbon atoms (14 oxygen atoms needed for the $7C \rightarrow 7CO_2$ oxidation) and 5 hydrogen atoms (5/2 oxygen atoms needed for the $5H \rightarrow 5/2 H_2O$). Compared with $14 + 5/2$ (i.e., 33/2 oxygen atoms), TNT has only 6 oxygen atoms to achieve complete oxidation. This deficit (i.e., 33/2 vs 6; i.e., 21/2 oxygen atoms, 21/4 oxygen molecules) must be written on the left-hand side of the TNT combustion equation as follows:

$$C_7H_5N_3O_6 + 21/4\, O_2 \rightarrow 7CO_2 + 5/2\, H_2O + 3/2\, N_2$$
$$(\text{Mol.Wt} = 227.1)$$
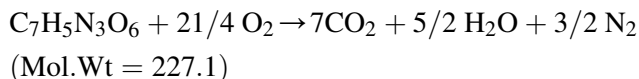
Therefore, 227.1 g of TNT requires 168 g of oxygen (corresponds to 21/2 oxygen atoms), and 100 g of TNT requires $168/227.1 \times 100 = 74$ g of oxygen. Therefore, the OB of TNT $= -74\%$.

For a CHNO explosive with the formula $C_xH_yN_wO_z$, the OB percentage can be found by a general formula as follows:

$$OB\% = \frac{100 \times \text{At.Wt.of oxygen}}{\text{Mol.Wt. of the compound}} \left(Z - 2x - \frac{y}{2} \right)$$

OB is one of the important parameters of HEMs. The ideal OB of an explosive compound is zero. When it has a negative OB, the products of explosion contain underoxidized CO and there may also be some H_2. It means that if there had been some more oxygen, we
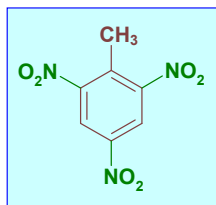

Figure 2.7
Trinitrotoluene.

could have got more heat by further oxidation of CO and H_2 to CO_2 and H_2O, respectively. In the case of compounds with positive OB, the extra oxygen evolved after complete oxidation reactions (e.g., NG) does not serve us any purpose. It has been there in the molecule as a sort of "dead weight."

Figure 2.8 shows that the ideal OB for an explosive is zero when maximum heat can be obtained by an explosive reaction from a given weight of explosive. However, from the OB values of several explosives, it is seen that, known explosives, barring NG, have negative OB values (e.g., nitrocellulose (NC) in the range of approximately -28%, TNT $= -74\%$, research and development explosive (RDX) $= -21.6\%$). Therefore, it is not possible to formulate a military explosive or propellant composition with zero OB. Most of these compositions have negative OB values. As we will see in subsequent sections, a factor that is as important as heat output is the number of moles of gases evolved from a unit weight of the explosive or propellant (n). The higher the value of n in the explosion/deflagration products, the higher will be the performance of the HEM. Naturally, for a gram of explosive or propellant, a higher value of n means a lower value for the average molecular weight (M) of gaseous products. The value of n plays a vital role in the field of explosives and propellants. Thus, if we get smaller molecules such as CO and H_2 instead of CO_2 and H_2O, we must remember that what we lost as heat output is compensated for, at least partly, by what we gain as work output due to higher values of n.

On the other hand, OB in commercial explosives cannot be very negative. They should have an OB close to zero. If it is negative, then the amount of toxic gases such as CO and in some cases nitrous oxide evolved will be unacceptable.
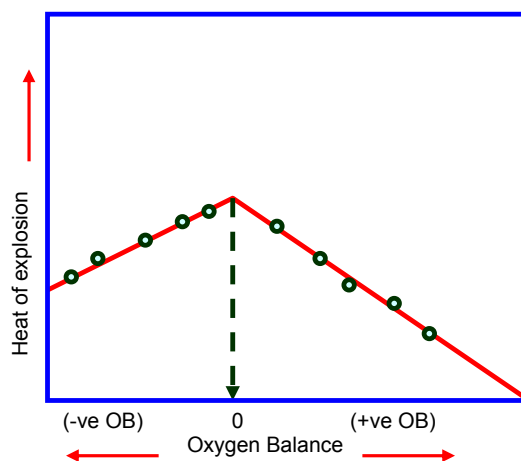

Figure 2.8
Plot of Heat of Explosion against Oxygen Balance (OB).

Worked Example 2.1

Calculate the following parameters for RDX: (1) OB, (2) heat of explosion, and (3) heat of combustion.

(Given: heats of formation of RDX, CO, CO_2, and $H_2O_{(l)}$ are $+16.09$, -26.7, -94.05, and -67.42 kcal/mol, respectively).

1. The molecular formula of RDX is $C_3H_6N_6O_6$, which corresponds to a molecular weight of 222.
   It needs three extra oxygen atoms to completely oxidize C and H to CO_2 and H_2O, respectively. The combustion equation is written as

   $$C_3H_6N_6O_6 + 3/2O_2 \rightarrow 3CO_2 + 3H_2O + 3N_2 \ (+\Delta H_c)$$

   222 g of RDX requires 48 g of oxygen.
   Therefore, 100 g of RDX requires $48/222 \times 100$ g oxygen $= 21.6\%$.
   Therefore, the OB of RDX $= -21.6\%$.
2. Heat of combustion (ΔH_c)
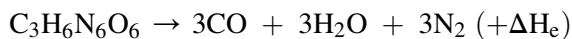   From the above equation, we can write

   $$\Delta H_c = \Sigma(\Delta H_f)\text{products} - \Sigma(\Delta H_f)\text{reactants}$$

   $$\Delta H_c = [(3 \times -94.05) + (3 \times -67.4)] - (16.09)$$

   $$= -500.5 \text{ kcal/mole} = -\frac{500,500 \text{ cal/g}}{222} = -2255 \text{ cal/g}$$

3. Heat of explosion (ΔH_e; in which no external oxygen participates in the reaction)
   The explosion reaction of RDX can be written as

   $$C_3H_6N_6O_6 \rightarrow 3CO + 3H_2O + 3N_2 \ (+\Delta H_e)$$

   $$\Delta H_e = \Sigma(\Delta H_f)\text{products} - \Sigma(\Delta H_f)\text{reactants}$$

   $$= [(3 \times -26.71) + (3 \times -67.4)] - (16.09)$$

   $$= -298.4 \text{ kcal/mole} = -\frac{298,400}{222} \text{ cal/g}$$

   $$= -1344 \text{ cal/g}$$

Compared with ΔH_e, ΔH_c is more by 68%.

2.3.5 Heat of Explosion: Dependence on Heat of Formation and Oxygen Balance

2.3.5.1 Balance

We have seen from Figure 2.8 that ΔH_e has a dependence on OB and has the maximum value at zero OB. ΔH_f values are of great importance for all HEMs. Even when new or potential compounds are to be targeted for synthesis of futuristic explosives, extensive computerized calculations are made to know their ΔH_f values. This is mostly because a positive value (or a low negative value) of ΔH_f for an explosive ensures that the explosive reaction gives out a large amount of heat.

Figure 2.9 qualitatively illustrates the effect of ΔH_f on ΔH_e. Explosive A is formed from its elements ($\Delta H_f = +x$) and later explodes to form stable products ($\Delta H_e = a$). A similar depiction is given for explosive B, which has a negative value for ΔH_f ($= -x$). Its heat of explosion ($\Delta H_e = b$) is much less than that of explosive A. Therefore, one expects higher ΔH_e values for an explosive that has a positive value of ΔH_f.

However, there can be a few exceptions. $Pb(N_3)_2$ is an endothermic compound ($\Delta H_f = +340$ cal/g), and NG is an exothermic compound ($\Delta H_f = -392$ cal/g). Their ΔH_e values are -381 and -1617 cal/g, respectively. This means that although $Pb(N_3)_2$ has a positive heat of formation, its heat output during explosion is far less than that of NG,

Figure 2.9
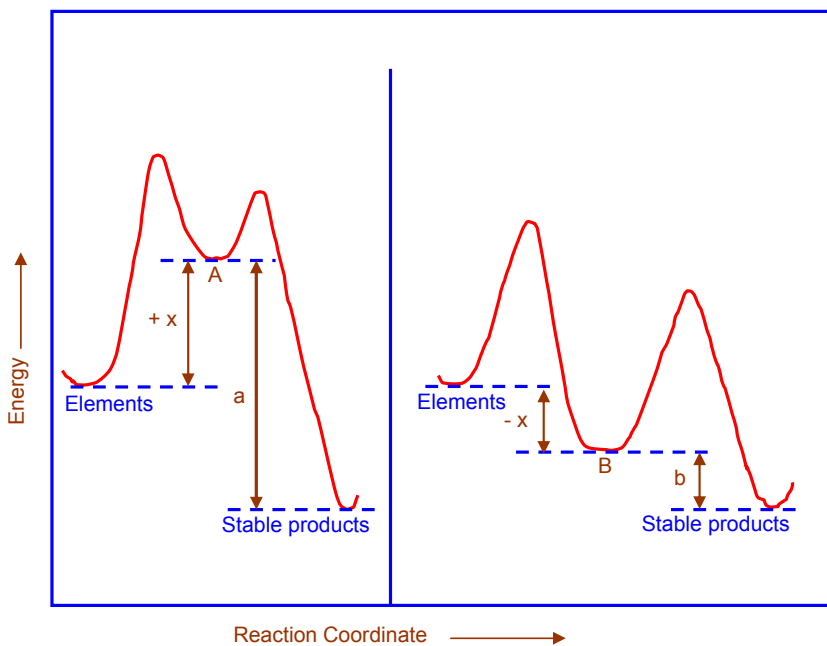Effect of ΔH_f on ΔH_e.

which has a negative heat of formation. This is because a molecule of NG has sufficient oxygen atoms that result the in highly exothermic oxidation of C and H atoms whereas, despite its positive ΔH_f value, $Pb(N_3)_2$ is not privileged even with a single oxygen atom, and the limited heat output it gives is due to the breakage of the energetic azide linkage.

The combined effect of ΔH_f and OB on ΔH_e was studied by Edward Baroody and colleagues. Figure 2.10 shows a plot of the ΔH_f and OB of some well-known CHNO explosives. It is seen that the higher the energy output from the compound, the more it shifts toward the top right-hand corner; in the reverse case, it is toward the bottom left-hand corner.

2.3.6 OB of Composite Explosives

Mostly, for military and industrial purposes, mixtures of different explosives and other chemicals are used rather than a single explosive. These are termed "composite explosives." A common example is composition B-3, which is made up of a 64/36 mixture of RDX and TNT. It can be calculated that this composition would have an OB of −40.5%. Taking another example, ANFO is a simple mixture of prilled ammonium nitrate (AN) and fuel oil (FO) at a nearly zero oxygen balanced ratio of 94/6 AN/FO. The 6% oil
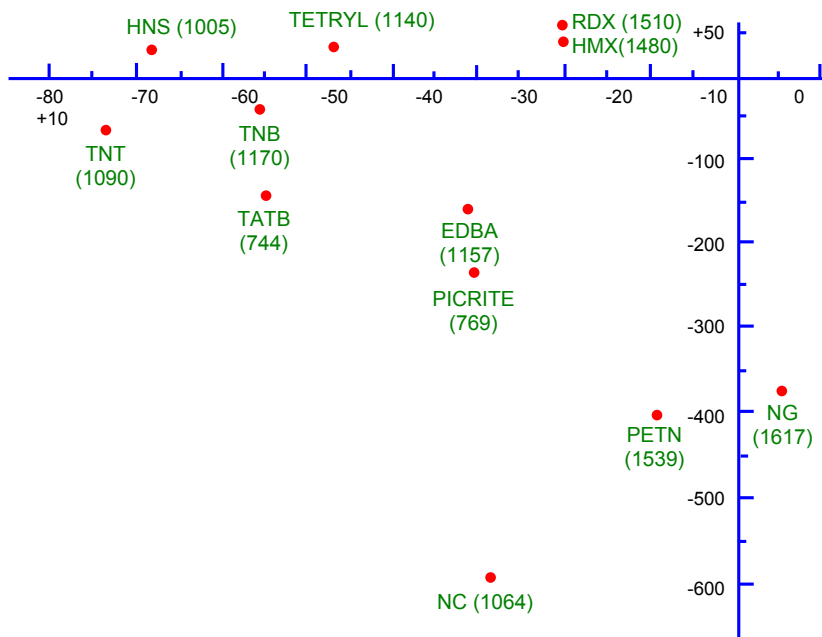

Figure 2.10
Effect of ΔH_f and Oxygen Balance (OB) on ΔH_e (x-Axis: OB%, y-Axis: ΔH_f [cal/g], ΔH_e Values in cal/g Are Given in Brackets).

is important enough to ANFO as to raise the heat of explosion from 0.35 kcal/g for prills alone to 0.89 kcal/g for the oxygen-balanced ANFO. The mixtures used for some common composite explosives and their OB are given in Table 2.2.

2.3.7 Hazard Assessment from OB

In a 1949 *Chemical Reviews* article, W. C. Lothrop and G. R. Handrick demonstrated quantitative correlation between OB and various measures of explosive effectiveness for several classes of organic explosives. This study drew upon the large database accumulated during the years of World War II explosive research. The properties of many explosive compounds were considered and correlated. The authors pointed out that the OB criterion is not only related to the power of new explosive compositions, but it also has a rough bearing on the hazards of their initiation (Table 2.3).

This table shows that as an explosive composition gets closer to zero OB, the hazard of initiation is more.

2.3.8 Composition of Gaseous Products

When an explosive detonates or a propellant burns, it is essential to know the composition of gaseous products formed for calculating ΔH_e and other performance parameters. Because many explosives have negative OB values, during the explosion, there is a stiff competition among C, H, and CO to grab the available oxygen in the explosive molecule.
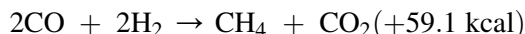
Table 2.2: Composite explosives and their oxygen balance (OB).

Commercial Name	Composition	Empirical Formula	OB%
AMATOL	80/20 AN/TNT	$C_{0.62}H_{4.44}N_{2.26}O_{3.53}$	1.1193
ANFO	94/6 AN/FO	$C_{0.365}H_{4.713}N_{2.0}O_{3.0}$	−1.6253
COMP A-3	91/9 RDX/WAX	$C_{1.87}H_{3.74}N_{2.46}O_{2.46}$	−50.3723
COMP B-3	64/36 RDX/TNT	$C_{6.851}H_{8.750}N_{7.650}O_{9.3}$	−40.4606
COMP C-4	91/5.3/2,1/1.6 RDX/ di(2-ethylhexyl)sebacate/ polyisobutylene/motor oil	$C_{1.82}H_{3.54}N_{2.46}O_{2.51}$	−46.3755

Table 2.3: Oxygen balance (OB) versus hazard rank.

OB Value	Hazard Rank
More positive than +160	Low
+160 to +80	Medium
+80 to −120	High
−120 to −240	Medium
More negative than −240	Low

Among the possible oxidation reactions (i.e., H → H_2O, C → CO, CO → CO_2), the order of preference appears to depend on the OB of the explosive and, to a certain extent, the density of loading. The situation becomes complex because of the shift in the chemical equilibrium due to side reactions such as the water gas reaction, as follows:

$$CO + H_2O \rightarrow CO_2 + H_2(+9.8 \text{ kcal})$$

$$2CO \rightarrow CO_2 + C(+41.2 \text{ kcal})$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O(+49.2 \text{ kcal})$$

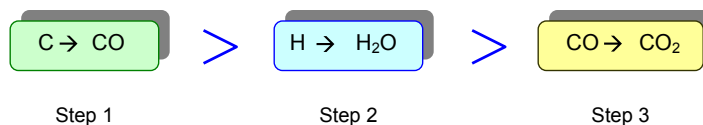$$2CO + 2H_2 \rightarrow CH_4 + CO_2(+59.1 \text{ kcal})$$
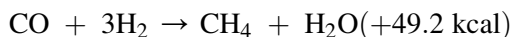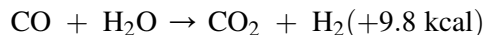
Although databanks and software have recently been developed for the computerized calculation of the exact or at least nearly exact composition of gaseous products, a good approximation by G. B. Kistiakowsky and E. B. Wilson follows to assume the order of preference of these oxidation reactions.

For explosives for which the OB is less than −40%:

H → H_2O	>	C → CO	>	CO → CO_2
Step 1		Step 2		Step 3
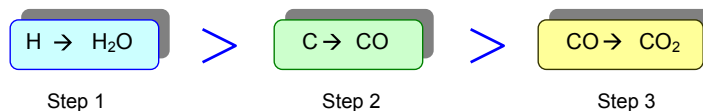
For explosives for which the OB is greater than −40%:

C → CO	>	H → H_2O	>	CO → CO_2
Step 1		Step 2		Step 3

In the case of detonation of explosives, particularly at higher density, Kamlet and Jacob assume a different order—formation of CO_2 is preferred to the formation of CO. The Kamlet−Jacob method makes this assumption for the estimation of the velocity of detonation (VOD) and the detonation pressure of explosives.

2.3.9 Significance and Limitations of OB

The OB can be used to optimize the composition of the mixture of the explosive. The family of explosives called "amatol" refers to mixtures of AN and TNT. AN has an OB of +20% and TNT has an OB of −74%, which is very deficient in oxygen; therefore, it would appear that the mixture yielding an OB of zero would also result in the best explosive properties. In actual practice, a mixture of 80% AN and 20% TNT by weight

yields an OB of $+1\%$, the best properties of all mixtures, and an increase in the strength of 30% over TNT.

The OB provides information on the types of gases liberated. The concept of OB is particularly useful as a first guideline when formulating explosives to produce a minimum of toxic fumes. An explosive with excess oxygen produces toxic nitric oxide and nitrogen dioxide; an explosive with an oxygen deficiency produces toxic CO. Explosives for use underground with poor ventilation should be formulated to produce a minimal total toxic effect. If the OB is large and negative, then there is not enough oxygen for CO_2 to be formed; consequently, toxic gases such as CO will be liberated. This is very important for commercial explosives because the amount of toxic gases liberated must be kept to a minimum.

Sensitivity, brisance (shattering power), and strength are properties resulting from complex explosive chemical reactions; therefore, a simple relationship such as OB cannot be depended upon to yield universally consistent results. When using OB to predict properties of one explosive relative to another, it is to be expected that one with an OB closer to zero will be the more brisant, powerful, and sensitive; however, many exceptions to this rule do exist.

2.3.10 Detonation Temperature/Flame Temperature

The temperature of the gas products on firing propellants in a gun is of considerable importance in the study of ballistics and the erosion of a gun barrel. Likewise, the detonation temperature in the case of high explosives is an important parameter because it is related to the power of those explosives. Let us understand the variation of detonation/flame temperatures under two different conditions—at constant volume and at constant pressure.

Case I (Constant Volume)

When a certain amount of explosive is initiated in a closed vessel that is thermally insulated, let the total heat evolved be x calories. This heat of explosion is used to increase the internal energy of the gases. Because the temperature is effectively a measure of the internal energy of a system, the heat of explosion increases the temperature of the products of explosion. The maximum temperature to which the decomposition products are raised is called the "detonation temperature" in the case of an explosive and the "flame temperature" when we talk about propellants. To be more specific, this temperature is also called the "adiabatic, isochoric flame temperature" (adiabatic, thermally insulated—no heat escapes from or enters inside of the system; isochoric, constant volume), abbreviated as T_v. The isochoric flame temperature of explosives varies from as low as 2500 °C in the case of nitroguanidine to 5000 °C in the case of NG.

Case II (Constant Pressure)

Let us imagine what would happen when the same amount of this explosive is initiated in a vessel that is fitted with a movable piston similar to that in an internal combustion engine. The same amount of heat produced (*x* calories) heats up the gaseous products to high pressures, but then these gases are now free to move the piston to do some work of expansion. Therefore, only a part of the heat is used to increase the internal energy of the gases (i.e., to the flame temperature), and the rest is converted into work. Obviously, because the amount of heat produced in both cases is the same, the flame temperature in case II—adiabatic, isobaric flame temperature, T_p (isobaric, same pressure)—would be less than T_v.

The above two cases can be written as

$$\text{Case} - \text{I} \quad \Delta H_e = \Delta E_v \quad (\text{Temp.} T_v) \tag{2.3}$$

$$\text{Case} - \text{II} \quad \Delta H_e = \Delta E_p + P\Delta V \quad (\text{Temp.} T_p) \tag{2.4}$$

where ΔE_v and ΔE_p represent the increase in internal energy of the gaseous products at constant volume and constant pressure, respectively. $P\Delta V$ represents the expansion work done by the gases at pressure P to effect an increase in volume by ΔV.

The term $P\Delta V$ is the useful work done by a system, and in the field of HEMs it does the work of blast in the case of high explosives, projectile propulsion in the case of gun propellants, and self-propulsion in the case of rocket propellants.

The relationship between T_p and T_v is as follows:

$$\frac{T_v}{T_P} = \gamma \tag{2.5}$$

where γ is the mean molar value of the ratio of specific heats of product gases at constant pressure (C_p) and at constant volume (C_v) (i.e., C_p/C_v of the product gases).

2.3.10.1 Calculation of Detonation/Flame Temperature

Let us assume that during an explosive reaction, n_1, n_2, and n_3 moles of CO, $H_2O_{(v)}$, and CO_2 are produced, respectively, and the flame temperature is T_v. After the heat of explosion (ΔH_e) is released, the gases cool to ambient temperature (T_a). This can be represented as

$$T_v \xrightarrow[\text{(at constant volume)}]{\text{Release of } \Delta H_e} T_a$$
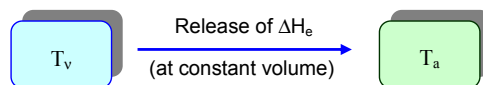
Conversely, we can imagine that the above gases are heated from T_a to T_v using the heat, ΔH_e. The amount of heat needed to heat each gas is obtained by multiplying the number

of moles of the gas produced, its molar heat capacity, and the increase in temperature. If $(C_v)_{CO}$, $(C_v)_{H_2O}$, and $(C_v)_{CO_2}$ are the molar heat capacities of CO, H_2O, and CO_2, respectively, then it can be written

$$\Delta H_e = n_1 (C_v)_{co} \left[T_v - T_a \right] + n_2 (C_v)_{H_2O} \left[T_v - T_a \right]$$
$$+ n_3 (C_v)_{CO_2} \left[T_v - T_a \right]$$

That is, $\Delta H_e = \Sigma C_v \times (T_v - T_a)$, where ΣC_v is the mean molar heat capacity of the product gases.

This above equation can be rearranged as follows:

$$T_v = \frac{\Delta H_e}{\sum C_v} + T_a \tag{2.6}$$

Because T_a and ΣC_v are constants, it is seen from Eqn (2.6) that T_v linearly increases with ΔH_e. This is illustrated in the worked example given below.

2.3.10.1.1 Calculation of T_v from Molar Internal Energies of the Products of Explosion

Standard tables are available (refer to *Explosives*, by Rudolf Meyer, 4th ed., Table No. 35) that give the molar internal energies of the reaction products in relation to temperature (Table 2.4). The best way to calculate T_v is to plot the calculated heat of explosion against various temperatures using the above table. From the linear plot, we can find out the value of T_v knowing the experimental value of ΔH_e.

Worked Example 2.2

Calculate the isochoric and isobaric flame temperatures of PETN.

(Given: The heat of explosion of PETN = 1510 cal/g)

Table 2.4: Molar internal energies of products $C_v(T - T_a)$; $T_a = 25\,°C$ ($\sim$ 300 K).

Temperature (K)	Molar Internal Energies of Explosion Products (kcal/mol)			
	N_2	H_2O	CO	CO_2
2500	13.15	18.43	13.33	24.34
3000	16.57	23.81	16.78	30.81
3500	20.05	29.37	20.27	37.43
4000	23.79	35.03	23.79	44.13
4500	27.08	40.76	27.33	50.88
5000	30.62	46.54	30.88	57.67

Reproduced with permission from: R. Meyer, J. Kohler, Explosives, VCH Publishers, Germany, 1993.

PETN, $C(CH_2ONO_2)_4$, or $C_5H_8N_4O_{12}$, undergoes the following explosive reaction:

$$C_5H_8N_4O_{12} \rightarrow 2N_2 + 4H_2O_{(v)} + 2CO + 3CO_2$$

(Mol.Wt=316.1)   (Total: 11 moles of gases)
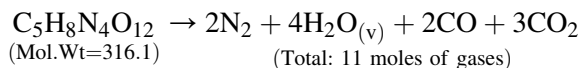
We need the heat of explosion value in the unit of kilocalories per mol.

$$\Delta H_e = 1510 \text{ cal/g} = \frac{1510}{1000} \times 316.1 = 477.3 \text{ kcal/mol}$$

The minimum and maximum values of flame temperature of explosives are approximately 2500 and 5000 K, respectively. We do not know the actual flame temperature of PETN, although we are certain that it should be somewhere between 2500 and 5000 K. Using Table 2.4, we can calculate the expected ΔH_e values of PETN had its flame temperature been 2500, 3000, 3500, 4000, 4500, or 5000 K.

For example, at 2500 K (or had the flame temperature been 2500 K), the expected cal.val output by the products $2N_2 + 4H_2O + 2CO + 3CO_2$ would be

$$\Delta H_{e(2500)} = 2(13.15) + 4(18.43) + 2(13.33) + 3(24.34) \text{ kcal/mol}$$
$$= 199.70 \text{ kcal/mol}.$$

A similar calculation yields ΔH_e values of 254.37, 310.41, 367.67, 424.50, and 482.17 kcal/mol at 3000, 3500, 4000, 4500, and 5000 K, respectively. A plot of cal.val versus assumed T_v (see Figure 2.11) yields a straight line.

Because the experimentally determined value for ΔH_e is 477.3 kcal/mol, it can be read out from the plot that the actual value for T_v is approximately 4960 K.

2.3.10.1.2 Calculation of T_p

Because T_p and T_v are related as $\frac{T_v}{T_p} = \gamma$, we should calculate the molar average value of γ for all of the products. The values of γ for N_2, H_2O, CO, and CO_2 are 1.404, 1.324, 1.404, and 1.304, respectively. The molar average of the products can be written as (remember that there are 11 moles of the product gases in all)

$$\gamma = \left(\frac{2}{11} \times 1.404\right) + \left(\frac{4}{11} \times 1.324\right) + \left(\frac{2}{11} \times 1.404\right) + \left(\frac{3}{11} \times 1.304\right)$$
$$= 1.348$$
$$T_p = T_v/\gamma = 4960/1.348 = 3680 \ K$$

The above method of calculating flame temperature can be applied to compositions of explosives and propellants once we know their ΔH_e values and the composition of the gaseous products.
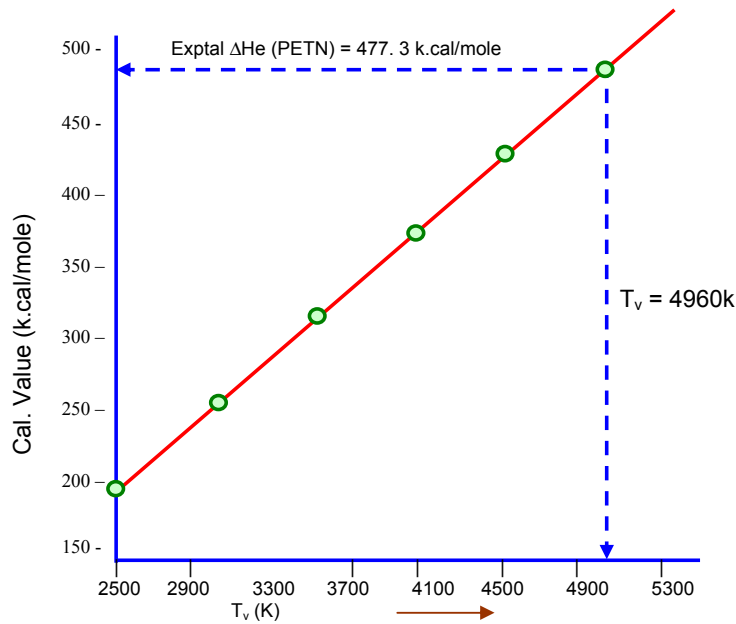
Figure 2.11
Plot of Calculated cal.val versus Different T_v Values.

2.3.10.1.3 Effects of C_v Values

There is an interesting observation that during an explosive decomposition, if the product gases have smaller molecular weights, then the flame temperature marginally increases. The smaller the molecule, the lesser is its heat capacity and, as a result (because $T_v = \Delta H_e / \Sigma C_v + T_a$), the flame temperature marginally increases.

2.3.10.1.4 Value of γ

The value of γ (of the product gases), which is the ratio of C_p to C_v, plays an important role in determining the energetic parameters of explosives and propellants. γ decreases with increasing temperature but increases with pressure. However, in a process of explosion/propellant burning, which is a high-temperature/high pressure phenomenon, this increase/decrease is almost compensated for and, with reasonable approximation, one can use the γ values of the product gases given for room temperature and ambient pressure at the conditions of explosion. This value is approximately 1.3−1.4 for most of the CHNO explosives.

However, at detonation/shock-wave zones in which the pressure ranges are phenomenally high, on the order of several hundreds of thousands of atmospheres, the value of γ sharply increases to approximately 3.

Note: "Detonation temperature" and "flame temperature" are almost the same for a given HEM because they refer to the temperature to which the products of explosion are adiabatically heated by the heat of explosion. However, the term "explosion temperature" (also sometimes referred to as "cook-off temperature") is often used to refer to the temperature at which the autoignition of an explosive commences when it is heated at a particular rate. For example, the detonation temperature of NC is approximately 3470 K whereas its explosion temperature is approximately 170 °C when it is heated at the rate of 5 °C/s. That is, when the temperature of NC reaches approximately 170 °C, the autoignition starts. There can be a slight variation in the values of the explosion temperature of an explosive depending on the heat exchange conditions and the geometry of the sample.

2.3.11 Gas Volume

When a certain quantity of explosive undergoes an explosive decomposition, it evolves high-pressure/high-temperature gaseous products. Because of the high pressure, the gases expand to reach the atmospheric pressure, and in the process of expansion, they do work. Because the volume of a (solid) explosive is negligible in comparison to that of the product gases, we can write

$$PV = nRT \tag{2.7}$$

where P, V, n, R, and T represent the final pressure after expansion, the final volume, the number of moles of the gases produced, the universal gas constant, and the final temperature, respectively. The volume of the gaseous products of expansion (V) is generally calculated at the pressure of 1 bar and 273 K (i.e., at normal temperature and pressure (NTP)). For explosives, the value of V varies from 700 to 1000 cc/g. That means that in the case of most of explosives, the explosion of 1 g of an explosive produces product gases that occupy a volume varying between 700 and 1000 cc when measured at atmospheric pressure and 273 K.

Worked Example 2.3

Calculate the number of moles and the volume of the gaseous products of explosion of RDX ($C_3H_6O_6N_6$).

The explosive reaction of RDX is given as

$$C_3H_6O_6N_6 \rightarrow 3CO + 3H_2O_{(v)} + 3N_2$$

$$(Mol.Wt = 222)$$
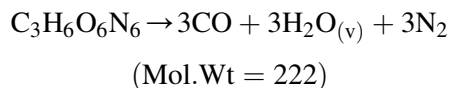
There are 9 moles of gaseous products, including H_2O, which is in vapor state. As a standard practice, H_2O is treated as vapor even when we calculate the total gas volume at NTP.

$$222 \text{ g of RDX evolves} \rightarrow 9 \text{ mol of gases (at NTP)}$$

$$\text{Therefore, } 1 \text{ g of RDX evolves} \rightarrow 9/222 \text{ mol of gases at NTP.}$$

$$(\text{Applying Avogadro's law}) \rightarrow \frac{9}{222} \times 22,400 \text{ cc of gases at NTP} = 908 \text{ cc.}$$

The gas volume of RDX explosion products $= 908$ cc/g.

It is seen from the gas equation that at a given temperature and pressure, the volume of a given gas directly depends on the number of moles of the gaseous products. Because the volume generation is tantamount to the work of expansion, we can say that an explosive that on decomposition produces more moles of the product gases (per gram of the explosive) possesses better work potential. More moles of gases per gram of explosive effectively means the product gases with lesser molecular weights.

2.3.12 The nRT Wonder

In Section 2.3.10, we presented the equation relating ΔH_e and ΔE at constant pressure as

$$\Delta H_e = \Delta E + P\Delta V$$

ΔV refers to the change in volume when a solid explosive is converted into product gases. As compared to the volume of product gases, the volume of the solid explosive can be neglected (we have seen above that 1 g of RDX, which occupies a volume of 0.56 cc, on explosion, gives product gases that occupy a volume of 908 cc). Therefore, in the above equation, ΔV can be replaced by V, the volume of the product gases; that is, $\Delta H_e = \Delta E + PV$, and because $PV = nRT$ (assuming ideal gas behavior),

$$\Delta H_e = \Delta E + nRT \tag{2.8}$$

nRT is actually the work factor of an explosive decomposition. This term is very important in the field of HEMs, and it manifests its importance in different forms under different nomenclatures. As we will see in the respective chapters, the nRT factor manifests itself as

- Specific energy, which decides the strength or power of a high explosive;
- Impetus, or force constant, in gun propellants, which would decide how much muzzle velocity and hence range can be imparted to a projectile; and
- A parameter in rocket propellants that is directly related to the specific impulse (I_{sp}), the ultimate energy index for any rocket propellant.

Although in the first two cases we deal with an almost constant-volume condition (flame temperature: T_v), in the case of rocket propellants we encounter a constant-pressure condition (flame temperature: T_p). These will be discussed in a little more detail in the respective chapters. The message is: "If we want an HEM with better work potential, then the value of nRT must be higher, implying that for a given weight of the explosive/propellant, it should produce more moles of product gases with higher flame temperature (isochoric or isobaric depending on the function)."

Energy of Formation (ΔE_f) versus Heat of Formation (ΔH_f):

We defined ΔH_f and explained its importance in Section 2.3.2. Now, having understood the difference between ΔH and ΔE being the energy transition involved under constant pressure and constant volume, respectively, let us see the relation between the energy of formation (ΔE_f) and the enthalpy of formation (ΔH_f).

"ΔH_f and ΔE_f are the quantities of heat absorbed or evolved when 1 mole of a compound is formed from its constituent elements at standard state (25 °C and 1 atm) at constant pressure and constant volume, respectively."

Worked Example 2.4

The enthalpy of formation of RDX is 76.1 cal/g. Calculate its energy of formation.

(Given: RDX: $C_3H_6N_6O_6$; molecular weight $= 222.1$.)

The chemical equation for the formation of RDX can be written as

$$3C + 3H_2 + 3N_2 + 3O_2 \rightarrow C_3H_6O_6N_6$$

Because C (carbon) and $C_3H_6O_6N_6$ (RDX) are solids under standard states, the change in the number of moles of gaseous compounds will be

$\Delta n =$ moles of the gaseous products $-$ moles of the gaseous reactants $= 0 - (0 + 3 + 3 + 3) = -9$.

Because $\Delta H = \Delta E + \Delta nRT$ (R $=$ universal gas constant $= 1.987$ cal/K/mol), and T $=$ standard temperature $= 25\,°C = 298$ K, then we can write $(76.1 \times 222.1) = \Delta E + (-9)(1.987)(298)$. (Please note that cal/g must be converted into cal/mol by multiplying by the molecular weight of RDX).

$16{,}902 = \Delta E - 5329$.

Therefore, $\Delta E = 22{,}231$ cal/mol.

$$= \frac{22{,}231}{222.1} \approx 100 \text{ cal/g}$$

Energy of formation (ΔE_f) of RDX $= 100$ cal/g.

On the basis of the data on the ΔE_f values of explosives and their explosive decomposition products, we can calculate their heat of explosion and perform a thermodynamic calculation of the decomposition reactions.

2.3.13 Pressure of Explosion

It was stated that when an explosive undergoes deflagration in a closed vessel, high pressure is produced because of the evolution of high-temperature gases in large amounts. This pressure is an important parameter because when the product gases expand to do some useful work, such as propulsion of a projectile through a gun barrel, the total amount of work done by the gases is directly proportional to this pressure. The pressure of explosion, P_e, is defined as the maximum static pressure achieved when a given weight of explosive is burned in a closed vessel of fixed volume assuming adiabatic conditions. The gas equation for this process is given as

$$P_e(V^* - \alpha) = nRT_e$$

where V^* is the volume of the closed vessel and α is the covolume correction necessitated by the fact that at such high pressures, a gas tends to be nonideal and a certain correction must be applied for the volume of gaseous molecules themselves. We will deal in more detail in subsequent chapters about the nonideal behavior of gaseous products formed during explosion during detonation and explosive deflagration.

(Note: The pressure of explosion should not be confused with detonation pressure. The latter refers to the pressure that exists at the *detonation zone* (detonation front) when a shock wave travels through the medium of the explosive, which will be discussed in the next chapter.)

2.3.14 Density

Density is one of the important characteristics of explosives and propellants. It will be shown later that an increase in density of a high explosive increases its VOD and brisance (destructive fragmentation effect). The actual density of an explosive, referred to as the "theoretical maximum density" (TMD), can be accurately determined by conventional methods. However, when an explosive composition is processed and filled, say in a warhead, the density of the composition is often slightly less because of very fine voids. That is why maximum care is taken to maximize the density of the high-energy composition to be close to the TMD.

In addition, in the case of propellants, the higher the density, the higher will be the performance output. For example, if the volume of a cartridge case of a small arms ammunition is limited, one would look for a propellant with high density so that more weight of the propellant can be loaded in it. In the case of rocket propellants, even if a

solid rocket propellant may be energetic, if its density is very low, then the weight of the rocket propellant grain loadable in a rocket motor of limited volume will be too little to be acceptable. Therefore, in the field of energetic materials, density is a parameter as important as energy itself.

2.3.14.1 Density and Molecular Structure

The density of an explosive should depend on the nature of the molecules and the way they are arranged or packed in a crystal lattice. In particular, the weight of a molecule and its volume (effective molar volume) should be a dominant factor. L. T. Eremenko established a linear relationship between the density of explosives (liquid and solid) and their hydrogen content, classified the explosives under 12 groups depending on their molecular structures (whether aliphatic or aromatic, with symmetrical or unsymmetrical substituents, etc.), and evolved an empirical equation as follows:

$$\rho = a_i - K_i H$$

where ρ represents the calculated density of the explosive at TMD. a_i and K_i are constants, the values of which depend on the molecular structure/group/homologue. H refers to the weight percentage of hydrogen in the molecule (normally %H is from 0 to 6). An error of not more than 2% in this method has been claimed.

To summarize, several vital parameters of HEMs dictate their ultimate performance characteristics. The inter-relationships among them are schematically shown in Figure 2.12.

Summary of Important Terms

1. Heat of reaction
   The quantity of heat evolved or absorbed during a chemical reaction is called the "heat of reaction."
2. Enthalpy of reaction
   If the chemical reactions occur at constant pressure, then the heat of reaction is often called the "enthalpy of reaction."
3. Endothermic reaction
   A reaction in which energy is supplied to the reactants from the surroundings to obtain the product is called an "endothermic reaction."
4. Exothermic reaction
   A reaction in which heat energy is evolved along with the products is called an "exothermic reaction."
5. Heat
   Heat is one form of energy and can be produced from work. However, it is not completely convertible into work. It can only partly be transformed into work. In this respect, heat differs from many other forms of energy.
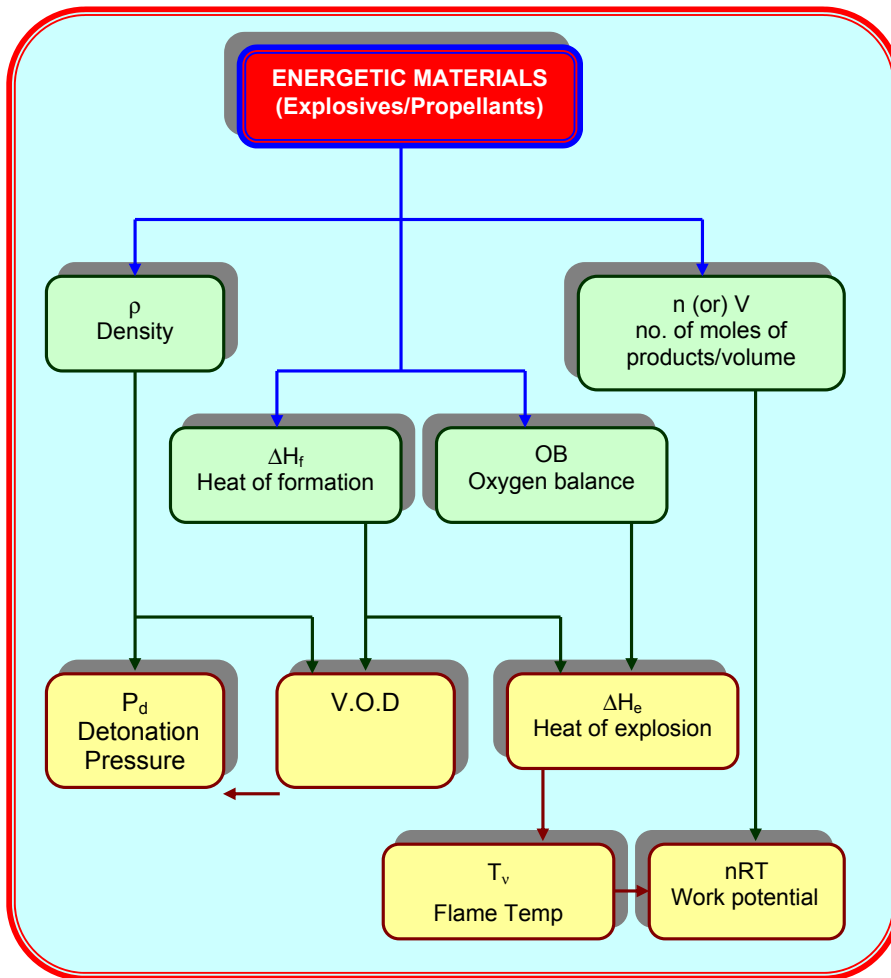
Figure 2.12
Inter-Relationship between Parameters and Performance Characteristics of High-Energy Materials.

6. Energy

The energy of a system may be defined as "any property that is capable of doing work." There are several forms of energy, including thermal energy (heat), mechanical energy, electrical energy, chemical energy, etc. Energy can be quantitatively converted into work and can be produced from work.

7. Internal energy

Internal energy is the total energy content of the system. It is due to the translational, vibrational, and rotational motions of the molecules and their mutual attraction (inter-molecular force) in a system.

8. Resonance

   Resonance is the possible existence of several types of bonding within a fixed skeleton structure of a molecule by the mobility of double bonds. In more modern terminology, the additional stability is brought about by the formation of a delocalized molecular orbital of π electrons.

9. Hess's law

   Hess law states that "If a chemical reaction is carried out in stages, the algebraic sum of the amounts of heat evolved in separate stages is equal to the total amount of heat evolved when the reaction occurs directly."

10. Heat of combustion (ΔH_c)

   It is defined as the heat evolved when 1 mole of a compound is completely burnt in excess of oxygen.

11. Oxygen balance

   The percentage excess or deficit of oxygen present in a compound required for its complete oxidation to CO_2, H_2O, etc., is known as the OB of that compound. OB is a method of quantifying how well an explosive provides its own oxidant.

12. Detonation temperature

   The maximum temperature to which the decomposition products are raised is called the "detonation temperature" in the case of explosives and "flame temperature" when we talk about propellants.

13. Adiabatic, isochoric flame temperature

   The flame temperature of the products of explosion of an explosive under adiabatic (thermally insulated), isochoric (constant volume) conditions. It is abbreviated as T_v.

14. Adiabatic, isobaric flame temperature

   Flame temperature of the products of explosion of an explosive under adiabatic, isobaric (constant pressure) conditions. It is abbreviated as T_p. T_p is less than T_v.

15. Explosion temperature/autoignition temperature

   The temperature at which the autoignition of an explosive commences when it is heated at a particular rate.

16. Pressure of explosion P_e

   The pressure of explosion (P_e) is defined as the maximum static pressure achieved when a given weight of explosive is burned in a closed vessel of fixed volume assuming adiabatic conditions.

Suggested Reading

Any standard book on Physical Chemistry would discuss various aspects of thermochemistry. Apart from this, the reader might refer to the following books.

[1] A. Bailey, S.G. Murray, Explosives, Propellants, and Pyrotechnics, Pergamon Press, Oxford, New York, 1988.

[2] Service Textbook of Explosives, Min. of Defence, Publication, UK, 1972.

[3] Structure and properties of energetic materials, in: D.H. Liebenberg, et al. (Eds.), Materials Research Society, 1993. Pennsylvania, USA.

[4] P.W. Cooper, Explosives Engineering, VCH, Publishers Inc., USA, 1996.

[5] B. Siegel, L. Schieler, Energetics of Propellant Chemistry, John Wiley & Sons. Inc., New York, 1964.

[6] S.F. Sarner, Propellant Chemistry, Reinhold publishing corporation, New York, 1966.

[7] L. Pauling, Nature of the Chemical Bond, third ed., Cornell University Press, Ithaca, 1960.

Questions

1. The heat of explosion of TNT is 1080 cal/g. If 1 kg of TNT detonates in 2 μs, how much power does it generate? (Answer: 2.2572×10^{12} W)
   (Note: The above question is hypothetical. The Second Law of Thermodynamics is very much there to ban us from converting the entire heat to useful work.)

2. Why can we describe explosives as metastable materials?

3. When an explosives chemist wants to synthesize a new, high-performing explosive, what parameters should his target molecule satisfy?

4. Why does one prefer to have a HEM with a positive heat of formation?

5. Calculate the OB of PETN. (Answer: 60.76%)

6. An explosive has a unique value of heat of combustion whereas its exact value of heat of explosion depends on the conditions of its experimental determination. Why?

7. Why does zero OB help to achieve highest value of heat of explosion?

8. What is meant by isochoric and isobaric flame temperatures (T_v and T_p respectively)? How are they related to each other? Why is T_v always more than T_p?

9. Calculate the isochoric and isobaric flame temperatures of HMX (molecular formula $C_4H_8N_8O_8$). (Given: Heat of explosion of HMX = 1480 cal/g.) (Hint: Use the molar internal energies table given in Section 2.3.7.1.)
   (Answer: $T_v \sim 4580$ K, $T_p \sim 3326$ K.)

10. What is the importance of the gas volume for an explosive? Calculate the volume of the gaseous products of the explosion of 1 g of NG (molecular formula $C_3H_5N_3O_9$) measured at NTP. Assume water as water vapor. (Answer: 715.1 mL)

11. Which parameter decides the work potential of an HEM? What different names does it assume for a high explosive, a gun propellant, and a rocket propellant?

12. Name some methods used for the theoretical prediction of the heat of formation of a molecule.

13. What is the general method used to measure the detonation temperature of a high explosive?

14. What is the difference between explosion temperature and flame temperature?

15. Define heat of formation (ΔH_f) and energy of formation (ΔE_f) and state how they are related to each other.

16. Define pressure of explosion (P_e) and write the gas equation for this process.