Chapter 19

Thermochemistry of explosives

19.1 INTRODUCTION

Thermochemistry is a subject in which the changes in internal heat of the reacting products is studied. Every explosion is a series of several reactions that take place in a particular sequence at extremely rapid speed. These reactions are invariably exothermic, i.e. heat is evolved in the reaction. In an explosion the ingredients of the chemicals, or mixtures of them, first decompose into elemental form and again recombine by consuming some of the energy evolved. Energy changes in explosive reactions are calculated either from known chemical laws or by analysis of the products.

This chapter deals with all such aspects of the chemical reaction of an explosive.

19.2 CHEMICAL NATURE OF EXPLOSIVES

As mentioned earlier, explosives are either pure chemicals with one type of molecules, or mixtures of many chemicals with different molecules.

Exceptions do exist but as said earlier almost all explosive chemicals comprise of carbon, hydrogen, nitrogen and oxygen.

Nitrogen is probably the most essential constituent of a chemical to attain the explosive nature. This is because nitrogen by itself is an inert gas. This means that it has least ability of sharing electrons with other atoms to form a molecule. In other words when a molecule is comprised of nitrogen, excessively high energy must be used to keep the bond intact. Such bonds are broken easily and are not reformed easily. Thus, a very high quantum of energy is released at extremely rapid speed when a chemical containing nitrogen decomposes.

It has also been noticed that generally for the organic explosive elements, the strength increases with increasing molar weight.

19.3 REACTIONS OF EXPLOSIVE CHEMICALS

Thermochemical studies of reactions have much greater importance in the case of explosive chemicals than other chemicals because of the extreme speed of the reactions.

This is because the end products of a chemical reaction of an explosive are extremely short-lived. Both pressure and heat of explosion fall within a few miniseconds. It is almost impossible to correctly measure their magnitudes experimentally. Therefore indirect or theoretical methods are required to be used to determine the maximum temperature and pressure values.

Whenever a chemical reaction takes place, it progresses in a particular sequence as shown in Table 19.1

In the very initial stage all the molecules contained in an explosive chemical or mixture thereof, decompose to form atoms. Once this happens the atoms start combining with each other in the priority steps shown in the table. When a chemical is formed in this manner it does not undergo decomposition again. This means that the sequence proceeds only in increasing priority number in the table.

If both the atoms required by a particular priority are not present the step is skipped and the reaction proceeds as per the next priority.

Let us take an example of picric acid.

In the initial step molecules of the elements are formed. Hence,

$$C_6H_2(OH)(NO_2)_3 \Rightarrow 6C + 3H + 3N + 7O$$

As the mixture does not contain any metal or chlorine there are no reactions as per priority step 1, 2 and 3.

As per step 4 the mixture gets converted into

$$6CO + 3H + 3N + O$$

As per step 5 the mixture gets converted into

$$6CO + H_2O + H + 3N$$

Table 19.1 Priorities of formation of end products of explosive reactions.

Priority	*Composition of the product mix*	*End products*	*End product phase*
1	A metal and chlorine	Metallic chloride	Solid
2	Hydrogen and Chlorine	HCl	Gas
3	A Metal and Oxygen	Metallic oxide	Solid
4	Carbon and Oxygen	CO	Gas
5	Hydrogen and Oxygen	H_2O	Gas
6	Carbon Monoxide and Oxygen	CO_2	Gas
7	Nitrogen	N_2	Gas
8	Excess Oxygen	O_2	Gas
9	Excess Hydrogen	H_2	Gas
10	Carbon	C	Gas

As there is no unreacted oxygen left in the mixture there is no reaction as per priority step 6 and the mixture remains

$$6CO + H_2O + H + 3N$$

As per step 7 the mixture gets converted into

$$6CO + H_2O + H + 1.5N_2$$

As there is no excess oxygen left in the mixture there is no reaction as per priority step 8 and the mixture remains

$$6CO + H_2O + H + 1.5N_2$$

As per step 9 the mixture gets converted into

$$6CO + H_2O + 0.5H_2 + 1.5N_2$$

Since there is no unreacted carbon left, the mixture remains

$$6CO + H_2O + 0.5H_2 + 1.5N_2$$

In the above equations the symbols such as $0.5H_2$ or $1.5N_2$ are correct because they do not represent molecules but represent moles each of which contains $6.02257 * 10^{27}$ molecules.

It must be specifically noted that the water formed after the explosive is in vapor i.e. gaseous form.

End products formed after the detonation of different explosives are given in Table 19.2.

The important aspects of the chemical reactions of explosives are:

1 Oxygen balance
2 Volume of products of explosion
3 Heat of explosion
4 Strength of explosive

Each of these aspects is detailed below.

19.3.1 Oxygen balance

An explosive does not use oxygen available from the atmosphere in its chemical reaction. If it is required to do so the reaction will be very slow and the material will not qualify to be called an explosive.

If the atoms contained in an explosive molecule are in such numbers that the oxygen molecules evolved can completely convert all metal atoms to metal oxide

Table 19.2 Characteristics of some chemical reactions of explosives and the end products.

Explosive name	*Chemical formula*	*End products*	*Q_v in J/kg*	*T_e in °C*	*f kg/cm^2*	*V in m/s*	*Trauzl expansion in cc/10 g*	*Energy potential in kg · m*
Gunpowder	$2KNO_3 + 3C + S$	$N_2 + 3CO_2 + K_2S$	2098	2090	291	–	30	2.1
Nitrocellulose	$C_{24}H_{29}O_9(NO_3)_{11}$	$20.5CO + 3.5CO_2 + 14.5H_2O + 5.5N_2$	5234	2800	981	6100	420	5.3
Nitroglycerin	$C_3H_5(NO_3)_3$	$3CO_2 + 2.5H_2O + 1.5N_2 + 0.25O_2$	6389	3360	964	8500	590	6.5
Ammonium Nitrate	NH_4NO_3	$2H_2O + N_2 + 0.5O_2$	1608	1100	500	4100	300	1.6
Trinitrotoluene	$C_7H_5(NO_2)_3$	$6CO + C + 2.5H_2 + 1.5N_2$	2714	2200	822	6800	260	2.8
Picric Acid	$C_6H_2(OH)(NO_2)_3$	$6CO + H_2O + 0.5H_2 + 1.5N_2$	3546	2717	977	7000	300	3.6
Ammonium Picrate	$C_6H_2(NO_2)_3ONH_4$	$6CO + H_2O + 2H_2 + 2N_2$	2604	1979	837	6500	230	2.6
Tetryl	$C_7H_5N_5O_8$	$7CO + H_2O + 2H_2 + 2N_2$	3802	2781	1062	7229	320	3.9
Mercury Fulminate	$Hg(ONC)_2$	$Hg + 2CO + N_2$	1759	4105	511	3920	213	1.8
Lead Azide	PbN6	$Pb + 3N_2$	2864	3180	791	5000	250	2.9

Q_v = Heat of explosion at constant volume, T_e = Temperature of explosion, f = Pressure exerted by 1 kg explosive in volume of explosive at explosion temperature, V = Velocity of detonation in m/s.

From Science of Explosives by Myers.

molecules, convert all carbon atoms to carbon dioxide molecules, convert all hydrogen atoms to water molecules and leave no oxygen atoms to form oxygen molecules, it is considered to have zero oxygen balance.

It has been noticed that the strength, brisance and sensitivity generally tend to be maximum when the explosive molecule has perfect oxygen balance.

The explosive molecule is said to have a positive oxygen balance if it holds more oxygen than is needed and a negative oxygen balance if it holds less oxygen than is needed for such conversion.

The oxygen balance can be calculated by using the following formula

$$OB = -(100\%) * (MW_o/MW_e) * [2C + H/2 + M - O]$$

where

MW_o = Molecular weight of oxygen
MW_e = Molecular weight of explosive
C = Number of carbon atoms in the explosive
H = Number of hydrogen atoms in the explosive
M = Number of metal atoms in the explosive
O = Number of oxygen atoms in the explosive

As an example, consider picric acid, the end products of which are

$$6C + 3H + 3N + 7O$$

It will need 12O to convert 6C into $6CO_2$ and 1.5O to convert 3H to $1.5H_2O$ i.e. a total of 13.5O. Since it already has 7O the additional need is for 6.5O.

By using the formula the oxygen balance of picric acid can be found as

$$OB = -100 * (15.999/229.1037) * (2 * 6 + 3/2 - 7) = 45.39\%$$

19.3.2 Volume of products of explosion

A mole is a scientific term given to a numerical quantity of molecules. The number of molecules contained in a mole is $6.02257 * 10^{27}$ and is often termed as Avogadro's Number. It can be shown that at NTP conditions i.e. temperature of 0°C and pressure of 101.325 kPa the volume of one mole of any gas equals to 22.3933 m^3.

Let us now consider the chemical decomposition of nitroglycerin. The chemical equation is as follows.

$$C_3H_5(NO_3)_3 \Rightarrow 3CO_2 + 2.5H_2O + 1.5N_2 + 0.25O_2$$

In a way this is an ideal explosive because it produces totally non-toxic end products and it has a positive balance of oxygen.

As indicated by the above equation one mole of nitroglycerin molecules produces a total of 7.25 g-moles of gas at 0°C. Hence, its volume at 0°C will be $7.25 \times 22.3933 = 162.3514$ L.

By using Charles' Law the volume for 20°C works out to 162.3514 * ((273.15 + 20)/273.15) = 174.2387 L.

19.3.3 Heat of explosion

Some energy is required for formation of each molecule. When a molecule of explosive breaks down, the energy required for its formation is released. Immediately a part of the energy is spent in formation of the end products of the reaction. Thus, the heat evolved in an explosion can be calculated as

$$\Delta E = \Delta E_{fe} - \Delta E_{fp}$$

where

ΔE = Energy evolved in kJ/mol

ΔE_{fe} = Energy required in kJ/mol for formation of the explosive

ΔE_{fp} = Energy required in kJ/mol for formation of the end products of the explosive reaction

For actual calculations, the heat of formation of some explosives and the end products of the reaction are given in Table 19.3.

As an example, let us calculate the heat of explosion of Trinitrotoluene i.e. TNT. From Table 19.3 we have

$$\Delta H_{fe} = -54.39 \text{ kJ/mol}$$

From Table 19.1 the end products of explosion of TNT are

$$6CO + C + 2.5H_2 + 1.5N_2$$

Table 19.3 Heat of formation of some explosive and the end products of explosive reactions.

Name of end product or explosive	*Chemical formula*	*Molecular weight*	*Formation energy in kJ/mol*
Oxygen molecule	O_2	31.998	0
Hydrogen molecule	H_2	2.0158	0
Nitrogen molecule	N_2	28.014	0
Carbon monoxide	CO	28.01	−111.8
Carbon dioxide	CO_2	44.009	−393.5
Water	H_2O	18.0148	−240.6
Nitroglycerin	$C_3H_5N_3O_9$	297.1313	−333.66
RDX	$C_3H_6N_6O_6$	222.1164	+83.82
PETN	$C_5H_8N_4O_{12}$	316.1342	−514.63
HMX	$C_4H_8N_8O_8$	296.1552	+104.77
Trinitrotoluene	$C_7H_5N_3O_6$	227.1315	−54.39
Tetryl	$C_7H_5N_5O_8$	287.1435	+38.91

Therefore,

$\Delta E_{fp} = 6(-111.8) + 1(0) + 2.5(0) + 1.5(0) = -670.8$

With this we get

$\Delta E = -54.39 - (-670.8) = 616.41$ kJ/mol

Since ΔE is positive the reaction is exothermic and heat is evolved and not absorbed.

Since one mole of TNT weighs 227.1435 grams the heat evolved by the explosion of one kg of TNT will work out to 616.41/0.2271435 = 2713.74 kJ.

19.3.4 Strength of explosive

As soon as an explosive is detonated, gases and other end products, and also a huge quantity of heat, evolves from the chemical reaction. The gases and heat do lot of work on the surroundings such as expansion of the blasthole, crushing of the rock in the peripheral wall of the blasthole, fragmenting of the rock mass, throwing of rock pieces etc. The capacity to do all this work is called the strength of the explosive.

From the basic principle, the strength of the explosive will be equal to the volume of gases evolved and the change in internal energy. In this regard the concept put forth by Berthelot is of great importance. Even Berthelot also knew that it is not a perfect concept hence it is called the Berthelot Approximation. It indirectly states that the strength of the explosive is proportional to the product of change in internal energy in the explosion and the volume of gases evolved in the explosion for each mole of the explosive.

From this an equation for the strength of any explosive can be written as

$S_t = 840 * \Delta n * \Delta E/(M_w)2$

where

S_t = Strength of Explosive as a percentage in relation to the strength of trinitrotoluene.

Δn = Volume of gases produced per mole by the reaction of the explosive.

ΔE = Change in internal energy due to chemical reaction.

M_w = Molecular weight of the explosive in g/mol.

The strength is relative to the strength of trinitrotoluene because the constant 840 accounts for the units and values of Δn and ΔE for trinitrotoluene.

Let us consider the example of RDX having chemical formula $C_3H_6N_6O_6$.

The steps of the chemical reaction of RDX explosion are:

Step 1: $C_3H_6N_6O_6 \Rightarrow 3C + 6H + 6N + 6O$
Step 4: $3C + 6H + 6N + 6O \Rightarrow 3CO + 6H + 6N + 3O$
Step 5: $3CO + 6H + 6N + 3O \Rightarrow 3CO + 3H_2O + 6N$
Step 7: $3CO + 3H_2O + 6N \Rightarrow 3CO + 3H_2O + 3N_2$

Thus, the end products of the explosion reaction of RDX are $3CO + 3H_2O + 3N_2$. All these products are in gaseous form hence 1 mole of RDX evolves 9 moles of gas. In other words, $\Rightarrow \Delta n = 9$.

For RDX we have $\Delta E_{fe} = 83.82$ and for the end products $DE_{fp} = 3(-111.8) + 3(-240.6) = -1057.2$.

Hence $\Delta E = 83.82 - (-1057.2) = 1141.02$.

This gives

$$S_t = 840 * 9 * 1141.02/(222.1164)^2 = 174.845\%$$

Thus, the strength of RDX is about 175% that of TNT.