CONTENTS

CHEMISTRY

Unit 8

Physical and chemical equilibrium

Claude Louis Berthollet, a Savoyard-French chemist, studied the mechanism of reversible chemical reaction and developed the theory of chemical equilibria. He also contributed to modern chemical nomenclature. He was the first to demonstrate the bleaching action of chlorine gas, and developed a solution of sodium hypochlorite that acts as a bleaching agent.

Learning Objectives

After studying this unit, the students will be able to

- describe the meaning of equilibrium
- explain the dynamic nature of equilibrium involved in physical and chemical processes
- state the law of mass action
- deduce the expression for equilibrium constants, K_C and K_P
- establish the relationship between K_P and K_C
- predict the extent of reaction using equilibrium constant
- state Le-Chatelier's principle
- explain the effect of various factors that affect a system at equilibrium.
- derive Van't Hoff equation.

8.1 Introduction

In our daily life, we observe several chemical and physical changes. For example, a banana gets ripened after few days, silver gets tarnished in few months and iron gets rusted slowly. These processes proceed in one direction. Now let us consider the transport of oxygen by hemoglobin in our body as an illustration for a reversible change. The hemoglobin combines with oxygen in lungs to form oxyhemoglobin. The oxy-hemoglobin has a tendency to form hemoglobin by releasing oxygen. In fact, in our lungs all the three species coexist.

Few chemical reactions proceed in only one direction whereas many reactions proceed in both the directions and these reactions are called reversible reactions.

In chemical reactions, the concentration of the reactants decreases and that of the products increases with time. In reversible reactions, initially the reaction proceeds towards the formation of the product. Upon formation of the product, the reverse reaction begins to take place. At a particular stage, the rate of the reverse reaction is equal to that of the forward reaction indicating a state of equilibrium.

It is desirable to know the three crucial aspects of chemical reactions namely the feasibility, the rate of the reaction and the extent of reaction. We know that the feasibility of a reaction is given by thermodynamics. Chemical kinetics will tell about the rate of the reaction. The equilibrium constant tells about the extent of a reaction which we will discuss in this chapter. We will also discuss the types of equilibrium, the significance of equilibrium constant and its relationship to thermodynamic quantities and the response of chemical equilibrium to change in the reaction conditions.

8.2. Physical and chemical equilibrium:

There are different types of equilibrium. For example, if two persons with same weight sit on opposite sides of a see-saw at equal distance from the fulcrum, then the see-saw will be stationary and straight and it is said to be in equilibrium.

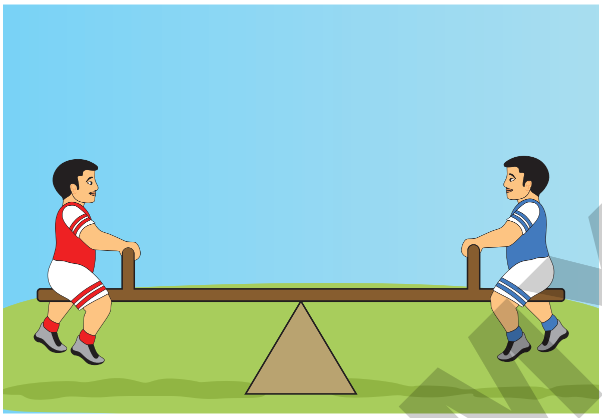


Fig. 8.1 Illustration of equilibrium

Another example of a state of equilibrium is the game of "tug-of-war." In this game a rope is pulled taut between two teams. There may be a situation when both the teams are pulling the rope with equal force and the rope is not moving in either direction. This state is said to be in equilibrium.

Fig. 8.2. Tug-of War

In reversible processes, the rate of two opposing reactions equals at a particular stage. At this stage the concentration of reactants and products do not change with time. This condition is not static and is dynamic, because both the forward and reverse reactions are still occurring with the same rate.

8.2.1 Physical equilibrium

A system in which the amount of matter constituting different phases does not change with time is said to be in physical equilibrium. This involves no perceptible physical change in the system. To understand the physical equilibrium let us analyse the following phase changes.

Solid-liquid equilibrium

Let us consider the melting of ice in a closed container at 273 K. This system will reach a state of physical equilibrium in which the amount of water in the solid phase and liquid phase does not change with time. In the process the total number of water molecules leaving from and returning to the solid phase at any instant are equal.

If some ice-cubes and water are placed in a thermos flask (at 273K and 1 atm pressure), then there will be no change in the mass of ice and water.

At equilibrium,

$$\text{Rate of melting of ice} = \text{Rate of freezing of water}$$

$$\boxed{H_2O\,(s) \rightleftharpoons H_2O\,(l)}$$

The above equilibrium exists only at a particular temperature and pressure. The temperature at which the solid and liquid phases of a substance are at equilibrium is called the melting point or freezing point of that substance.

Liquid - Vapour equilibrium

Similarly, there exists an equilibrium between the liquid phase and the vapour phase of a substance. For example, liquid water is in equilibrium with its vapour at 373 K and1 atm pressure in a closed vessel.

$$\boxed{H_2O\,(l) \rightleftharpoons H_2O\,(g)}$$

Here
Rate of evaporation = Rate of condensation

The temperature at which the liquid and vapour phases are at equilibrium is called the boiling point and condensation point of the liquid.

Solid - Vapour equilibrium

Consider a system in which the solid sublimes to vapour. In this process also, equilibrium can be established between these two phases. When solid iodine is placed in a closed transparent vessel, after sometime,the vessel gets filled up with violet vapour due to sublimation of iodine. Initially, the intensity of the violet colour increases, after sometime it decreases and finally it becomes constant, as the following equilibrium is attained.

$$\boxed{I_2\,(s) \rightleftharpoons I_2(g)}$$

More examples

$$\boxed{\begin{array}{c}\text{Camphor (s)} \rightleftharpoons \text{Camphor (g)} \\ NH_4Cl\,(s) \rightleftharpoons NH_4\,Cl\,(g)\end{array}}$$

8.2.2 Equilibrium involving dissolution of solids or gases in liquids

Solid in liquids

When you add sugar to water at a particular temperature, it dissolves to form sugar solution. If you continue to add much sugar, you will reach a stage at which the added sugar remains as solid and the resulting solution is called a saturated solution. Here, as in the previous cases a dynamic equilibrium is established between the solute molecules in the solid phase and in the solution phase.

$$\boxed{\text{Sugar (Solid)} \rightleftharpoons \text{Sugar (Solution)}}$$

In this process

Rate of dissolution of solute = Rate of crystallisation of solute

Gas in liquids

When a gas dissolves in a liquid under a given pressure, there will be an equilibrium between gas molecules in the gaseous state and those dissolved in the liquid.

Example:

In carbonated beverages the following equilibrium exists.

$$\boxed{CO_2\,(g) \rightleftharpoons CO_2\,(\text{Solution})}$$

Henry's law is used to explain such gas-solution equilibrium processes.

8.3. Chemical Equilibrium

Similar to physical processes chemical reactions gradually attain a state of equilibrium after sometime. Let us consider a general reversible reaction.

$$\boxed{A+B \rightleftharpoons C+D}$$

Initially only A and B are present. Soon, a few molecules of the products C and D are formed by the forward reaction. As the concentration of the products increases, more products collide and react in the backward direction. This leads to an increase in the rate of backward reaction. As the rate of reverse reaction increases, the rate of the forward reaction decreases. Eventually, the rate of both reactions becomes equal.

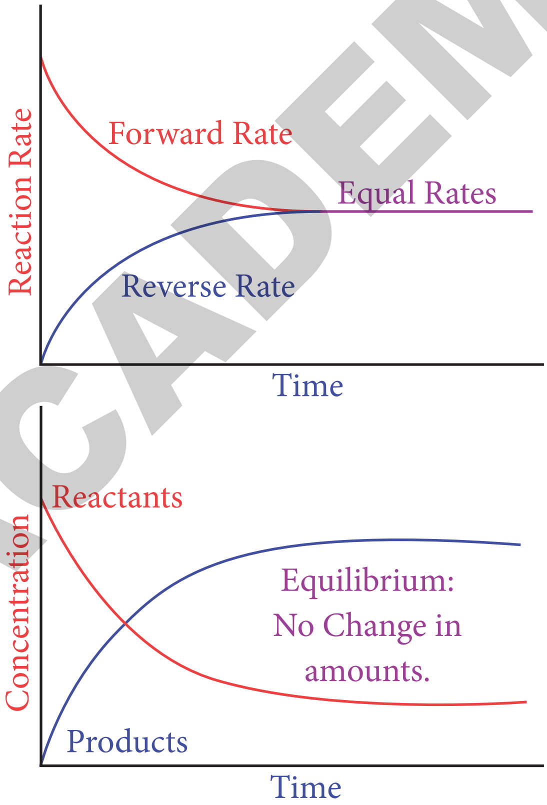


Figure: 8.3 Attainment of equilibrium state for the variation of the rates of forward and backward reactions with time.

8.4. Dynamic nature of equilibrium:

Let us consider, a situation in multi storey building, people are moving from first floor to second floor and vice versa. Assume that a certain number people moves up from first floor to second floor in a specific time, and the same number of people moves down from second floor to the first floor in the same time. Now, the rate of movement of people from first to second floor equals the rate of movement of people from second to first floor, and hence the number of people in each floor will remain the same. Thus the population of people on the two floors is in a dynamic equilibrium Let us extend this analogy to understand dynamic nature of equilibrium.

Chemical reactions which are reversible do not cease, when equilibrium is attained. At equilibrium the forward and the backward reactions are proceeding at the same rate and no macroscopic change is observed. So chemical equilibrium is in a state of dynamic equilibrium.

For example,

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$$

8.5 Homogeneous and heterogeneous equilibria

8.5.1 Homogeneous equilibrium

In a homogeneous equilibrium, all the reactants and products are in the same phase.

For example:

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$$

In the above equilibrium, H_2, I_2 and HI are in the gaseous state.

Similarly, for the following reaction, all the reactants and products are in homogeneous solution phase.

$$\begin{gathered} CH_3COOCH_3(aq)+H_2O(aq) \\ \rightleftharpoons \\ CH_3COOH(aq)+CH_3OH\,(aq) \end{gathered}$$

8.5.2 Heterogeneous equilibrium

If the reactants and products of a reaction in equilibrium, are in different phases, then it is called as heterogeneous equilibrium.

Example:

$$H_2O\,(l) \rightleftharpoons H_2O\,(g)$$

$$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$$

8.6 Law of mass action

In 1864 two Norwegian chemists namely Maximilian Guldberg and Peter Waage formulated the law of mass action, based on the experimental studies of many reversible reactions. The law states that,

"At any instant, the rate of a chemical reaction at a given temperature is directly proportional to the product of the active masses of the reactants at that instant".

$$\text{Rate}\ \alpha\ [\text{Reactant}]^x$$

where, x is the stoichiometric coefficient of the reactant and the square bracket represents the active mass (concentration) of the reactants.

$$\text{Active mass} = \left(\frac{n}{V}\right) \text{mol dm}^{-3} \text{(or) mol L}^{-1}$$

where n is the number of moles and V is the volume of the container (dm^3 or L)

8.6.1 Equilibrium constants (K_p and K_C):

Let us consider a reversible reaction,

$$\boxed{xA + yB \rightleftharpoons lC + mD}$$

where, A and B are the reactants, C and D are the products and x,y, l and m are the stoichiometric coefficients of A, B, C and D, respectively.

Applying the law of mass action, the rate of the forward reaction,

$$\boxed{r_f \propto [A]^x [B]^y \text{ (or) } r_f = k_f [A]^x [B]^y}$$

Similarly, the rate of the backward reaction,

$$\boxed{\begin{gathered} r_b \propto [C]^l [D]^m \\ \text{(or)} \\ r_b = k_b [C]^l [D]^m \end{gathered}}$$

where k_f and k_b are proportionality constants

At equilibrium,

$$\boxed{\begin{aligned} &\text{Rate of forward reaction } (r_f) \\ &= \text{Rate of backward reaction } (r_b) \\ &k_f [A]^x [B]^y = k_b [C]^l [D]^m \\ \text{or} \quad &\frac{k_f}{k_b} = \frac{[C]^l [D]^m}{[A]^x [B]^y} = K_c \end{aligned}}$$

where, K_c is the equilibrium constant in terms of concentration (active mass).

At a given temperature, the ratio of the product of active masses of reaction products raised to the respective stoichiometric coefficients in the balanced chemical equation to that of the reactants is a constant, known as equilibrium constant. Later when we study chemical kinetics we will learn that this is only approximately true.

If the reactants and products of the above reaction are in gas phase, then the equilibrium constant can be written in terms of partial pressures as indicated below,

$$\boxed{k_p = \frac{p_C^l \times p_D^m}{p_A^x \times p_B^y}}$$

Where, p_A, p_B, p_C, and p_D are the partial pressures of the gas A, B, C and D, respectively.

8.6.2 Relation between K_p and K_c

Let us consider the general reaction in which all reactants and products are ideal gases.

$$\boxed{xA + yB \rightleftharpoons lC + mD}$$

The equilibrium constant, K_c is

$$\boxed{k_c = \frac{[C]^l [D]^m}{[A]^x [B]^y} \qquad (1)}$$

and K_p is,

$$\boxed{k_p = \frac{p_C^l \times p_D^m}{p_A^x \times p_B^y} \qquad (2)}$$

The ideal gas equation is

$$PV = nRT$$

or

$$P = \frac{n}{V}RT$$

Since

Active mass = molar concentration = n/V

P = active mass × RT

Based on the above expression the partial pressure of the reactants and products can be expressed as,

$$p_A^x = [A]^x [RT]^x$$

$$p_B^y = [B]^y [RT]^y$$

$$p_C^l = [C]^l [RT]^l$$

$$p_D^m = [D]^m [RT]^m$$

On substitution in Eqn. 2,

$$k_p = \frac{[C]^l [RT]^l [D]^m [RT]^m}{[A]^x [RT]^x [B]^y [RT]^y} \qquad (3)$$

$$k_p = \frac{[C]^l [D]^m [RT]^{l+m}}{[A]^x [B]^y [RT]^{x+y}}$$

$$k_p = \frac{[C]^l [D]^m}{[A]^x [B]^y} [RT]^{(l+m) - (x+y)} \qquad (4)$$

By comparing equation (1) and (4), we get

$$k_p = K_c (RT)^{(\Delta n_g)} \qquad (5)$$

where,

Δn_g is the difference between the sum of number of moles of products and the sum of number of moles of reactants in the gas phase.

The following relations become immediately obvious.

When $\Delta n_g = 0$

$K_p = K_c (RT)^0 = K_c$

Example:

$H_2(g) + I_2(g) \rightleftharpoons 2HI\ (g)$

$N_2\ (g) + O_2\ (g) \rightleftharpoons 2NO(g)$

When $\Delta n_g = +ve$

$K_p = K_c\ (RT)^{+ve}$

$K_p > K_c$

$2NH_3(g) \rightleftharpoons N_2\ (g) + 3H_2\ (g)$

$PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2\ (g)$

When $\Delta n_g = -ve$

$K_p = K_c\ (RT)^{-ve}$

$K_p < K_c$

Example:

$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O\ (g)$

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3\ (g)$

Table 8.1 Relation between equilibrium constants for some reversible reactions

Reversible reactions	Equilibrium constant
For the forward reaction $x\,A + yB \rightleftharpoons lC + mD$	K_c

If the reaction is reversed, $lC+mB \rightleftharpoons xA+yB$	$K_c^{'} = \frac{1}{K_c}$
$A \overset{K_1}{\rightleftharpoons} B \quad B \overset{K_2}{\rightleftharpoons} C$ $C \overset{K_3}{\rightleftharpoons} D \quad A \overset{K_4}{\rightleftharpoons} D$	$K_4 = K_1K_2K_3$

8.6.3 Equilibrium constants for heterogeneous equilibrium

Consider the following heterogeneous equilibrium.

$$CaCO_3\ (s) \rightleftharpoons CaO\ (s) + CO_2\ (g)$$

The equilibrium constant for the above reaction can be written as

$$k_c = \frac{[CaO(s)][CO_2(g)]}{CaCO_3\ (s)}$$

A pure solid always has the same concentration at a given temperature, as it does not expand to fill its container. i.e. it has same number of moles L^{-1} of its volume. Therefore, the concentration of a pure solid is a constant. The above expression can be modified as follows

$$K_c = [CO_2\ (g)]$$

$$\text{or}$$

$$K_p = p_{CO_2}$$

The equilibrium constant for the above reaction depends only the concentration of carbon dioxide and not the calcium carbonate or calcium oxide. Similarly, the active mass (concentration) of the pure liquid does not change at a given temperature. Consequently, the concentration terms of pure liquids can also be excluded from the expression of the equilibrium constant.

For example,

$$CO_2(g) + H_2O\ (l) \rightleftharpoons H+(aq) + HCO_3^-\ (aq)$$

Since, H_2O (l) is a pure liquid the Kc can be expressed as

$$K_C = \frac{[H^+(aq)][HCO_3^-(aq)]}{[CO_2(g)]}$$

Example

Write the K_p and K_c for the following reactions

1) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
2) $2CO(g) \rightleftharpoons CO_2(g) + C(S)$
3) $Ag_2O(S) + 2NH_3(aq) \rightleftharpoons 2AgNO_3(aq) + H_2O(l)$

1) $$K_C = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]}$$

$$K_P = \frac{P^2_{SO_3}}{P^2_{SO_2} \times PO_2}$$

2) $$\therefore\ K_C = \frac{[CO_2]}{[CO]^2} \text{ and } K_P = \frac{P_{CO_2}}{P^2_{CO}}$$

3) $$K_C = \frac{[AgNO_3]^2}{[NH_3]^2}$$

Evaluate Yourself

1) Consider the following reaction

$$\mathbf{Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons [Fe(SCN)]^{2+}(aq)}$$

A solution is made with initial Fe^{3+}, SCN^- concentration of 1×10^{-3}M and 8×10^{-4} M respectively. At equilibrium $[Fe(SCN)]^{2+}$ concentration is 2×10^{-4}M. Calculate the value of equilibrium constant.

2) The atmospheric oxidation of NO

$$\mathbf{2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)}$$

was studied with initial pressure of 1 atm of NO and 1 atm of O_2. At equilibrium, partial pressure of oxygen is 0.52 atm calculate K_p of the reaction.

8.7 Application of equilibrium constant

The knowledge of equilibrium constant helps us to

1. predict the direction in which the net reaction will take place
2. predict the extent of the reaction and
3. calculate the equilibrium concentrations of the reactants and products.

It is to be noted that these constants do not provide any information regarding the rates of the forward or reverse reactions.

8.7.1 Predicting the extent of a reaction

The value of equilibrium constant, K_c tells us the extent of a reaction, i.e., it indicates how far the reaction has proceeded towards product formation at a given temperature.

A large value of K_c indicates that the reaction reaches equilibrium with high product yield. On the other hand, a low value of K_c indicates that the reaction reaches equilibrium with low product formed. In general, if the K_c is greater than the 10^3, the reaction proceeds nearly to completion. If it is less than 10^{-3},the reaction rarely proceeds. If the K_c is in the range 10^{-3} to10^3, significant amount of both reactants and products are present at equilibrium.

Table8.2 Dependence of extent of reaction on Kc

Value of K_C	$K_C < 10^{-3}$	$10^{-3} < K_C < 10^3$	$K_C > 10^3$
Relative concentrations of reactants and products	[Products] << [Reactants]	Significant quantity of Products and Reactants	[Products] >> [Reactants]
Extent of reaction	Reaction makes a little progress in the forward direction	Both the forward and backward reactions reaction make significant progress	Reaction nearly goes to completion
Prediction	Reverse reaction is favoured	Neither forward nor reverse reaction predominates	Forward reaction is favoured
Examples	Decomposition of water at 500 K $2H_2O(g) \rightleftharpoons 2H_2(g) + O_2\,(g)$ $K_C = 4.1 \times 10^{-48}$ Oxidation of nitrogen at 1000 K $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $K_C = 1\times 10^{-30}$	Dissociation of bromine monochloride at 1000 K $2BrCl(g) \rightleftharpoons Br_2(g) + Cl_2(g)$ $K_C = 5$ Formation HI at 700 K $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ $K_C = 57.0$	Formation of HCl at 300K $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl\,(g)$ $K_C = 4 \times 10^{31}$ Oxidation of carbon monoxide at 1000 K $2CO(g) + O_2\,(g) \rightleftharpoons 2CO_2(g)$ $K_C = 2.2 \times 10^{22}$

Example

Consider the following equilibrium reactions and relate their equilibrium, constants

i) $N_2 + O_2 \rightleftharpoons 2NO \,;\, K_1$
ii) $2NO + O_2 \rightleftharpoons 2NO_2 \,;\, K_2$
iii) $N_2 + 2O_2 \rightleftharpoons 2NO_2 \,;\, K_3$

$$K_1 = \frac{[NO]^2}{[N_2][O_2]}$$

$$K_2 = \frac{[NO_2]^2}{[NO]^2[O_2]}$$

$$\text{Now } K_1 \times K_2 = \frac{[NO]^2}{[N_2][O_2]} \times \frac{[NO_2]^2}{[NO]^2\,[O_2]}$$

$$= \frac{[NO_2]^2}{[N_2][O_2]^2} = K_3$$

$$\therefore\ K_3 = K_1 \times K_2$$

8.7.2 Predicting the direction of a reaction

From the knowledge of equilibrium constant, it is possible to predict the direction in which the net reaction is taking place for a given concentration or partial pressure of reactants and products.

Consider a general homogeneous reversible reaction,

$$xA + yB \rightleftharpoons lC + mD$$

For the above reaction under non-equilibrium conditions, reaction quotient 'Q' is defined as the ratio of the product of active masses of reaction products raised to the respective stoichiometric coefficients in the balanced chemical equation to that of the reactants.

Under non-equilibrium conditions, the reaction quotient Q can be calculated using the following expression.

$$Q = \frac{[C]^l\,[D]^m}{[A]^x\,[B]^y}$$

As the reaction proceeds, there is a continuous change in the concentration of reactants and products and also the Q value until the reaction reaches the equilibrium. At equilibrium Q is equal to K_c at a particular temperature. Once the equilibrium is attained, there is no change in the Q value. By knowing the Q value, we can predict the direction of the reaction by comparing it with Kc.

- If $Q = K_c$, the reaction is in equilibrium state.
- If $Q > K_c$, the reaction will proceed in the reverse direction i.e., formation of reactants.
- If $Q < K_c$, the reaction will proceed in the forward direction i.e., formation of products.

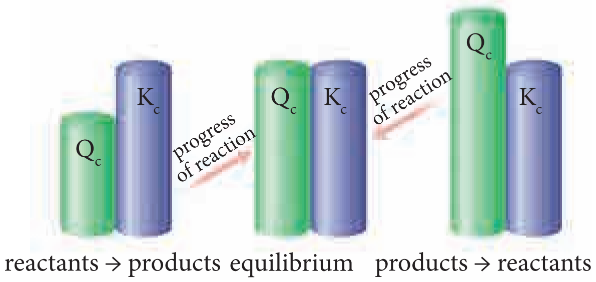


Fig: 8.4 Predicting the direction of a reaction

Example 1

The value of K_c for the following reaction at 717 K is 48.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

At a particular instant, the concentration of H_2, $I_2$and HI are found to be 0.2 mol L^{-1}, 0.2 mol L^{-1} and 0.6 mol L^{-1} respectively. From the above information we can predict the direction of reaction as follows.

$$\boxed{Q = \frac{[HI]^2}{[H_2][I_2]} = \frac{0.6\times0.6}{0.2\times0.2} = 9}$$

Since Q< K_c, the reaction will proceed in the forward direction.

Example 2

The value of Kc for the reaction

$$\boxed{N_2O_4\,(g) \rightleftharpoons 2NO_2(g)}$$

Kc = 0.21 at 373 K. The concentrations N_2O_4 and NO_2 are found to be 0.125 mol dm^{-3} and 0.5 mol dm^{-3} respectively at a given time. From the above information we can predict the direction of reaction as follows.

$$\boxed{Q = \frac{[NO_2]^2}{[N_2O_4]} = \frac{0.5\times0.5}{0.125} = 2}$$

The Q value is greater than Kc. Hence, the reaction will proceed in the reverse direction until the Q value reaches 0.21

Evaluate Yourself

3) The following water gas shift reaction is an important industrial process for the production of hydrogen gas.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

At a given temperature K_p = 2.7. If 0.13 mol of CO, 0.56 mol of water, 0.78 mol of CO_2 and and 0.28 mol of H_2 are introduced into a 2 L flask, and find out in which direction must the reaction proceed to reach equilibrium

8.7.3 Calculation of concentration of reactants and products at equilibrium

If the equilibrium concentrations of reactants and products are known for a reaction, then the equilibrium constant can be calculated and vice versa.

Let us consider the formation of HI in which, 'a' moles of hydrogen and 'b' moles of iodine gas are allowed to react in a container of volume V. Let 'x' moles of each of H_2 and I_2 react together to form 2x moles of HI.

$$\boxed{H_2\,(g) + I_{2\,(g)} \rightleftharpoons 2HI_2(g)}$$

	H_2	I_2	HI
Initial number of moles	a	b	0
number of moles reacted	x	x	0
Number of moles at equilibrium	a-x	b-x	2x
Active mass or molar concentration at equilibrium	$\frac{a-x}{V}$	$\frac{b-x}{V}$	$\frac{2x}{V}$

Applying law of mass action,

$$K_C = \frac{[HI]^2}{[H_2][I_2]}$$

$$= \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-x}{V}\right)} = \frac{4x^2}{(a-x)(b-x)}$$

The equilibrium constant K_p can also be calculated as follows:

We know the relationship between the K_c and K_p

$$\boxed{K_P = K_C\,(RT)^{(\Delta n_g)}}$$

Here the

$$\Delta n(g) = n_p - n_r = 2 - 2 = 0$$

Hence Kp = Kc

$$K_p = \frac{4x^2}{(a-x)(b-x)}$$

Solved Problem

One mole of H_2 and one mole of I_2 are allowed to attain equilibrium. If the equilibrium mixture contains 0.4 mole of HI. Calculate the equilibrium constant.

Given data:

$[H_2] = 1$ mole $\qquad [I_2] = 1$ mole

At equilibrium, [HI] = 0.4 mole Kc= ?

Solution:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

	H_2	I_2	HI
Initial number of moles	1	1	–
Number of moles at equilibrium	1-x	1-x	2x = 0.4. x=0.2
	0.8	0.8	0.4

$$\therefore K_C = \frac{[HI]^2}{[H_2][I_2]} = \frac{0.4 \times 0.4}{0.8 \times 0.8} = 0.25$$

Dissociation of PCl_5:

Consider that 'a' moles of PCl_5 is taken in a container of volume V. Let 'x' moles of PCl_5 be dissociated into x moles of PCl_3 and x moles of Cl_2.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

	PCl_5	PCl_3	Cl_2
Initial number of moles	a	0	0
number of moles dissociated	x	0	0
Number of moles at equilibrium	a-x	x	x
Active mass or molar concentration at equilibrium	$\frac{a-x}{V}$	$\frac{x}{V}$	$\frac{x}{V}$

Applying law of mass action,

$$K_C = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{a-x}{V}\right)} = \frac{x^2}{(a-x)V}$$

The equilibrium constant K_p can also be calculated as follows:

We know the relationship between the Kc and Kp

$$K_P = K_C(RT)^{(\Delta n_g)}$$

Here the

$$\Delta ng = n_p - n_r = 2 - 1 = 1$$

Hence Kp = Kc (RT)

We know that PV = nRT

$$RT = \frac{PV}{n}$$

Where n is the total number of moles at equilibrium.

n = (a-x) + x + x = (a+x)

$$K_p = \frac{x^2}{(a-x)V}\,\frac{PV}{n}$$

$$K_p = \frac{x^2}{(a-x)V}\,\frac{PV}{(a+x)}$$

$$K_p = \frac{x^2P}{(a-x)\,(a+x)}$$

Synthesis of ammonia:

Let us consider the formation of ammonia in which, 'a' moles nitrogen and 'b' moles hydrogen gas are allowed to react in a container of volume V. Let 'x' moles of nitrogen react with 3x moles of hydrogen to give 2x moles of ammonia.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

	N_2	H_2	NH_3
Initial number of moles	a	b	0
number of moles reacted	x	3x	0
Number of moles at equilibrium	a-x	b-3x	2x
Active mass or molar concentration at equilibrium	$\frac{a-x}{V}$	$\frac{b-3x}{V}$	$\frac{2x}{V}$

Applying law of mass action,

$$K_C = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$= \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-3x}{V}\right)^3}$$

$$= \frac{\left(\frac{4x^2}{V^2}\right)}{\left(\frac{a-x}{V}\right)\left(\frac{b-3x}{V}\right)^3}$$

$$K_C = \frac{4x^2V^2}{(a\text{-}x)\,(b\text{-}3x)^2}$$

The equilibrium constant K_p can also be calculated as follows:

$$K_p = K_C(RT)^{(\Delta n_g)}$$

$$\Delta n_g = n_p - n_r = 2 - 4 = -2$$

$$K_p = \frac{4x^2V^2}{(a-x)\,(b-3x)^3}(RT)^{-2}$$

Total number of moles at equilibrium,

n= a-x + b-3x+ 2x = a+b-2x

$$K_p = \frac{4x^2V^2}{(a-x)\,(b-3x)^3} \times \left[\frac{PV}{n}\right]^{-2}$$

$$K_p = \frac{4x^2V^2}{(a-x)\,(b-3x)^3} \times \left[\frac{n}{PV}\right]^{2}$$

$$K_p = \frac{4x^2V^2}{(a-x)\,(b-3x)^3} \times \left[\frac{a+b-2x}{PV}\right]^{2}$$

$$K_p = \frac{4x^2\,(a+b-2x)^2}{P^2\,(a-x)\,(b-3x)^3}$$

Solved Problems:

1. The equilibrium concentrations of NH_3, N_2 and H_2 are 1.8 × 10^{-2} M, 1.2 × 10^{-2} M and 3 × 10^{-2}M respectively. Calculate the equilibrium constant for the formation of NH_3 from N_2 and H_2. [Hint: M= mol lit^{-1}]

Given data:

$[NH_3] = 1.8 \times 10^{-2}\,M$

$[N_2] = 1.2 \times 10^{-2}\,M$

$[H_2] = 3 \times 10^{-2}\,M$

$K_c = ?$

Solution:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

$$K_C = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{1.8\times10^{-2}\times1.8\times10^{-2}}{1.2\times10^{-2}\times3\times10^{-2}\times3\times10^{-2}\times3\times10^{-2}}$$

$$= 1\times10^{3}\ l^{2}\ \mathrm{mol}^{-2}$$

2. The equilibrium constant at 298 K for a reaction is 100.

$$A + B \rightleftharpoons C + D$$

If the initial concentration of all the four species is 1 M, the equilibrium concentration of D (in mol lit^{-1}) will be

Given data:

$[A] = [B] = [C] = [D] = 1\,M$

$K_c = 100$

$[D]_{eq} = ?$

Solution:

Let x be the no moles of reactants reacted

	A	B	C	D
Initial concentration	1	1	1	1
At equilibrium (as per reaction stoichiometry	1-x	1-x	1+x	1+x

$$K_C = \frac{[C][D]}{[A][B]}$$

$$100 = \frac{(1+x)(1+x)}{(1-x)(1-x)}$$

$$\sqrt{100} = \sqrt{\frac{(1+x)(1+x)}{(1-x)(1-x)}}$$

$$10 = \frac{1+x}{1-x}$$

$$10(1-x) = 1+x$$

$$10 - 10x - 1 - x = 0$$

$$9 - 11x = 0$$

$$11x = 9$$

$$x = \frac{9}{11} = 0.818$$

$[D]$ eq = 1+x = 1 + 0.818 = 1.818M

Evaluate Yourself

4) 1 mol of PCl_5, kept in a closed container of volume 1 dm^3 and was allowed to attain equilibrium at 423 K. Calculate the equilibrium composition of reaction mixture. (The K_c value for PCl_5 dissociation at 423 K is 2)

8.8 Le-Chatelier's Principle

Many chemical reactions that have industrial importance such as synthesis of ammonia are reversible in nature. It is important to know the reaction conditions to produce maximum yield. If a system at equilibrium is disturbed by modifying the reaction conditions, then the system adjusts itself the new conditions to re-establish the equilibrium.

The effect of change in reaction conditions such as temperature, pressure and concentration etc… on a system at equilibrium can be predicted by Le Chatelier-Braun principle.

It states that "If a system at equilibrium is disturbed, then the system shifts itself in a direction that nullifies the effect of that disturbance."

8.8. 1 Effect of concentration

At equilibrium, the concentration of the reactants and the products does not change. The addition of more reactants or products to the reacting system at equilibrium causes an increase in their respective concentrations.

According to Le Chatelier's principle, the effect of increase in concentration of a substance is to shift the equilibrium in a direction that consumes the added substance.

Let us consider the reaction

$$\boxed{H_2(g) + I_2(g) \rightleftharpoons 2HI(g)}$$

The addition of H_2 or I_2 to the equilibrium mixture, disturbs the equilibrium. In order to minimize the stress, the system shifts the reaction in a direction where $H_2$and I_2 are consumed. i.e., the formation of additional HI would balance the effect of added reactant. Hence, the equilibrium shifts to the right (forward direction) i.e. the forward reaction takes place until the equilibrium is re-established. Similarly, removal of HI (product) also favours the forward reaction.

If HI is added to the equilibrium mixture, the concentration HI is increased, and system proceeds in the reverse direction to nullify the effect of increase in concentration of HI .

Let us explain the effect change in concentration by considering the formation of HI from H_2 and I_2. At equilibrium, the concentrations of HI, H_2 and I_2 are 1 M, 0.2 M and 0.1 M respectively.

$$\boxed{K_C = \frac{[HI]^2}{[H_2][I_2]} = \frac{1\times 1}{0.2\times 0.1} = 50}$$

The equilibrium was disturbed by adding 0.1 M iodine to the reaction mixture. After sometime, the concentration of HI is found to be 1.092 M. Let us verify whether the system proceeds to re-establish the equilibrium according to Le Chatelier's principle.

	H_2	I_2	HI
Concentration at equilibrium	0.2	0.1	1
Disturbance (Addition of 0.1 M iodine)		+0.1	
Concentration immediately after the addition of iodine	0.2	0.2	1
Change in concentration	-x	-x	2x
New concentration	0.2-x	0.2-x	1+2x

Now,

Concentration HI = 1+2x = 1.092 M

2x = 0.092

x = 0.046 M

Therefore, the concentration of hydrogen and iodine at this stage,

$$[H_2] = 0.2 - X = 0.2 - 0.046 = 0.154$$

$$[I_2] = 0.2 - X = 0.2 - 0.046 = 0.154$$

The reaction quotient Q at this stage,

$$\boxed{Q = \frac{[HI]^2}{[H_2][I_2]} = \frac{1.096 \times 1.096}{0.154 \times 0.154} \approx 50}$$

The Q value is equal to Kc value.

So, we can conclude that the system has reestablished the equilibrium at this stage and the addition of iodine results in the increase in the HI concentration.

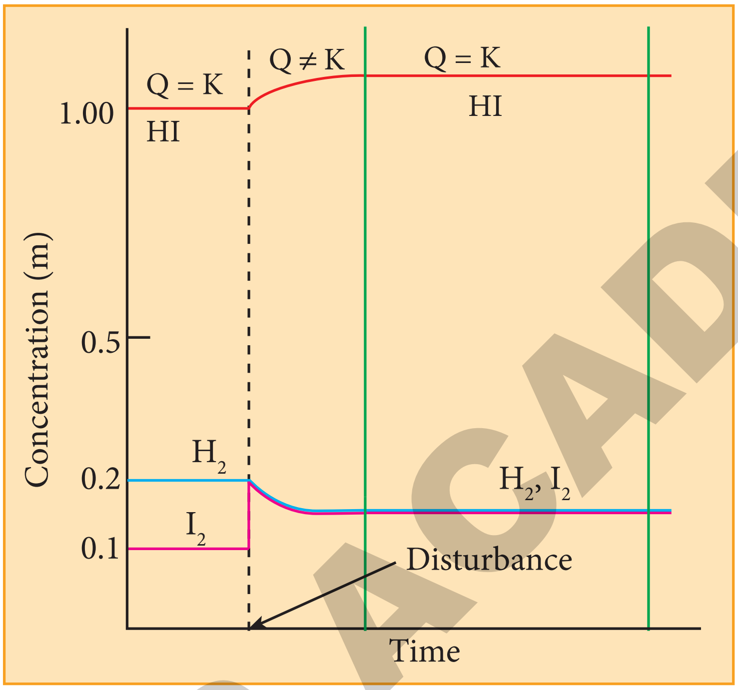


Figure 8.5 Effect of addition of iodine on formation of HI

DO YOU KNOW?

In the large scale of production of CaO from $CaCO_3$, constant removal of CO_2 from the kiln drives the reaction to completion. As in the case of manufacture of NH_3 by the Haber's process, NH_3 is liquefied and removed so that the reaction keeps moving in forward direction.

8.8.2 Effect of pressure

The change in pressure has significant effect only on equilibrium systems with gaseous components. When the pressure on the system is increased, the volume decreases proportionately and the system responds by shifting the equilibrium in a direction that has fewer moles of gaseous molecules.

Let us consider the synthesis of ammonia from nitrogen and hydrogen.

$$\boxed{N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)}$$

Let the system be allowed to attain equilibrium in a cylinder with a piston. If we press the piston down to increase the pressure, the volume decreases. The system responds to this effect by reducing the number of gas molecules. i.e. it favours the formation of ammonia. If we pull the piston upwards to reduce the pressure, the volume increases. It favours the decomposition of ammonia

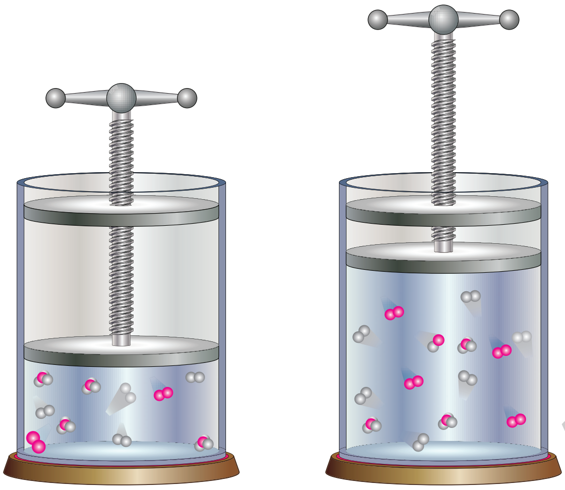


Figure 8.6 Effect of pressure on ammonia synthesis.

However, when the total number of the moles of the gaseous reactants and the gaseous products are equal, the change in pressure has no effect on system at equilibrium.

Let us consider the following reaction

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

2 moles of reactants $\Rightarrow$ 2 moles of product

Here, the number of moles of reactants and products are equal. So, the pressure has no effect on such equilibrium with $\Delta n_g = 0$.

8.8. 3 Effect of temperature

If the temperature of a system at equilibrium is changed, the system responds by shifting the equilibrium in the direction that attempts to nullify the effect of temperature.

Let us consider the formation of ammonia.

$$N_2(g) + 3H_2(g) \underset{\text{endothermic}}{\overset{\text{exothermic}}{\rightleftharpoons}} 2NH_3(g) \quad \Delta H = -92.2\ \text{kJ}$$

In this equilibrium, the forward reaction is exothermic i.e. the heat is liberated while the reverse reaction is endothermic i.e. the heat is absorbed.

If the temperature of the system is increased (by supplying heat energy), the system responds by decomposing some of the ammonia molecules to nitrogen and hydrogen by absorbing the supplied heat energy. Similarly, the system responds to a drop in the temperature by forming more ammonia molecules from nitrogen and hydrogen, which releases heat energy.

We have already learnt that the change in pressure or concentration causes a change in the equilibrium concentration such that the equilibrium constant remains the same. However, in case of change in temperature, the equilibrium is reestablished with a different equilibrium constant.

8.8.4 Effect of a catalyst

Addition of a catalyst does not affect the state of the equilibrium. The catalyst increases the rate of both the forward and the reverse reactions to the same extent. Hence, it does not change the equilibrium composition of the reaction mixture.

However, it speeds up the attainment of equilibrium by providing a new pathway having a lower activation energy.

For example, in the synthesis of NH_3 by the Haber's process iron is used as a catalyst. Similarly, in the contact process of manufacturing SO_3, platinum or V_2O_5 is used as a catalyst.

8.8.5 Effect of inert gas

When an inert gas (i.e, a gas which does not react with any other species involved in equilibrium) is added to an equilibrium system at constant volume, the total number of moles of gases present in the container increases, that is, the total pressure of gases increases. the partial pressure of the reactants and the products are unchanged. Hence at constant volume, addition of inert gas has no effect on equilibrium.

Table 8.3: Effect of concentration, pressure, temperature, catalyst and Inert gas on equilibrium

Condition	Stress	Direction in which equilibrium shifts
Concentration	Addition of reactants (increase in reactant concentration)	Forward reaction
	Removal of products (decrease in product concentration)	
	Addition of products (increase in product concentration)	Reverse reaction
	Removal of reactants (decrease in reactant concentration)	
Pressure	Increase of pressure (Decrease in volume)	Reaction that favours fewer moles of the gaseous molecules
	Decrease of pressure (Increase in volume)	Reaction that favours more moles of the gaseous molecules
Temperature(Alters equilibrium constants)	Increase (High T)	Towards endothermic reaction
	decrease (Low T)	Towards exothermic reaction
Catalyst (Speeds up the attainment of equilibrium)	Addition of catalyst	No effect
Inert gas	Addition of inert gas at constant volume	No effect

8.9 Van't Hoff Equation

This equation gives the quantitative temperature dependence of equilibrium constant (K). The relation between standard free energy change (ΔG°) and equilibrium constant is

$$\Delta G^{\circ} = -RT\ln K \qquad (1)$$

We know that

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \qquad (2)$$

Substituting (1) in equation (2)

$$-RT\ln K = \Delta H^{\circ} - T\Delta S^{\circ}$$

Rearranging

$$\ln K = \frac{-\Delta H^{o}}{RT} + \frac{\Delta S^{o}}{R} \qquad (3)$$

Differentiating equation (3) with respect to temperature,

$$\frac{d(\ln K)}{dT} = \frac{\Delta H^{o}}{RT^{2}} \qquad (4)$$

Equation 4 is known as differential form of van't Hoff equation.

On integrating the equation 4, between T_1 and T_2 with their respective equilibrium constants K_1 and K_2.

$$\int_{K_1}^{K_2} d(\ln K) = \frac{\Delta H^{o}}{R}\int_{T_1}^{T_2}\frac{dT}{T^{2}}$$

$$[\mathrm{In}K]_{K_1}^{K_2} = \frac{\Delta H^{o}}{R}\left[-\frac{1}{T}\right]_{T_1}^{T_2}$$

$$\mathrm{In}\,K_2 - \mathrm{In}\,K_1 = \frac{\Delta H^{o}}{R}\left[-\frac{1}{T_2} + \frac{1}{T_1}\right]$$

$$\mathrm{In}\frac{K_2}{K_1} = \frac{\Delta H^{o}}{R}\left[\frac{T_2 - T_1}{T_2T_1}\right]$$

$$\log\frac{K_2}{K_1} = \frac{\Delta H^{o}}{2.303\,R}\left[\frac{T_2 - T_1}{T_2T_1}\right] \qquad \text{............ (5)}$$

Equation 5 is known as integrated form of van't Hoff equation.

Problem:

For an equilibrium reaction K_p = 0.0260 at 25°C ΔH=32.4kJmol^{-1}, calculate K_p at 37° C

Solution :

T_1=25 + 273 = 298 K

T_2 = 37 + 273 = 310 K

ΔH = 32.4 KJmol^{-1} = 32400 Jmol^{-1}

R=8.314 JK^{-1} mol^{-1}

K_{P1}= 0.0260

K_{p2} = ?

$$\log\frac{K_2}{K_1} = \frac{\Delta H^{o}}{2.303\,R}\left[\frac{T_2 - T_1}{T_2T_1}\right]$$

$$\log\frac{K_2}{K_1} = \frac{32400}{2.303\times 8.314}\left(\frac{310-298}{310\times 298}\right)$$

$$= \frac{32400\times 12}{2.303\times 8.314\times 310\times 298}$$

$$= 0.2198$$

$$\frac{K_2}{K_1} = \text{anti}\log 0.2198 = 1.6588$$

$$K_2 = 1.6588\times 0.026 = 0.0431$$

Evaluate Yourself

5) The equilibrium constant for the following reaction is 0.15 at 298 K and 1 atm pressure.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g);$$

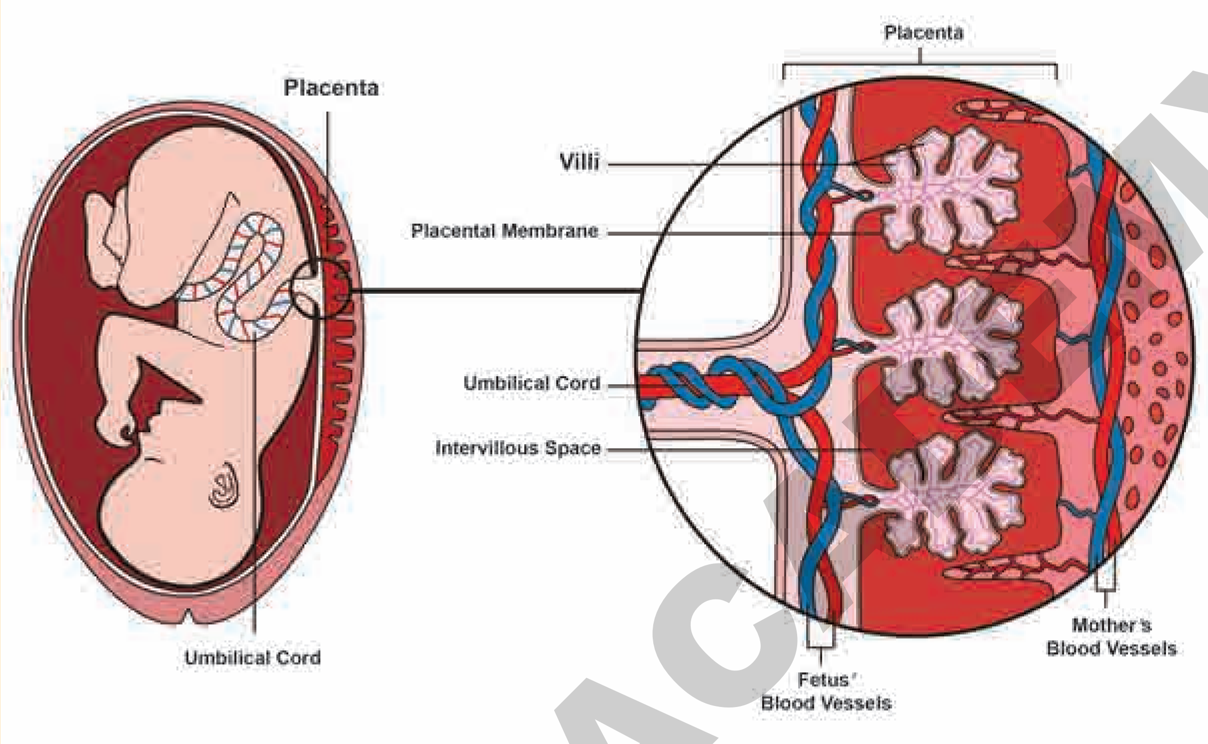
$$\Delta H^{o}_{f} = 57.32\ \text{KJmol}^{-1}$$

The reaction conditions are altered as follows.

a) The reaction temperature is altered to 100° C keeping the pressure at 1 atm, Calculate the equilibrium constant.

DO YOU KNOW?

How does oxygen exchanges between maternal and fetal blood in a pregnant women?



In a pregnant women, the oxygen supply for fetus is provided by the maternal blood in the placenta where the blood vessels of both mother and fetus are in close proximity. Both fetal and maternal hemoglobin binds to oxygen reversibly as follows.

$$\text{Hb(mother)} + O_2 \rightleftharpoons \text{HbO}_2 \text{ (mother)}$$

$$\text{Hb(fetus)} + O_2 \rightleftharpoons \text{HbO}_2 \text{ (Fetus)}$$

In the above two equilibriums, the equilibrium constant value for the oxygenation of fetal hemoglobin is higher, which is due to its higher affinity for oxygen compared to the adult hemoglobin. Hence in placenta, the oxygen from the mother's blood is effectively transferred to the fetal hemoglobin

SUMMARY

- In our daily life, we observe several chemical and physical changes.
- In some chemical reactions, at a particular stage, the rate of the reverse reaction is equal to that of the forward reaction indicating a state of equilibrium.

There are different types of equilibrium.

Physical equilibrium

Chemical Equilibrium

- Chemical reactions which are reversible do not cease, when equilibrium is attained. At equilibrium the forward and the backward reactions are proceeding at the same rate and no macroscopic change is observed. So chemical equilibrium is in a state of dynamic equilibrium.
- The rate law states that, "At any instant, the rate of a chemical reaction at a given temperature is directly proportional to the product of the active masses of the reactants at that instant".
- The value of equilibrium constant, Kc tells us the extent of a reaction, i.e., it indicates how far the reaction has proceeded towards product formation at a given temperature.
- Under non-equilibrium conditions, reaction quotient 'Q' is defined as the ratio of the product of active masses of reaction products raised to the respective stoichiometric coefficients in the balanced chemical equation to that of the reactants.
- Le-Chatelier's Principle "If a system at equilibrium is disturbed, then the system shifts itself in a direction that nullifies the effect of that disturbance."
- The effect of change in reaction conditions such as temperature, pressure and concentration etc… on a system at equilibrium can be predicted by Le Chatelier-Braun principle.
- vant Hoff equation This equation gives the quantitative temperature dependence of equilibrium constant (K).

Evaluation

1. If K_b and K_f for a reversible reactions are 0.8×10^{-5} and 1.6×10^{-4} respectively, the value of the equilibrium constant is,

a) 20 b) 0.2×10^{-1}

c) 0.05 d) none of these

2. At a given temperature and pressure, the equilibrium constant values for the equilibria

$$3A_2 + B_2 + 2C \xrightleftharpoons{K_1} 2A_3BC \text{ and}$$

$$A_3BC \xrightleftharpoons{K_2} {}^3\!/_2[A_2] + \frac{1}{2}B_2 + C$$

The relation between K_1 and K_2 is

a) $K_1 = \frac{1}{\sqrt{K_2}}$ b) $K_2 = K_1^{-1/2}$

c) $K_1^2 = 2K_2$ d) $\frac{K_1}{2} = K_2$

3. The equilibrium constant for a reaction at room temperature is K1 and that at 700 K is K2. If K1 > K2, then

a) The forward reaction is exothermic

b) The forward reaction is endothermic

c) The reaction does not attain equilibrium

d) The reverse reaction is exothermic

4. The formation of ammonia from $N_2(g)$ and $H_2(g)$ is a reversible reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + \text{Heat}$$

What is the effect of increase of temperature on this equilibrium reaction

a) equilibrium is unaltered

b) formation of ammonia is favoured

c) equilibrium is shifted to the left

d) reaction rate does not change

5. Solubility of carbon dioxide gas in cold water can be increased by

a) increase in pressure

b) decrease in pressure

c) increase in volume

d) none of these

6 Which one of the following is incorrect statement ?

a) for a system at equilibrium, Q is always less than the equilibrium constant

b) equilibrium can be attained from either side of the reaction

c) presence of catalyst affects both the forward reaction and reverse reaction to the same extent

d) Equilibrium constant varied with temperature

7. K_1 and K_2 are the equilibrium constants for the reactions respectively.

$$N_2(g) + O_2(g) \xrightleftharpoons{K_1} 2NO(g)$$

$$2NO(g) + O_2(g) \xrightleftharpoons{K_2} 2NO_2\,(g)$$

What is the equilibrium constant for the reaction $NO_2(g) \rightleftharpoons \frac{1}{2}N_2(g) + O_2(g)$

a) $\dfrac{1}{\sqrt{K_1K_2}}$ b) $(K_1 = K_2)^{1/2}$

c) $\dfrac{1}{2K_1K_2}$ d) $\left(\dfrac{1}{K_1K_2}\right)^{3/2}$

8. In the equilibrium,

$$2A(g) \rightleftharpoons 2B(g) + C_2(g)$$

the equilibrium concentrations of A, B and C_2 at 400 K are 1×10^{-4} M, 2.0×10^{-3} M, 1.5×10^{-4} M respectively. The value of K_C for the equilibrium at 400 K is

a) 0.06 b) 0.09

c) 0.62 d) 3×10^{-2}

9. An equilibrium constant of 3.2×10^{-6} for a reaction means, the equilibrium is

a) largely towards forward direction

b) largely towards reverse direction

c) never established

d) none of these

10. $\dfrac{K_C}{K_P}$ for the reaction,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \text{ is}$$

a) $\dfrac{1}{RT}$ b) $\sqrt{RT}$

c) RT d) $(RT)^2$

11. For the reaction AB (g) ⇌ A(g) + B(g), at equilibrium, AB is 20% dissociated at a total pressure of P, The equilibrium

constant K_P is related to the total pressure by the expression

a) $P = 24\ K_P$ b) $P = 8\ K_P$

c) $24\ P = K_P$ d) none of these

12. In which of the following equilibrium, K_P and K_C are not equal?

a) $2\ NO(g) \rightleftharpoons N_2(g) + O_2(g)$

b) $SO_2\ (g) + NO_2 \rightleftharpoons SO_3(g) + NO(g)$

c) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

d) $PCl_5\ (g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

13. If x is the fraction of PCl_5 dissociated at equilibrium in the reaction

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$

then starting with 0.5 mole of PCl_5, the total number of moles of reactants and products at equilibrium is

a) 0.5 – x b) x + 0.5

c) 2x + 0.5 d) x + 1

14. The values of K_{P_1} and K_{P_2} for the reactions

$X \rightleftharpoons Y + Z$

$A \rightleftharpoons 2B$ are in the ratio 9 : 1 if degree of dissociation and initial concentration of X and A be equal then total pressure at equilibrium P_1, and P_2 are in the ratio

a) 36 : 1 b) 1 : 1

c) 3 : 1 d) 1 : 9

15. In the reaction,

$Fe\ (OH)_3\ (s) \rightleftharpoons Fe^{3+}(aq) + 3OH^-(aq)$,

if the concentration of OH^- ions is decreased by ¼ times, then the equilibrium concentration of Fe^{3+} will

a) not changed

b) also decreased by ¼ times

c) increase by 4 times

d) increase by 64 times

16. Consider the reaction where $K_P = 0.5$ at a particular temperature

$PCl_5(g) \rightleftharpoons PCl_3\ (g) + Cl_2\ (g)$

if the three gases are mixed in a container so that the partial pressure of each gas is initially 1 atm, then which one of the following is true

a) more PCl_3 will be produced

b) more Cl_2 will be produced

c) more PCl_5 will be produced

d) none of these

17. Equimolar concentrations of H_2 and I_2 are heated to equilibrium in a 1 litre flask. What percentage of initial concentration of H_2 has reacted at equilibrium if rate constant for both forward and reverse reactions are equal

a) 33% b) 66%

c) $(33)^2$ % d) 16.5 %

18. In a chemical equilibrium, the rate constant for the forward reaction is 2.5×10^2 and the equilibrium constant is 50. The rate constant for the reverse reaction is,

a) 11.5 b) 5

c) 2×10^2 d) 2×10^{-3}

19. Which of the following is not a general

characteristic of equilibrium involving physical process

a) Equilibrium is possible only in a closed system at a given temperature

b) The opposing processes occur at the same rate and there is a dynamic but stable condition

c) All the physical processes stop at equilibrium

d) All measurable properties of the system remains constant

20. For the formation of Two moles of $SO_3(g)$ from SO_2 and O_2, the equilibrium constant is K_1. The equilibrium constant for the dissociation of one mole of SO_3 into SO_2 and O_2 is

a) $1/K_1$ b) K_1^2

c) $\left(\frac{1}{K_1}\right)^{1/2}$ d) $\frac{K_1}{2}$

21. Match the equilibria with the corresponding conditions,

i) Liquid ⇌ Vapour

ii) Solid ⇌ Liquid

iii) Solid ⇌ Vapour

iv) Solute (s) ⇌ Solute (Solution)

1) melting point

2) Saturated solution

3) Boiling point

4) Sublimation point

5) Unsaturated solution

	(i)	(ii)	(iii)	(iv)
(a)	1	2	3	4
(b)	3	1	4	2
(c)	2	1	3	4
(d)	3	2	4	5

22. Consider the following reversible reaction at equilibrium, $A + B \rightleftharpoons C$, If the concentration of the reactants A and B are doubled, then the equilibrium constant will

a) be doubled b) become one fourth

c) be halved d) remain the same

23. $[Co(H_2O)_6]^{2+}$ (aq) (pink) + $4Cl^-$ (aq) ⇌ $[CoCl_4]^{2-}$ (aq) (blue)+ 6 H_2O (*l*)

In the above reaction at equilibrium, the reaction mixture is blue in colour at room temperature. On cooling this mixture, it becomes pink in colour. On the basis of this information, which one of the following is true ?

a) $\Delta H > 0$ for the forward reaction

b) $\Delta H = 0$ for the reverse reaction

c) $\Delta H < 0$ for the forward reaction

d) Sign of the ΔH cannot be predicted based on this information.

24. The equilibrium constants of the following reactions are :

$N_2 + 3H_2 \rightleftharpoons 2NH_3$; K_1

$N_2 + O_2 \rightleftharpoons 2NO$; K_2

$H_2 + ½O_2 \rightleftharpoons H_2O$; K_3

The equilibrium constant (K) for the reaction ;

$2NH_3 + 5/2\, O_2 \xrightleftharpoons{K} 2NO + 3H_2O$, will be

a) $K_2^3 K_3 / K_1$ b) $K_1 K_3^3 / K_2$

c) $K_2 K_3^3 / K_1$ d) $K_2 K_3 / K_1$

25. A 20 litre container at 400 K contains CO_2 (g) at pressure 0.4 atm and an excess of SrO (neglect the volume of solid SrO). The volume of the container is now decreased by moving the movable piston fitted in the container. The maximum volume of the container, when pressure of CO_2 attains its maximum value will be :

Given that : $SrCO_3$ (S) $\rightleftharpoons$ SrO (S) + CO_2(g)

K_P = 1.6 atm (NEET 2017)

a) 2 litre b) 5 litre

c) 10 litre d) 4 litre

26. If there is no change in concentration, why is the equilibrium state considered dynamic ?

27. For a given reaction at a particular temperature, the equilibrium constant has constant value. Is the value of Q also constant ? Explain.

28. What the relation between K_P and K_C. Give one example for which K_P is equal to K_C.

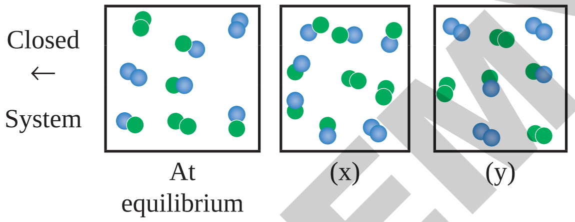
29. For a gaseous homogeneous reaction at equilibrium, number of moles of products are greater than the number of moles of reactants. Is K_C is larger or smaller than K_P.

30. When the numerical value of the reaction quotient (Q) is greater than the equilibrium constant (K), in which direction does the reaction proceed to reach equilibrium ?

31. For the reaction,

$A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$; ΔH is –ve.

the following molecular scenes represent different reaction mixture (A – green, B – blue)



i) Calculate the equilibrium constant K_P and (K_C).

ii) For the reaction mixture represented by scene (x), (y) the reaction proceed in which directions ?

iii) What is the effect of increase in pressure for the mixture at equilibrium.

32. State Le-Chatelier principle.

33. Consider the following reactions,

a) $H_2(g) + I_2(g) \rightleftharpoons 2\,HI$

b) $CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2(g)$

c) $S(s) + 3F_2\,(g) \rightleftharpoons SF_6\,(g)$

In each of the above reaction find out whether you have to increase (or) decrease the volume to increase the yield of the product.

34. State law of mass action.

35. Explain how will you predict the direction of a equilibrium reaction.

36. Derive a general expression for the equilibrium constant K_P and K_C for the reaction

$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$

37. Write a balanced chemical equation for a equilibrium reaction for which the equilibrium constant is given by expression

$$K_C = \frac{[NH_3]^4\,[O_2]^5}{[NO]^4\,[H_2O]^6}$$

38. What is the effect of added inert gas on the reaction at equilibrium.

39. Derive the relation between K_P and K_C.

40. One mole of PCl_5 is heated in one litre closed container. If 0.6 mole of chlorine is found at equilibrium, calculate the value of equilibrium constant.

41. For the reaction

$SrCO_3(s) \rightleftharpoons SrO(s) + CO_2(g)$,

the value of equilibrium constant $K_P = 2.2 \times 10^{-4}$ at 1002 K. Calculate K_C for the reaction.

42. To study the decomposition of hydrogen iodide, a student fills an evacuated 3 litre flask with 0.3 mol of HI gas and allows the reaction to proceed at 500 ^{0}C. At equilibrium he found the concentration of HI which is equal to 0.05 M. Calculate K_C and K_P.

43. Oxidation of nitrogen monoxide was studied at 200 ^{0}C with initial pressures of 1 atm NO and 1 atm of O_2. At equilibrium partial pressure of oxygen is found to be 0.52 atm calculate K_P value.

44. 1 mol of CH_4, 1 mole of CS_2 and 2 mol of H_2S are 2 mol of H_2 are mixed in a 500 ml flask. The equilibrium constant for the reaction $K_C = 4 \times 10^{-2}$ mol^2 lit^{-2}. In which direction will the reaction proceed to reach equilibrium ?

45. At particular temperature $K_C = 4 \times 10^{-2}$ for the reaction

$H_2S(g) \rightleftharpoons H_2(g) + \frac{1}{2} S_2(g)$

Calculate K_C for each of the following reaction

i) $2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$

ii) $3H_2S(g) \rightleftharpoons 3H_2(g) + \frac{3}{2} S_2(g)$

46. 28 g of Nitrogen and 6 g of hydrogen were mixed in a 1 litre closed container. At equilibrium 17 g NH_3 was produced. Calculate the weight of nitrogen, hydrogen at equilibrium.

47. The equilibrium for the dissociation of XY_2 is given as,

$2XY_2(g) \rightleftharpoons 2XY(g) + Y_2(g)$

if the degree of dissociation x is so small compared to one. Show that

$2K_P = PX^3$ where P is the total pressure and K_P is the dissociation equilibrium constant of XY_2.

48. A sealed container was filled with 1 mol of $A_2(g)$, 1 mol $B_2(g)$ at 800 K and total pressure 1.00 bar. Calculate the amounts of the components in the mixture at equilibrium given that K = 1 for the reaction

$A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$

49. Deduce the Vant Hoff equation.

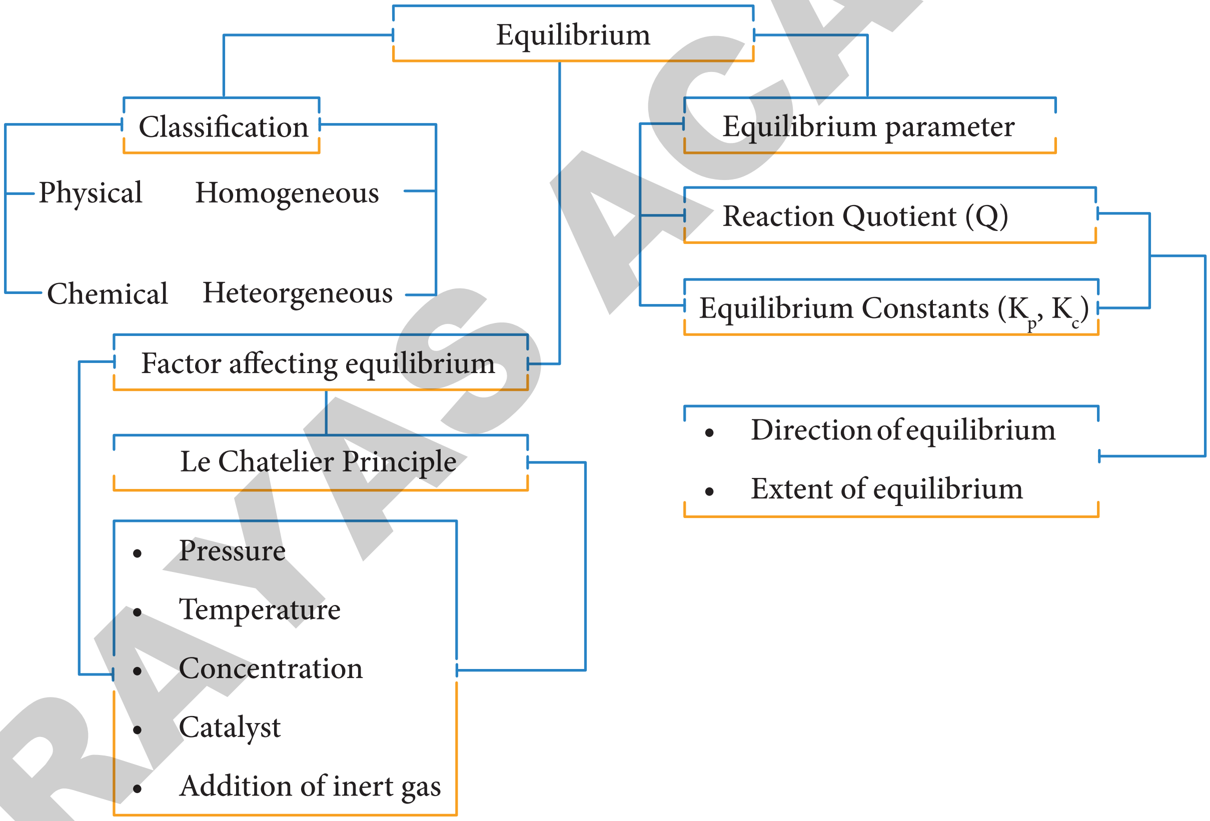
50. The equilibrium constant K_p for the reaction

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is 8.19×10^2 at 298 K and 4.6×10^{-1} at 498 K. Calculate ΔH^0 for the reaction.

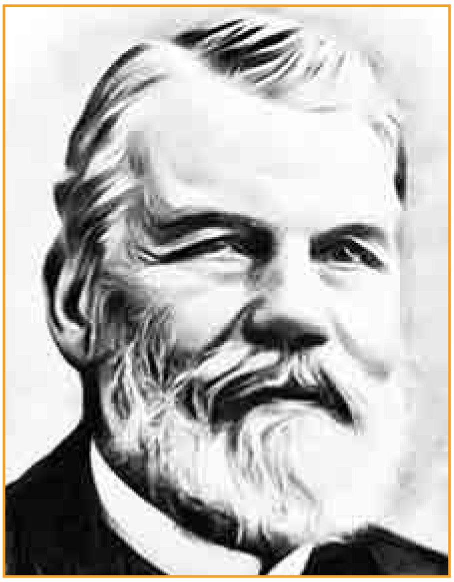
51. The partial pressure of carbon dioxide in the reaction

$CaCO_3$ (s) $\rightleftharpoons$ CaO (s) + $CO_2(g)$ is 1.017×10^{-3} atm at 500^0 C. Calculate K_p at 600^0c C for the reaction. ΔH for the reaction is 181 KJ mol^{-1} and does not change in the given range of temperature.

CONCEPT MAP



Unit 9 Solutions



François - Marie Raoult

François - Marie Raoult was a French chemist who conducted research into the behaviour of solutions, especially their physical properties.

In his first research paper, he described the action of solutes in depressing the freezing point of the solutions. He also gave a relation between the vapour pressure of the solution with the molecular wight of the solute.

Learning Objectives

After studying this unit students will be able to

- describe the formation of different types of solutions
- express the concentration of a solution in different units
- prepare solutions of required concentrations by diluting the stock solution
- state Henry's and Raoult's Law
- explain the deviation of real solutions from Raoult's Law
- correlate colligative properties of solutions with the molar masses of their solutes
- explain the abnormal colligative properties
- define Van't Hoff factor and calculate degree of dissociation / association

9.1 INTRODUCTION

There are many chemicals that play an important role in our daily life. All these chemicals are in different physical forms, viz solid, liquid and gas. If we do close examination on their composition, we could find that most of them are mixtures and rarely pure substances. One more interesting aspect is that most of the mixtures are homogeneous irrespective of their physical state and such homogeneous mixtures are called as solutions.

Sea water is one of the naturally existing solutions which covers more than 70% of the earth's surface. We cannot imagine life on earth without sea water. It contains many dissolved solids, mostly NaCl. Another important naturally occurring solution is air. Air is a homogeneous mixture of nitrogen, oxygen, carbon dioxide, and other trace gases. Even solid material such as brass is a homogeneous mixture of copper and zinc.

In the above examples the solutions are in different physical states viz... liquid (sea water), gas (air) and solid (alloys), and one common property of all the above is their homogeneity. The homogeneity implies uniform distribution of their constituents or components throughout the mixture. In this chapter, we learn about the solutions and their properties.

9.2 Types of solutions

A solution is a homogeneous mixture of two or more substances, consisting of atoms, ions or molecules. The compound that is present in largest amount in a homogeneous mixture is called the solvent, and the others are solutes. For example, when a small amount of NaCl is dissolved in water, a homogeneous solution is obtained. In this solution, Na^+ and Cl^- ions are uniformly distributed in water. Here water is the solvent as the amount of water is more compared to the amount of NaCl present in this solution, and the NaCl is the solute.

The commonly used solutions are the solutions in which a solid solute is dissolved in a liquid solvent. However, solute or solvent can be in any of the three states of matter (solid, liquid, gas). If the water is used as the solvent,the resultant solution is called as an aqueous solution. If solvents (Benzene, CCl_4, ether etc.,) other than water is used, then the resultant solution is called as a non-aqueous solution.

The following table illustrates the different type of solutions based on the physical state of the solute and solvent.

Table 9.1 Types and examples of solutions

S. No.	State of solution	Solute	Solvent	Examples
1	Gaseous solution	Gas	Gas	Air (A mixture of nitrogen, oxygen and other gases)
		Liquid	Gas	Humid oxygen (Oxygen containing water)
		Solid	Gas	Camphor in nitrogen gas
2	Liquid solutions	Gas	Liquid	CO_2 dissolved in water (carbonated water)
		Liquid	Liquid	Ethanol dissolved in water
		Solid	Liquid	Salt water
3	Solid solutions	Gas	Solid	Solution of H_2 in palladium
		Liquid	Solid	Amalgam of potassium (used for dental filling)
		Solid	Solid	Gold alloy (of copper used in making Jewelery)

9.3 Expressing concentration of solutions

In our life we have come across many solutions of varying strengths or concentrations such as mouthwash, antiseptic solutions, household disinfectants etc... Have you ever noticed the concentration of the ingredients present in those solutions? For example, chlorhexidine mouthwash solution contains 0.2 % (w/v) chlorhexidine gluconate; The concentration of the commercially available hydrogen peroxide is 3% (w/v). Similarly, other terms such as ppm (TDS of water), molar and normal (laboratory reagents) are used to express the concentration of the solution. The concentration of a solution gives the amount of solute present in a given quantity of solvent. As we have seen, there are different ways of expressing the concentration of a solutions. Let us learn the different concentration terms and to prepare a solution of a specific concentration.

Table 9.2 Different concentration units and their illustrations

S. No.	Concentration term	Expression	Illustration
1	Molality (m)	$\frac{\text{Number ofmoles of solute}}{\text{Mass of the solvent (in kg)}}$	The molality of the solution containing 45 g of glucose dissolved in 2 kg of water $\frac{\text{Number ofmoles of solute}}{\text{Mass of the solvent (in kg)}} = \frac{\left(\frac{45}{180}\right)}{2}$ $= \frac{0.25}{2} = 0.125\text{ m}$
2	Molarity (M)	$\frac{\text{Number ofmoles of solute}}{\text{Volume of solution (in L)}}$	5.845 g of sodium chloride is dissolved in water and the solution was made up to 500 mL using a standard flask. The strength of the solution in molarity is $\frac{\text{Number ofmoles of solute}}{\text{Volume of solution (in L)}} = \frac{\left(\frac{5.845}{58.45}\right)}{0.5}$ $\frac{0.1}{0.5} = 0.2\text{ M}$
3	Normality (N)	$\frac{\text{Number of gram equivalents of solute}}{\text{Volume of solution (in L)}}$	3.15 g of oxalic acid dihydrate, is dissolved in water and the solution was made up to 100 mL using a standard flask. The strength of the solution in normality is $= \frac{\text{Number of gram equivalents of solute}}{\text{Volume of solution (in L)}}$ $= \frac{\left(\frac{\text{mass of oxalic acid}}{\text{Equivalent mass of oxalic acid}}\right)}{\text{volume of solution (inL)}} = \frac{\left(\frac{3.15}{63}\right)}{0.1}$ $= \frac{0.05}{0.1} = 0.5\text{ N}$

S. No.	Concentration term	Expression	Illustration
4	Formality (F)	$\frac{\text{Number of Formula weight of solute}}{\text{Volume of solution (in L)}}$	5.85g of sodium chloride is dissolved in water and the solution was made up to 500 mL using a standard flask. The strength of the solution in formality is $\text{formality} = \frac{\text{Number of Formula weight of solute}}{\text{Volume of solution (in L)}}$ $= \frac{5.85}{58.5 \times 0.5\text{L}}$ $= 0.2\text{ F}$
4	Mole fraction (of a component) (x)	$\frac{\text{Number of moles of the component}}{\text{Total number of moles of all the components present in solution}}$ Consider a solution containing two components A and B whose mole fractions are x_A and x_B, respectively. Let the number of moles of the two components A and B be n_A and n_B, respectively. $x_A = \frac{n_A}{n_A + n_B}$ and $x_B = \frac{n_B}{n_A + n_B}$ Now, $x_A + x_B = \frac{n_A}{n_A + n_B} + \frac{n_B}{n_A + n_B} = 1$	0.5 mole of ethanol is mixed with 1.5 moles of water. The mole fraction of ethanol in the above solution is $= \frac{\text{Number of moles of the ethanol}}{\text{Total number of moles of ethanol and water}}$ $= \frac{0.5}{1.5+0.5} = \frac{0.5}{2.0} = 0.25$ The mole fraction of water in the above solution is $= \frac{\text{Number of moles of water}}{\text{Total number of moles of ethanol and water}}$ $= \frac{1.5}{2.0} = 0.75$ The mole fraction of water can also be calculated as follows mole fraction of water + mole fraction of ethanol = 1; mole fraction of water = 1 – mole fraction of ethanol = 1-0.25 = 0.75
5	Mass percentage (% w/w)	$\frac{\text{Mass of the solute (in g)}}{\text{Mass of solution (in g)}} \times 100$	Neomycin, aminoglycoside antibiotic cream contains 300 mg of neomycin sulphate the active ingredient, in 30g of ointment base. The mass percentage of neomycin is $\frac{\text{Mass of the neomycin sulphate (in g)}}{\text{Mass of solution (in g)}} \times 100$ $= \frac{0.3\text{ g}}{30\text{ g}} \times 100 = 1\%\text{ w/w}$

S. No.	Concentration term	Expression	Illustration
6	Volume percentage (% v/v)	$\frac{\text{Volume of the solute (in mL)}}{\text{Volume of solution (in mL)}}\times 100$	50 mL of tincture of benzoin, an antiseptic solution contains 10 mL of benzoin. The volume percentage of benzoin $=\frac{\text{Volume of the benzoin (in mL)}}{\text{Volume of solution (in mL)}}\times 100$ $=\frac{10}{50}\times 100 = 20\%\ v/v$
7	Mass by volume percentage (% w/v)	$\frac{\text{Mass of the solute (in g)}}{\text{Volume of solution (in mL)}}\times 100$	A 60 mL of paracetamol pediatric oral suspension contains 3g of paracetamol. The mass percentage of paracetamol is $\frac{\text{Mass of the paracetamol (in g)}}{\text{Volume of solution (in mL)}}\times 100 =$ $=\frac{3}{60}\times 100 = 5\%\ w/v$
8	Parts per million (ppm)	$\frac{\text{Number of parts of the component}}{\text{Total number of parts of all components}}\times 10^6$ $=\frac{\text{Mass of the solute}}{\text{Mass of the solution}}\times 10^6$	50 mL of tap water contains 20 mg of dissolved solids. The TDS value in ppm is $\frac{\text{Mass of the dissolved solids}}{\text{Mass of the water}}\times 10^6$ $\frac{20\times 10^{-3}\ g}{50\ g}\times 10^6 = 400\ ppm$

Evaluate Yourself

1) If 5.6 g of KOH is present in (a) 500 mL and (b) 1 litre of solution, calculate the molarity of each of these solutions.

2) 2.82 g of glucose is dissolved in 30 g of water. Calculate the mole fraction of glucose and water.

3) The antiseptic solution of iodopovidone for the use of external application contains 10 % w/v of iodopovidone. Calculate the amount of iodopovidone present in a typical dose of 1.5 mL.

4) A litre of sea water weighing about 1.05 kg contains 5 mg of dissolved oxygen (O_2). Express the concentration of dissolved oxygen in ppm.

The concentration of a solution is expressed in different units. The choice of unit depends on the type of measurement applied. For example,in complexometric titrations involving EDTA, the reaction between EDTA and the metal ions takes place in the 1:1 mole ratio and hence molar solutions are used in this titrations. In the redox and neutralisation titrations we use normality. The mole fraction is used to calculate the partial pressure of gases and the vapour pressure of solutions. The percentage units are used to express the active ingredients present in therapeutics, and the ppm is used to express the quantity of solutes present in small amounts in solutions.

9.3.1 Standard solutions and working standards

A standard solution or a stock solution is a solution whose concentration is accurately known. A standard solution of required concentration can be prepared by dissolving a required amount of a solute, in a suitable amount of solvent. Its done by transforming a known amount of a solute to a standard flask of definite volume. A small amount of water is added to the flask and shaken well to dissolve the salt.. Then water is added to the flask to bring the solution level to the mark indicated at the top end of the flask. The flask is stoppered and shaken well to make concentration uniform.

At the time of experiment, the solution with required concentration is prepared by diluting the stock solution. This diluted solution is usually called working standard. A known volume of stock solution is transferred to a new container and brought to the calculated volume. The necessary volumes of the stock solution and final volume can be calculated using the following expression.

$$C_s V_s = C_w V_w \qquad (9.1)$$

Where the C_s &V_s are concentration and the volume of the stock solution and C_w & V_w are concentration and the volume of the working standard, respectively.

9.3.2 Advantages of using standard solutions:

1. The error due to weighing the solute can be minimised by using concentrated stock solution that requires large quantity of solute.

2. We can prepare working standards of different concentrations by diluting the stock solution, which is more efficient since consistency is maintained.

3. Some of the concentrated solutions are more stable and are less likely to support microbial growth than working standards used in the experiments.

Example Problem

1. What volume of 4M HCl and 2M HCl should be mixed to get 500 mL of 2.5 M HCl?

Let the volume of 4M HCl required to prepare 500 mL of 2.5 MHCl = x mL

Therefore, the required volume of 2M HCl = (500 - x) mL

We know from the equation (9.1)

$$\begin{aligned} C_1V_1 + C_2V_2 &= C_3V_3 \\ (4x)+2(500-x) &= 2.5 \times 500 \\ 4x+1000-2x &= 1250 \\ 2x &= 1250 - 1000 \\ x &= \frac{250}{2} \\ &= 125 \text{ mL} \end{aligned}$$

Hence, volume of 4M HCl required = 125 mL

Volume of 2M HCl required = (500 - 125) mL= 375 mL

Evaluate Yourself

5) Describe how would you prepare the following solution from pure solute and solvent

   (a) 1 L of aqueous solution of 1.5 M $CoCl_2$.

   (b) 500 mL of 6.0 % (V/V) aqueous methanol solution.

6) How much volume of 6 M solution of NaOH is required to prepare 500 mL of 0.250 M NaOH solution.

9.4 Solubility of the solutes

Solubility of a solute is the maximum amount of solute that can be dissolved in a specific amount of solvent at a specified temperature. When maximum amount of solute is dissolved in a solvent, any more addition of solute will result in precipitation at a given temperature and pressure. Such a solution is called as a saturated solution. The solubility of a substance at a given temperature is defined as the amount of the solute that can be dissolved in 100 g of the solvent at a given temperature to form a saturated solution.

9.4.1 Factors influencing the solubility

The solubility of a solute generally depends on the nature of the solute and the solvent in which it is dissolved. It also depends on the temperature and pressure of the solution.

Nature of solute and solvent:

Sodium chloride, an ionic compound, dissolves readily in a polar solvent such as water, but it does not dissolve in non-polar organic solvents such as benzene or toluene. Many organic compounds dissolve readily in organic solvents and do not dissolve in water. Different gases dissolve in water to different extents: for example, ammonia is more soluble than oxygen in water.

Effect of temperature:

Solid solute in liquid solvent:

Generally, the solubility of a solid solute in a liquid solvent increases with increase in temperature. When the temperature is increased, the average kinetic energy of the molecules of the solute and the solvent increases. The increase in kinetic energy facilitates the solvent molecules to break the intermolecular attractive forces that keep the solute molecules together and hence the solubility increases.

When a solid is added to a solvent, it begins to dissolve. i.e. the solute leaves from the solid state (dissolution). After some time, some of the dissolved solute returns back to the solid state (recrystallisation). If there is excess of solid present, the rate of both these processes becomes equal at a particular stage. At this stage an equilibrium is established between the solid solute molecules and dissolved solute molecules.

$$\boxed{\text{Solute (solid)} \leftrightarrows \text{Solute (dissolved)}}$$

According to Le-Chatelier principle, if the dissolution process is endothermic, the increase in temperature will shift the equilibrium towards left i.e solubility increases. for an exothermic reaction, the increase in temperature decreases the solubility. The solubilities of ammonium nitrate, calcium chloride, ceric sulphate nano-hydrate and sodium chloride in water at different temperatures are given in the following graph.

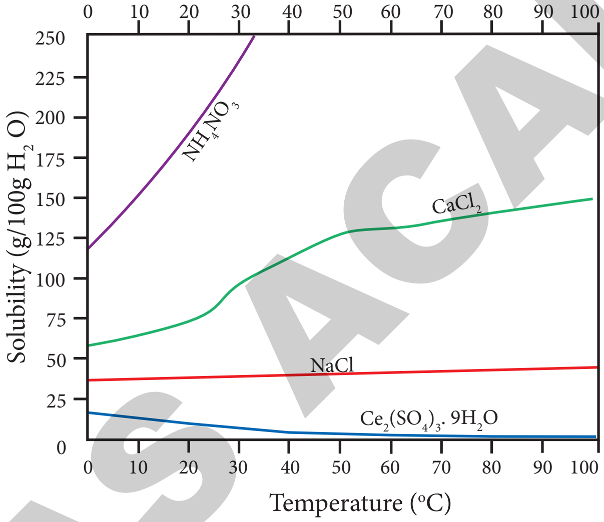


Figure 9. 1 Plot of solubility versus temperature for selective compounds

The following conclusions are drawn from the above graph.

- The solubility of sodium chloride does not vary appreciably as the maximum solubility is achieved at normal temperature. In fact, there is only 10 % increase in solubility between 0 ° to 100 °C.
- The dissolution process of ammonium nitrate is endothermic, the solubility increases steeply with increase in temperature.
- In the case of ceric sulphate, the dissolution is exothermic and the solubility decreases with increase in temperature.
- Even though the dissolution of calcium chloride is exothermic, the solubility increases moderately with increase in temperature. Here, the entropy factor also plays a significant role in deciding the position of the equilibrium.

Gaseous solute in liquid solvent:

In the case of gaseous solute in liquid solvent, the solubility decreases with increase in temperature. When a gaseous solute dissolves in a liquid solvent, its molecules interact with solvent molecules with weak intermolecular forces. When the temperature increases, the average kinetic energy of the molecules present in the solution also increases. The increase in kinetic energy breaks the weak intermolecular forces between the gaseous solute and liquid solvent which results in the release of the dissolved gas molecules to the gaseous state. Moreover, the dissolution of most of the gases in liquid solvents is an exothermic process, and in such processes, the increase in temperature decreases the dissolution of gaseous molecules.

Activity:

Open the soda bottle and put a balloon over it. The balloon will inflate with the released carbon dioxide from the soda. Carry out the same experiment by placing the soda bottle in a container of hot water. You will observe the balloon is inflated much faster now. This shows the decrease in solubility of gases in solution with increase in temperature. In the rivers where hot water is discharged from industrial plants, the aquatic lives are less sustained due to the decreased availability of dissolved oxygen.

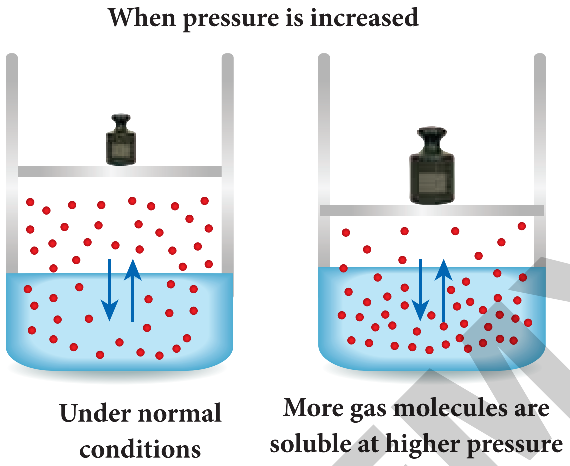


Figure 9.2 Effect of pressure on solubility

Effect of pressure:

Generally the change in pressure does not have any significant effect in the solubility of solids and liquids as they are not compressible. However, the solubility of gases generally increases with increase of pressure.

Consider a saturated solution of a gaseous solute dissolved in a liquid solvent in a closed container. In such a system, the following equilibrium exists.

Gas (in gaseous state) ⇆ Gas (in solution)

According to Le-Chatelier principle, the increase in pressure will shift the equilibrium in the direction which will reduce the pressure. Therefore, more number of gaseous molecules dissolves in the solvent and the solubility increases.

9.5 Henry's law

William Henry investigated the relationship between pressure and solubility of a gaseous solute in a particular solvent. According to him, “the partial pressure of the gas in vapour phase (vapour pressure of the solute) is directly proportional to the mole fraction(x) of the gaseous solute in the solution at low concentrations". This statement is known as Henry's law.

Henry's law can be expressed as,

$$p_{\text{solute}} \ \alpha \ x_{\text{solute in solution}} \qquad (9.1)$$

$$p_{\text{solute}} = K_H x_{\text{solute in solution}} \qquad (9.2)$$

Here, p_{solute} represents the partial pressure of the gas in vapour state which is commonly called as vapour pressure. x_{solute} in solution represents the mole fraction of solute in the solution. K_H is a empirical constant with the dimensions of pressure. The value of 'K_H' depends on the nature of the gaseous solute and solvent. The above equation is a straight-line in the form of y=mx. The plot partial pressure of the gas against its mole fraction in a solution will give a straight line as shown in fig 9.3. The slope of the straight line gives the value of K_H.

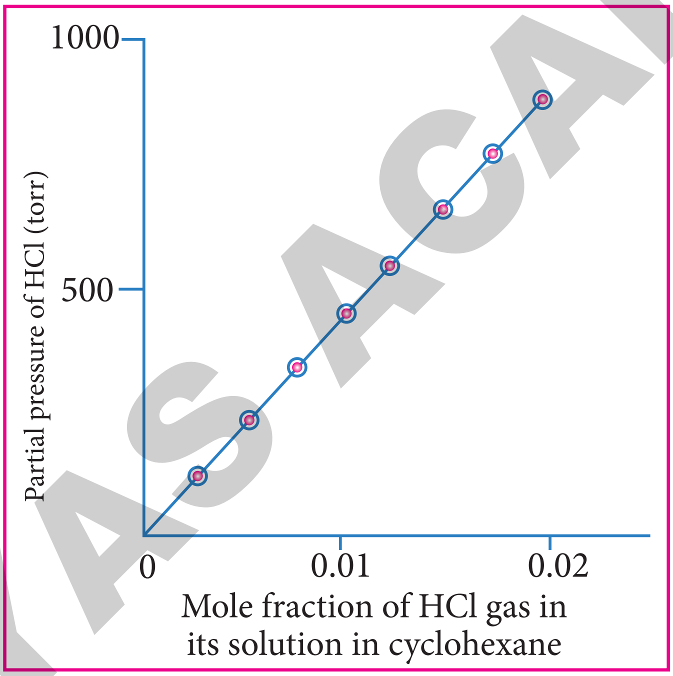


Figure 9.3 Solubility of HCl gas in cyclohexane at 293 K.

DO YOU KNOW?

Why the carbonated drinks are stored in a pressurized container?

We all know that the carbonated beverages contain carbon dioxide dissolved in them. To dissolve the carbon dioxide in these drinks, the CO_2 gas is bubbled through them under high pressure. These containers are sealed to maintain the pressure. When we open these containers at atmospheric pressure, the pressure of the CO_2 drops to the atmospheric level and hence bubbles of CO_2 rapidly escape from the solution and show effervescence. The burst of bubbles is even more noticeable, if the soda bottle is in warm condition.

DO YOU KNOW?

Why deep-sea divers use air diluted with helium gas in their air tanks?

The professional deep-sea divers carry a compressed air tank for breathing at high pressure under water. The normal compressed air contains nitrogen and oxygen and these gases are not very soluble in blood and other body fluids at normal pressure. As the pressure at that depth is far greater than the surface atmospheric pressure, more nitrogen dissolves in the blood and other body fluids when the diver breathes from tank. When the diver ascends to the surface, the pressure decreases, the dissolved nitrogen comes out of the blood and other body fluids quickly forming bubbles in the blood stream. These bubbles restrict blood flow, affect the transmission of nerve impulses and can even burst the capillaries or block them. This condition is called "the bends", which are painful and dangerous to life. Now a days, to avoid such dangerous condition, the professional divers, use air diluted with helium gas (about 11.7% Helium, 56.2% Nitrogen and 32.1% Oxygen), because of lower solubility of helium in the blood than nitrogen. Moreover, because of small size of helium atoms they can pass through cell walls without damaging them. The excess oxygen dissolved in the blood is used in metabolism and does not cause the condition of bends

9.5.1 Limitations of Henry's law

- Henry's law is applicable at moderate temperature and pressure only.
- Only the less soluble gases obeys Henry's law
- The gases reacting with the solvent do not obey Henry's law. For example, ammonia or HCl reacts with water and hence does not obey this law.

$$\boxed{NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-}$$

- The gases obeying Henry's law should not associate or dissociate while dissolving in the solvent.

Example Problem 2:

0.24 g of a gas dissolves in 1 L of water at 1.5 atm pressure. Calculate the amount of dissolved gas when the pressure is raised to 6.0 atm at constant temperature.

$p_{solute} = K_H x_{solute\ in\ solution}$

At pressure 1.5 atm,

$p_1 = K_H x_1$------------(1)

At pressure 6.0 atm,

$p_2 = K_H x_2$------------(2)

Dividing equation (1) by (2)

From equation $p_1/p_2 = x_1/x_2$

$1.5/6.0 = 0.24/x_2$

Therefore $x_2 = 0.24 \text{ x } 6.0/1.5 = 0.96$ g/L

Evaluate Yourself

7) Calculate the proportion of O_2 and N_2 dissolved in water at 298 K. When air containing 20% O_2 and 80% N_2 by volume is in equilibrium with it at 1 atm pressure. Henry's law constants for two gases are $K_H(O_2) = 4.6 \text{ x } 10^4$ atm and $K_H(N_2) = 8.5 \text{ x } 10^4$ atm.

8) Explain why the aquatic species are more comfortable in cold water during winter season rather than warm water during the summer.

9.6 Vapour pressure of liquid

Generally, liquids have a tendency to evaporate. If the kinetic energy of molecules in the liquid state overcomes the intermolecular force of attraction between them, then the molecules will escape from the liquid state. This process is called 'evaporation' and it happens on the surface of the liquid.

If evaporation is carried out in a closed container then the vapour remains in contact with the surface of the liquid. These vapour molecules are in continuous random motion during which they collide with each other and also with the walls of the container. As the collision is inelastic, they lose their energy and as result the vapour returns back to liquid state. This process is called as 'condensation'.

Evaporation and condensation are continuous processes. If the process is carried out in a closed system, a stage is reached when the rate of evaporation becomes equal to the rate of condensation. Thus, an equilibrium is established between liquid and its vapour. The pressure of the vapour in equilibrium with its liquid is called vapour pressure of the liquid at the given temperature. The vapour pressure of a liquid depends on its nature, temperature and the surface area. The following simple apparatus demonstrates the measurement of vapour pressure of a liquid.

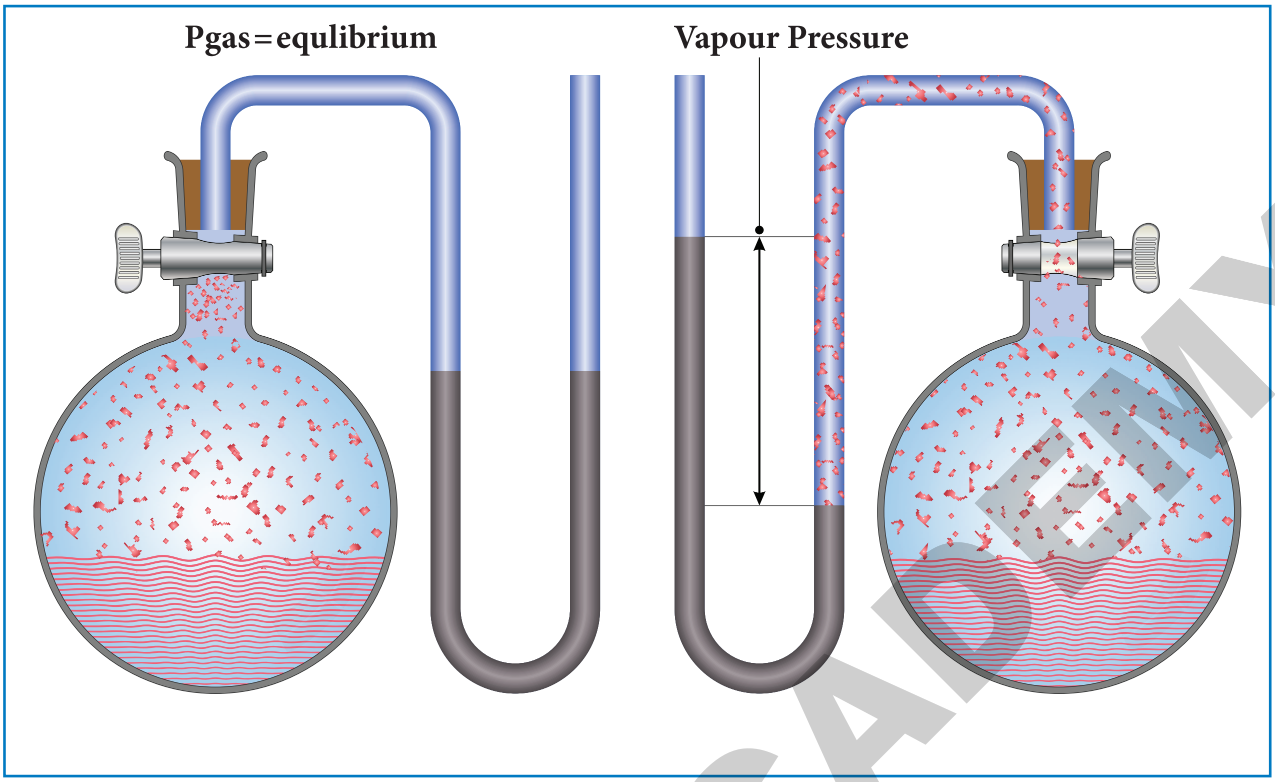


Figure 9.4 : a) A closed round bottomed flask in which ethanol is in equilibrium with its vapour. b) In the same setup the vapour is allowed to escape through a U tube filled with mercury. The escaped vapour pushes the mercury in the U tube and the difference in mercury level gives the vapour pressure of ethanol present in the RB flask.

9.7 Vapour pressure of liquid solutions

When a solute (of any physical state - solid, liquid or gas) is dissolved in a liquid solvent the resultant solution is called a liquid solution. The solution which contains only two components (one solvent and one solute) is called a binary solution. We have already discussed the solution of a gaseous solute in liquid solvent under Henry's law.

9.7.1 Vapour pressure of binary solution of liquid in liquids

Now, let us consider a binary liquid solution formed by dissolving a liquid solute 'A' in a pure solvent 'B' in a closed vessel. Both the components A and B present in the solution would evaporate and an equilibrium will be established between the liquid and vapour phases of the components A and B.

The French chemist Raoult, proposed a quantitative relationship between the partial pressures and the mole fractions of two components A & B, which is known as Raoult's Law. This law states that "in the case of a solution of volatile liquids, the partial vapour pressure of each component (A & B) of the solution is directly proportional to its mole fraction".

According to Raoult's law,

$$p_A \alpha\, x_A \qquad (9.3)$$

$$p_A = k\, x_A$$

when $x_A = 1$, $k = p^\circ_A$

where p°_A is the vapour pressure of pure component 'A' at the same temperature.

Therefore,

$$p_A = p^\circ_A x_A \qquad (9.4)$$

Similarly, for component 'B'

$$p_B = p^\circ_B\, x_B \qquad (9.5)$$

x_A and x_B are the mole fraction of the components A and B respectively.

According to Dalton's law of partial pressure the total pressure in a closed vessel will be equal to the sum of the partial pressures of the individual components.

Hence,

$$P_{total} = p_A + p_B \qquad (9.6)$$

Substituting the values of p_A and p_B from equations (9.4) and (9.5) in the above equation,

$$P_{total} = x_A p^\circ_A + x_B p^\circ_B \qquad (9.7)$$

We know that $x_A + x_B = 1$ or $x_A = 1 - x_B$

Therefore,

$$P_{total} = (1 - x_B)\, p^\circ_A + x_B p^\circ_B \qquad (9.8)$$

$$P_{total} = p^\circ_A + x_B(p^\circ_B - p^\circ_A) \qquad (9.9)$$

The above equation is of the straight-line equation form y = mx+c. The plot of P_{total} versus x_B will give a straight line with $(p^\circ_B - p^\circ_A)$ as slope and p°_A as the y intercept.

Let us consider the liquid solution containing toluene (solute) in benzene (solvent).

The variation of vapour pressure of pure benzene and toluene with its mole fraction is given in the graph.

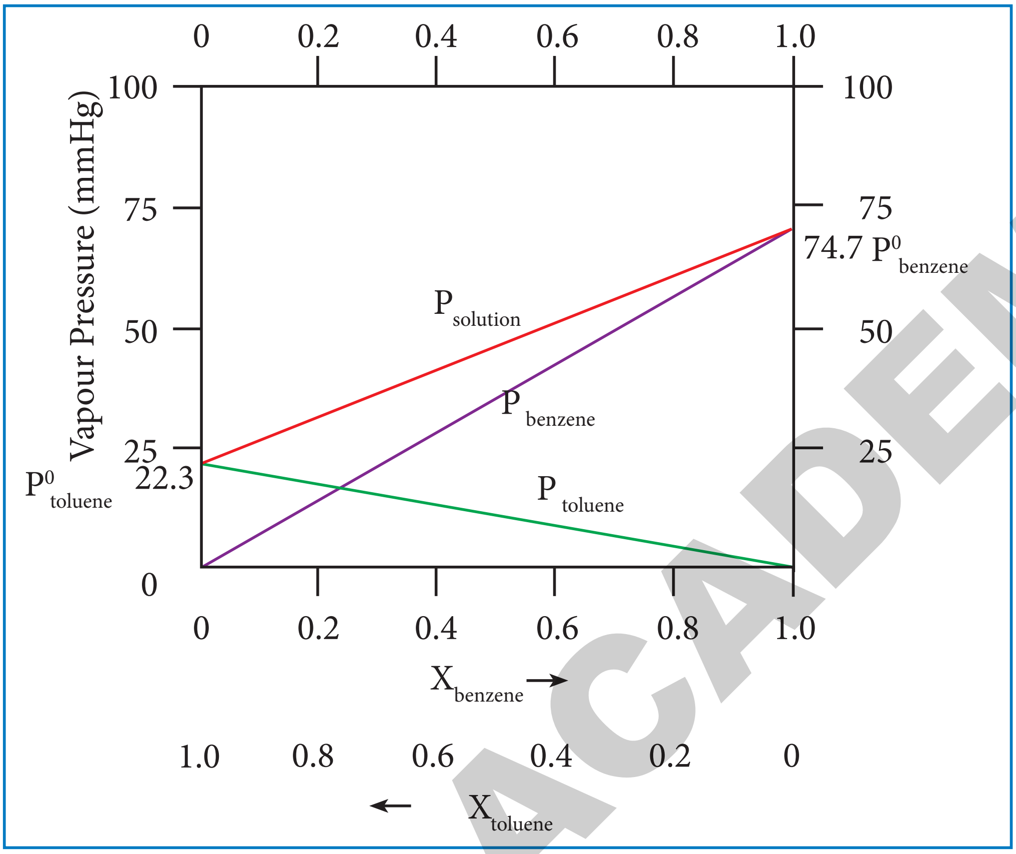


Figure 9.5 Solution of benzene in toluene obeying Raoult's law.

The vapour pressures of pure toluene and pure benzene are 22.3 and 74.7 mmHg, respectively. The above graph shows, the partial vapour pressure of the pure components increases linearly with the increase in the mole fraction of the respective components. The total pressure at any composition of the solute and solvent is given by the following straight line (represented as red line) equation.

$$P_{solution} = p^{\circ}_{toluene} + x_{benzene}(p^{\circ}_{benzene} - p^{\circ}_{toluene}) \qquad (9.10)$$

9.7.2 Vapour pressure of binary solution of solids in liquids

When a nonvolatile solute is dissolved in a pure solvent, the vapour pressure of the pure solvent will decrease. In such solutions, the vapour pressure of the solution will depend only on the solvent molecules as the solute is nonvolatile.

For example, when sodium chloride is added to the water, the vapour pressure of the salt solution is lowered. The vapour pressure of the solution is determined by the number of molecules of the solvent present in the surface at any time and is proportional to the mole fraction of the solvent.

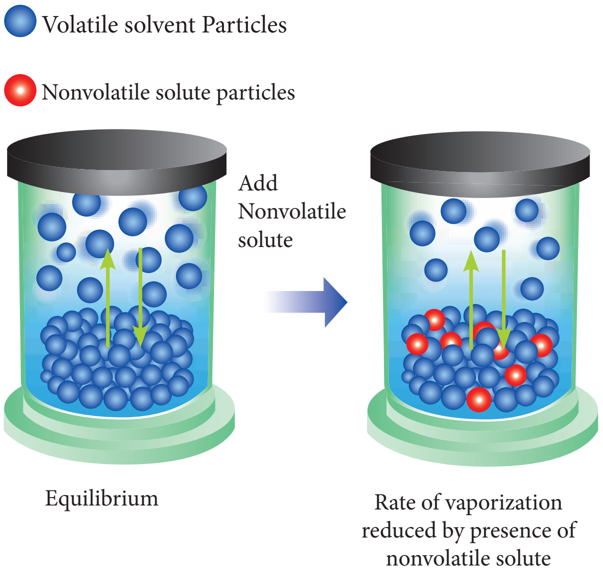


Fig 9.6 Rate of vapourization reduced by presence of nonvolatile solute.

$$P_{solution} \propto x_A \quad (9.11)$$

Where x_A is the mole fraction of the solvent

$$P_{solution} = k\,x_A \quad (9.12)$$

When $x_A = 1, \quad K = P^o_{solvent}$

($P^o_{solvent}$ is the partial pressure of pure solvent)

$$P_{solution} = P^o_{solvent}\,x_A \quad (9.13)$$

$$\frac{P_{solution}}{P^o_{solvent}} = x_A \quad (9.14)$$

$$1 - \frac{P_{solution}}{P^o_{solvent}} = 1 - x_A \quad (9.15)$$

$$\frac{P^o_{solvent} - P_{solution}}{P^o_{solvent}} = x_B \quad (9.16)$$

Where x_B is the fraction of the solute

$(\because x_A + x_B = 1, x_B = 1 - x_A)$

The above expression gives the relative lowering of vapour pressure. Based on this expression, Raoult's Law can also be stated as "the relative lowering of vapour pressure of an ideal solution containing the nonvolatile solute is equal to the mole fraction of the solute at a given temperature".

Comparison of Raoult's law and Henry's law

According to Raoult's law, for a solution containing a nonvolatile solute

$$p_{solute} = p^o_{solute}\,x_{solute} \quad (9.17)$$

According to Henry's law:

$$p_{solute} = K_H\,x_{solute\ in\ solution} \quad (9.18)$$

The difference between the above two expressions is the proportionality constant p^o_A (Raoults Law) and K_H.(Henry's Law). Henry's law is applicable to solution containing gaseous solute in liquid solvent, while the Raoults Law is applicable to nonvolatile solid solute in a liquid solvent. If the solute is non volatile then the Henry's law constant will become equal to the vapour of the pure solvent (p^o_A) and thus, Raoult's law becomes a special case of Henry's law. For very dilute solutions the solvent obeys Raoult's law and the solute obeys Henry's law.

9.8 Ideal and non-ideal solutions

9.8.1 Ideal Solutions:

An ideal solution is a solution in which each component i.e. the solute as well as the solvent obeys the Raoult's law over the entire range of concentration. Practically no solution is ideal over the entire range of concentration. However, when the concentration of solute is very low, the dilute solution behaves ideally. If the two components present in the solution (A and B) are identical in size, structure, and having almost similar intermolecular attractive forces between them (i.e. between A-A, B-B and B-A) and then the solution tends to behave like an ideal solution.

For an ideal solution

i) there is no change in the volume on mixing the two components (solute & solvents). ($\Delta V_{mixing} = 0$)

ii) there is no exchange of heat when the solute is dissolved in solvent ($\Delta H_{mixing} = 0$).

iii) escaping tendency of the solute and the solvent present in it should be same as in pure liquids.

Examples for ideal solutions: benzene & toluene; n-hexane & n-heptane; ethyl bromide &ethyl iodide; chlorobenzene & bromobenzene.

9.8.2 Non-ideal solutions

The solutions which do not obey Raoult's law over the entire range of concentration, are called non-ideal solutions. For a non-ideal solution, there is a change in the volume and enthalpy upon mixing. i.e. $\Delta H_{mixing} \neq 0$ & $\Delta V_{mixing} \neq 0$. The deviation of the non-ideal solutions from the Raoult's law can either be positive or negative.

Non-ideal solutions - positive deviation from Rauolt's Law:

The nature of the deviation from the Rauolt's law can be explained in terms of the intermolecular interactions between solute (A) and solvent (B). Consider a case in which the intermolecular attractive forces between A and B are weaker than those between the molecules of A (A-A) and molecules of B (B-B). The molecules present in such a solution have a greater tendency to escape from the solution when compared to the ideal solution formed by A and B, in which the intermolecular attractive forces (A-A, B-B, A-B) are almost similar. Consequently, the vapour pressure of such non-ideal solution increases and it is greater than the sum of the vapour pressure of A and B as predicted by the Raoult's law. This type of deviation is called positive deviation.

Here, $p_A > p^\circ_A x_A$ and $p_B > p^\circ_B x_B$.

Hence $p_{total} > p^\circ_A x_A + p^\circ_B x_B$ (9.19)

Let us understand the positive deviation by considering a solution of ethyl alcohol and water. In this solution the hydrogen bonding interaction between ethanol and water is weaker than those hydrogen bonding interactions amongst themselves (ethyl alcohol-ethyl alcohol and water-water interactions). This results in the increased evaporation of both components from the aqueous solution of ethanol. Consequently, the vapour pressure of the solution is greater than the vapour pressure predicted by Raoult's law. Here, the mixing process is endothermic i.e. $\Delta H_{mixing} > 0$ and there will be a slight increase in volume ($\Delta V_{mixing} > 0$).

Examples for non-ideal solutions showing positive deviations: Ethyl alcohol & cyclohexane, Benzene & acetone, Carbon tetrachloride & chloroform, Acetone & ethyl alcohol, Ethyl alcohol & water.

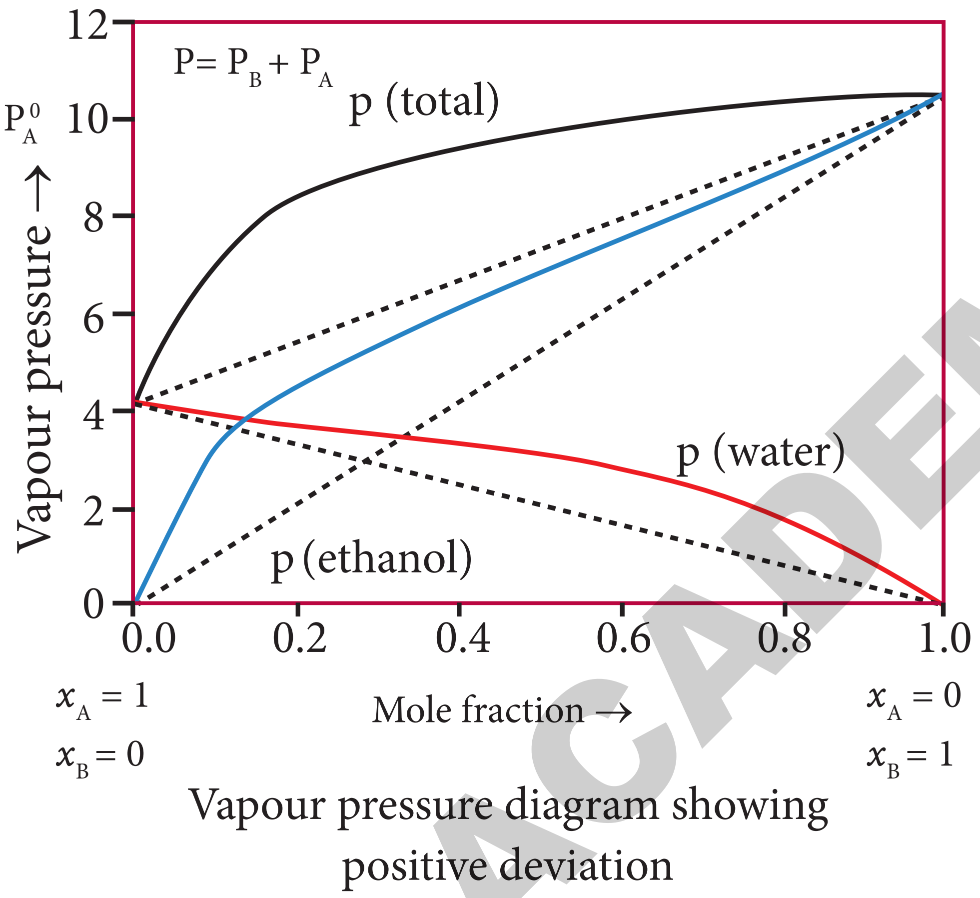


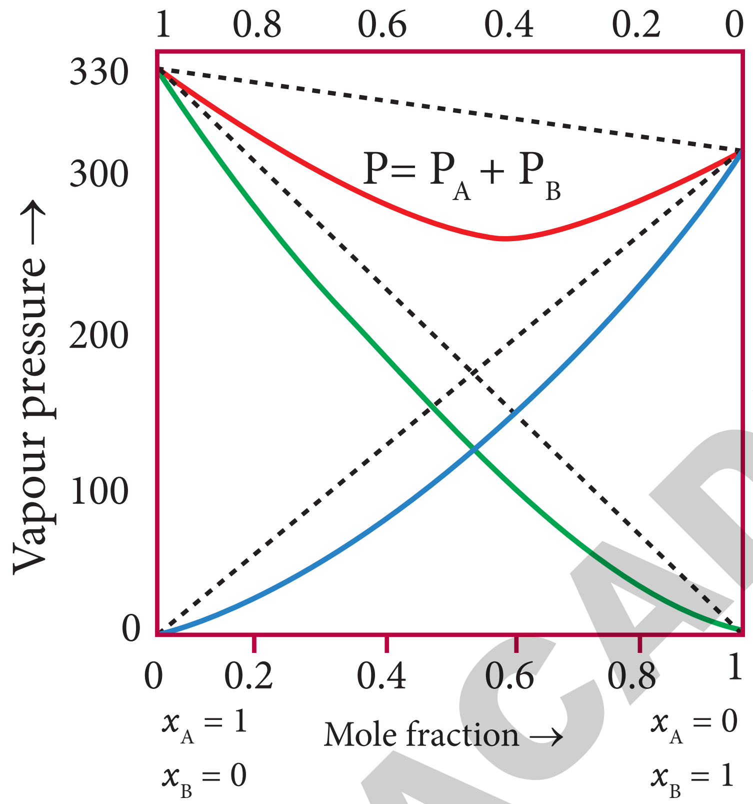
Figure 9.7 Positive deviations from Raoult's law. The dotted line (-----) is ideal behavior and the solid lines (_____) is actual behavior

Non-ideal solutions - negative deviation from Rauolt's Law:

Let us consider a case where the attractive forces between solute (A) and solvent (B) are stronger than the intermolecular attractive forces between the individual components (A-A & B-B). Here, the escaping tendency of A and B will be lower when compared with an ideal solution formed by A and B. Hence, the vapour pressure of such solutions will be lower than the sum of the vapour pressure of A and B. This type of deviation is called negative deviation. For the negative deviation $p_A < p^\circ_A x_A$ and $p_B < p^\circ_B x_B$.

Let us consider a solution of phenol and aniline. Both phenol and aniline form hydrogen bonding interactions amongst themselves. However, when mixed with aniline, the phenol molecule forms hydrogen bonding interactions with aniline, which are stronger than the hydrogen bonds formed amongst themselves. Formation of new hydrogen bonds considerably reduce the escaping tendency of phenol and aniline from the solution. As a result, the vapour pressure of the solution is less and there is a slight decrease in volume ($\Delta V_{mixing} < 0$) on mixing. During this process evolution of heat takes place i.e. $\Delta H_{mixing} < 0$ (exothermic)

Examples for non-ideal solutions showing negative deviation: Acetone + chloroform, Chloroform + diethyl ether, Acetone + aniline,Chloroform + Benzene.



Vapour pressure diagram showing negative deviation

Figure 9.8 Negative deviation from Raoult's law. The dotted line (-----) is ideal behavior and the solid lines (_____) is actual behaviour

9.8.3 Factors responsible for deviation from Raoult's law

The deviation of solution from ideal behavior is attributed to the following factors.

i) Solute-solvent interactions

For an ideal solution, the interaction between the solvent molecules (A-A),the solute molecules (B-B) and between the solvent & solute molecules (A-B) are expected to be similar. If these interactions are dissimilar, then there will be a deviation from ideal behavior.

ii) Dissociation of solute

When a solute present in a solution dissociates to give its constituent ions, the resultant ions interact strongly with the solvent and cause deviation from Raoult's law.

For example, a solution of potassium chloride in water deviates from ideal behavior because the solute dissociates to give K^+ and Cl^- ion which form strong ion-dipole interaction with water molecules.

$$KCl\,(s) + H_2O\,(l) \rightarrow K^+(aq) + Cl^-(aq)$$

iii) Association of solute

Association of solute molecules can also cause deviation from ideal behaviour. For example, in solution, acetic acid exists as a dimer by forming intermolecular hydrogen bonds, and hence deviates from Raoult's law.

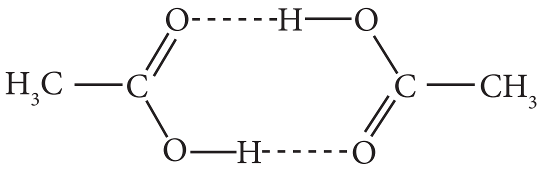


Fig 9.9 Acetic acid (dimer)

iv) Temperature

An increase in temperature of the solution increases the average kinetic energy of the molecules present in the solution which causes decrease in the attractive force between them. As result, the solution deviates from ideal behaviour.

v) Pressure

At high pressure the molecules tend to stay close to each other and therefore there will be an increase in their intermolecular attraction. Thus, a solution deviates from Raoult's law at high pressure.

vi) Concentration

If a solution is sufficiently dilute there is no pronounced solvent-solute interaction because the number of solute molecules are very low compared to the solvent. When the concentration is increased by adding solute, the solvent-solute interaction becomes significant. This causes deviation from the Raoult's law.

Evaluate Yourself

9) Calculate the mole fractions of benzene and naphthalene in the vapour phase when an ideal liquid solution is formed by mixing 128 g of naphthalene with 39 g of benzene. It is given that the vapour pressure of pure benzene is 50.71 mmHg and the vapour pressure of pure naphthalene is 32.06 mmHg at 300 K.

9.9 Colligative properties

Pure water is tasteless. When you add sugar it becomes sweet, while addition of salt makes it salty. It implies that the properties of a solution depend on the nature of solute particles present in the solution. However, for an ideal dilute solution, the properties, namely, relative lowering of vapour pressure, elevation of boiling point, depression in freezing point and osmotic pressure do not depend on the chemical nature of the solute but depends only on the number of solute particles (ions/molecules) present in the solution. These four properties are known as colligative properties. Though the magnitude of these properties are small, they have plenty of practical applications. For example the osmotic pressure is important for some vital biological systems.

Relative lowering of vapour pressure (ΔP)

The vapour pressure of a solution containing a nonvolatile, non-electrolyte solute is always lower than the vapour pressure of the pure solvent. Consider a closed system in which a pure solvent is in equilibrium with its vapour. At equilibrium the molar Gibbs free energies of solvent in the liquid and gaseous phase are equal ($\Delta G = 0$). When a solute is added to this solvent, the dissolution takes place and its free energy (G) decreases due to increase in entropy. In order to maintain the equilibrium, the free energy of the vapour phase must also decrease. At a given temperature, the only way to lower the free energy of the vapour is to reduce its pressure. Thus the vapour pressure of the solution must decrease to maintain the equilibrium.

We know that from the Raoult's law the relative lowering of the vapour pressure is equal to the mole fraction of the solute (equation 9.10)

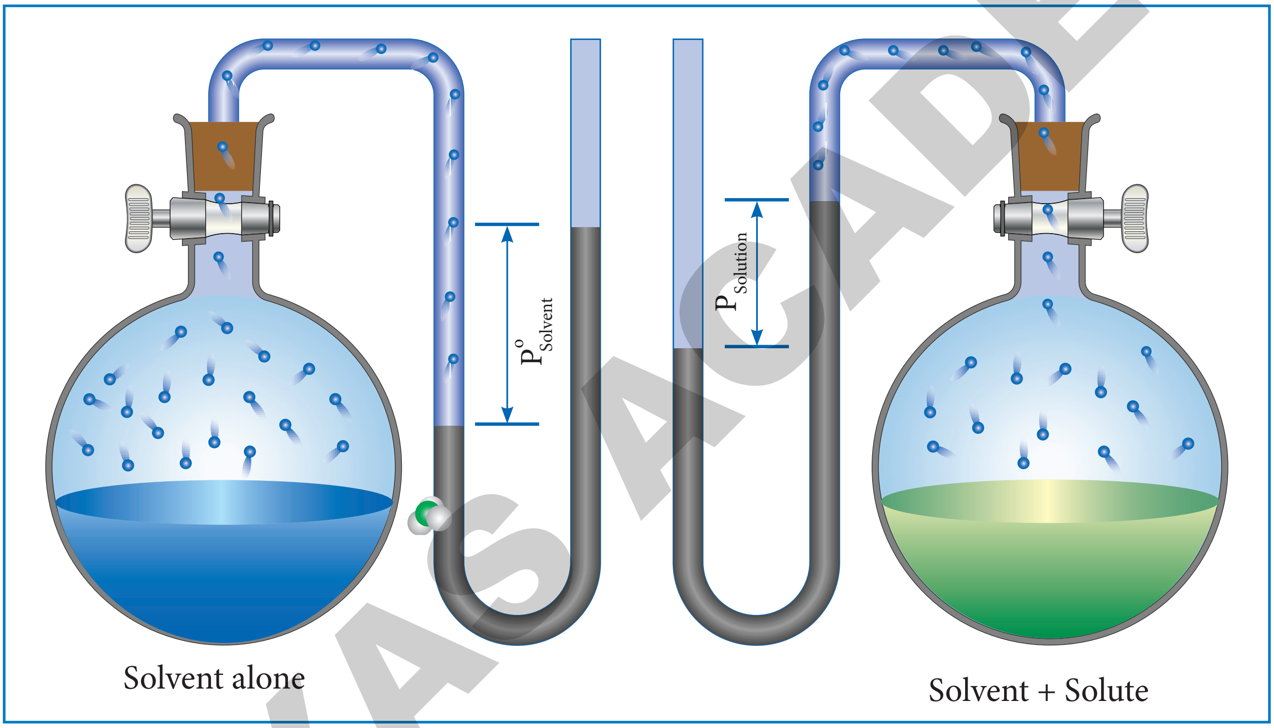


Figure 9.10 Measuring relative lowering of vapour pressure

From the above equation,it is clear that the relative lowering of vapour pressure depends only on the mole fraction of the solute (x_B) and is independent of its nature. Therefore, relative lowering of vapour pressure is a colligative property.

Determination of molar mass weights from relative lowering of vapour pressure

The measurement of relative lowering of vapour pressure can be used to determine the molar mass of a nonvolatile solute. For this purpose, a known mass of the solute is dissolved in a known quantity of solvent. The relative lowering of vapour pressure is measured experimentally.

According to Raoult's law the relative lowering of vapor pressure is,

$$\frac{P^0_{solvent} - P_{solution}}{P^0_{solvent}} = x_B$$

Let w_A and w_B be the weights of the solvent and solute respectively and their corresponding molar masses are M_A and M_B, then the mole fraction of the solute x_B is

$$x_B = \frac{n_B}{n_A + n_B} \qquad (9.20)$$

Here, n_A & n_B are the moles of the solvent and the solute respectively. For dilute solutions $n_A >> n_B$. Hence $n_A + n_B \approx n_A$. Now

$$x_B = \frac{n_B}{n_A}$$

Number of moles of solvent and the solute are,

$$n_A = \frac{w_A}{M_A}, n_B = \frac{w_B}{M_B}$$

$$\text{Therefore, } x_B = \frac{\frac{w_B}{M_B}}{\frac{w_A}{M_A}} \qquad (9.21)$$

Thus,

$$\text{Relative lowering of vapor pressure} = \frac{\frac{w_B}{M_B}}{\frac{w_A}{M_A}}$$

$$\text{Relative lowering of vapor pressure} = \frac{w_B \times M_A}{w_A \times M_B} \qquad ....(9.22)$$

From the equation (9.35) the molar mass of the solute (M_B) can be calculated using the known the values of w_A, w_B, M_A and the measured relative lowering of vapour pressure.

Example Problem3:

An aqueous solution of 2 % nonvolatile solute exerts a pressure of 1.004 bar at the boiling point of the solvent. What is the molar mass of the solute when P°_A is 1.013 bar?

$$\frac{\Delta P}{P^{\circ}_A} = \frac{W_B \text{ x } M_A}{M_B \text{ x } W_A}$$

In a 2 % solution weight of the solute is 2 g and solvent is 98 g

$\Delta P = P^{\circ}_A - P_{solution} = 1.013 - 1.004 \text{ bar} = 0.009$ bar

$$M_B = \frac{P^{\circ}_A \text{ x } W_B \text{ x} M_A}{\Delta P \text{ x } W_A}$$

$M_B = 2 \text{ x } 18 \text{ x } 1.013/(98 \text{ x } 0.009)$

$= 41.3 \text{ g mol}^{-1}$

Evaluate Yourself

10) Vapour pressure of a pure liquid A is 10.0 torr at 27°C . The vapour pressure is lowered to 9.0 torr on dissolving one gram of B in 20 g of A. If the molar mass of A is 200 then calculate the molar mass of B.

Elevation of boiling point

Boiling point is an important physical property of a liquid. The boiling point of a liquid is the temperature at which its vapour pressure becomes equal to the atmospheric pressure (1 atm). When a nonvolatile solute is added to a pure solvent at its boiling point, the vapour pressure of the solution is lowered below 1 atm. To bring the vapour pressure again to 1 atm, the temperature of the solution has to be increased. As a result,the solution boils at a higher temperature (T_b) than the boiling point of the pure solvent (T°_b). This increase in the boiling point is known as elevation of boiling point. A plot of vapour pressure versus temperature for water and an aqueous solution is given below

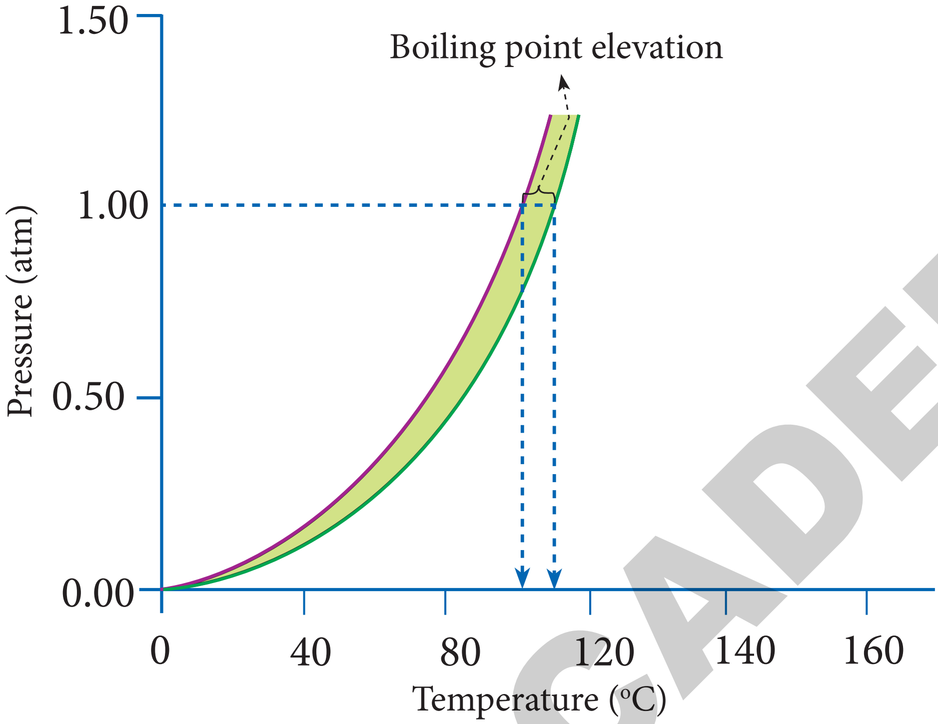


Figure 9.11 Elevation in boiling point

The vapour pressure of the solution increases with increase in temperature as shown in the above figure. The variation of vapour pressure with respect to temperature for pure water is given by the violet coloured curve. At 100 ^{0}C the vapour pressure of water is equal to 1 atm. Hence the boiling point of water is 100 ^{0}C (T_b^o). When a solute is added to water, the vapour pressure of the resultant solution is lowered. The variation of vapour pressure with respect to temperature for the solution is given by green curve. From the graph, it evident the vapour pressure of the solution is equal to 1 atm pressure at the temperature T_b which is greater than T_b^o. The difference between these two temperatures (T_b-T_b^o) gives the elevation of boiling point.

The elevation of boiling point (ΔT_b)= T_b - T_b^o

The elevation of boiling point is directly proportional to the concentration of the solute particles.

$\Delta T_b \; \alpha \; m$ (9.23)

m is the concentration of solution expressed in molality.

$\Delta T_b = K_b \, m$ (9.24)

Where K_b = molal boiling point elevation constant or Ebullioscopic constant.

If m=1, then $\Delta T_b = K_b$;

Hence, the K_b is equal to the elevation in boiling point for 1 molal solution. K_b is calculated by the following expression

$$K_b = \frac{RT^2\ M_{solvent}}{\Delta H_{vapourisation}}$$

Table 9.3 Molal boiling point elevation constant 'K_b' for some solvents

S. No.	Solvent	T_b° (K)	K_b (K kg mol^{-1})
1.	Water	373.15	0.52
2.	Ethanol	351.5	1.20
3.	Benzene	353.3	2.53
4.	Chloroform	334.4	3.63
5.	Ether	307.8	2.02
6.	Carbon tetrachloride	350.0	5.03
7.	Carbon disulphide	319.4	2.42
8.	Acetic acid	391.1	2.93
9.	Cyclohexane	353.74	2.79

Problem:

0.75 g of an unknown substance is dissolved in 200 g water. If the elevation of boiling point is 0.15 K and molal elevation constant is 7.5 K Kg mol^{-1} then, calculate the molar mass of unknown substance

$$\Delta T_b = K_b\, m$$

$$= K_b \times W_2 \times 1000 / M_2 \times W_1$$

$$M_2 = K_b \times W_2 \times 1000 / \Delta T_b \times W_1$$

$$= 7.5 \times 0.75 \times 1000 / 0.15 \times 200$$

$$= 187.5 \text{ g mol}^{-1}$$

Evaluate Yourself

11) 2.56 g of Sulphur is dissolved in 100g of carbon disulphide. The solution boils at 319. 692 K . What is the molecular formula of Sulphur in solution The boiling point of CS_2 is 319. 450K. Given that K_b for CS_2 = 2.42 K Kg mol^{-1}

Depression in freezing point

Freezing point of a substance is another important physical property like boiling point. Freezing point is defined as "the temperature at which the solid and the liquid states of the substance have the same vapour pressure". At freezing point, the solid and liquid phases of the substance are in equilibrium. For example, the freezing point of water is 0 ˚C. At this temperature the ice and the water are in equilibrium. When a nonvolatile solute is added to water at its freezing point, the freezing point of the solution is lowered from 0 ˚C. The lowering of the freezing point of the solvent when a solute is added is called depression in freezing point (ΔT_f).

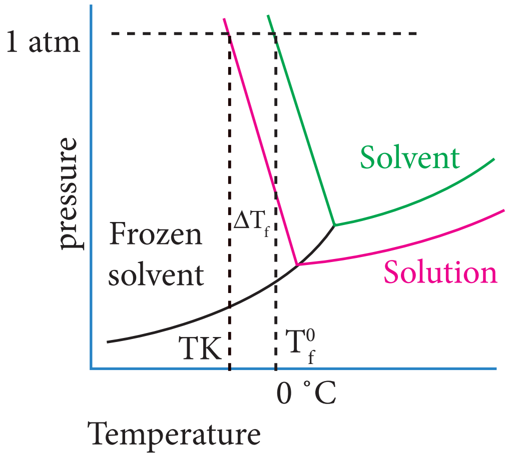


Fig 9.12 Depression in freezing point

From the above graph, we infer that the freezing point (T_f^0) is 0 ˚C as the vapour pressure at this temperature is 1 atm (atmospheric pressure). The vapour pressure versus temperature curve for the solution indicates that the freezing point (T_f) is lower than the 0 ˚C. The depression in freezing temperature (ΔT_f) can be expressed as,

$$\Delta T_f = T_f^o - T_f$$

The experimental results show that the depression in freezing point is directly proportional to the molal concentration of the solute particles.

Hence,

$$\Delta T_f \alpha \ m$$

$$\Delta T_f = K_f \ m \quad (9.25)$$

Here, 'm' = is the molality of the solution

K_f = molal freezing point depression constant or cryoscopic constant.

If m=1 then $\Delta T_f = K_f$

The K_f is equal to the depression in freezing point for 1 molal solution

Table 9.4 Molal freezing point depression constant for some solvents

S. No.	Solvent	Freezing point (K)	K_f (K.kg. mol^{-1})
1.	Water	273.0	1.86
2.	Ethanol	155.7	1.99
3.	Benzene	278.6	5.12
4.	Chloroform	209.6	4.79
5.	Carbon disulphide	164.2	3.83
6.	Ether	156.9	1.79
7.	Cyclohexane	279.5	20.0
8.	Acetic acid	290.0	3.90

Determination of molar mass of solute from depression in freezing point

If the solution is prepared by dissolving w_B g of solute in w_A g of solvent, then the molality is,

$$m = \frac{\text{Number of moles of solute} \times 1000}{\text{weight of solvent in grams}} \quad \text{............}(9.26)$$

$$\text{Number of moles of solute} = \frac{w_B}{M_B} \quad \text{............}(9.27)$$

Where, M_B=molar mass of the solute

Therefore,

$$m = \frac{w_B \times 1000}{M_B \times w_A} \quad \text{...............}(9.28)$$

and,

$$\Delta T_f = \frac{K_f \times w_B \times 1000}{M_B \times w_A} \quad \text{...............}(9.29)$$

molar mass can be calculated using (9.29)

$$M_B = \frac{K_b \times w_B \times 1000}{\Delta T_b \times w_A} \quad \text{...............}(9.30)$$

Example Problem - 5

Ethylene glycol ($C_2H_6O_2$) can be at used as an antifreeze in the radiator of a car. Calculate the temperature when ice will begin to separate from a mixture with 20 mass percent of glycol in water used in the car radiator. K_f for water = 1.86 K Kg mol^{-1} and molar mass of ethylene glycol is 62 g mol^{-1}.

Weight of solute (W_2) = 20 mass percent of solution means 20 g of ethylene glycol

Weight of solvent (water) W_1 = 100 -20 = 80 g

$\Delta T_f = K_f\, m$

$$= \frac{K_f \times W_2 \times 1000}{M_2 \times W_1}$$

$$= \frac{1.86 \times 20 \times 1000}{62 \times 80}$$

= 7.5 K

The temperature at which the ice will begin to separate is the freezing of water after the addition of solute i.e 7.5 K lower than the normal freezing point of water (273-7.5K) = 265.5 K

Evaluate Yourself

12) 2g of a non electrolyte solute dissolved in 75 g of benzene lowered the freezing point of benzene by 0.20 K. The freezing point depression constant of benzene is 5.12 K Kg mol^{-1}. Find the molar mass of the solute.

Osmosis and osmotic pressure

Many biological processes depend on osmosis, which is a spontaneous process by which the solvent molecules pass through a semi permeable membrane from a solution of lower concentration to a solution of higher concentration. The name osmosis is derived from the Greek word '*osmos*' which means 'to push'. It is also important to know that the semipermeable membrane selectively allows certain molecules in the solution to pass through it but not others.

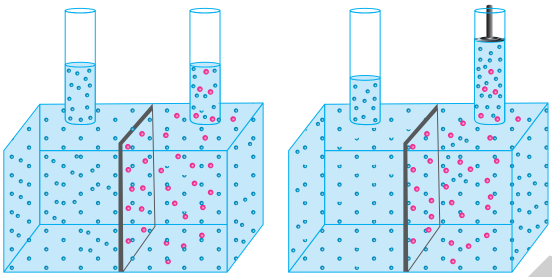


Figure 9.13 Osmosis and osmotic pressure

Let us consider a simple apparatus as shown in the above figure. A semipermeable membrane separates a chamber into two compartments. Water (pure solvent) is added to the first compartment and the aqueous NaCl (solution) is added to the second compartment such that the liquid levels on the both sides are equal. Since there is a difference in concentration between the liquids present in the two compartments, the water molecules move from first compartment to second compartment through the semipermeable membrane. The membrane allows only the water molecules to pass through it in either direction but not allows the NaCl. The net flow of water is into the sodium chloride solution and hence increases its volume. This decreases its concentration and also creates a pressure difference between the compartments. This pressure difference, push some of the water molecules back to the solvent side through the semipermeable membrane until an equilibrium is established. At the equilibrium, the rate of movement of solvent molecules on both directions are equal. The pressure difference at the equilibrium is called osmotic pressure (π). Thus, osmotic pressure can be defined as "the pressure that must be applied to the solution to stop the influx of the solvent (to stop osmosis) through the semipermeable membrane" van't Hoff found out that for dilute solutions, the osmotic pressure is directly proportional to the molar concentration of the solute and the temperature of the solution. He proposed the following equation to calculate osmotic pressure which is now called as van't Hoff equation.

$$\pi = cRT \quad ....9.31$$

Here,

c = Concentration of the solution in molarity

T = Temperature

R = Gas constant

Determination of molar mass from osmotic pressure

According to van't Hoff equation

$$\pi = cRT$$

$$c = \frac{n}{V}$$

Here, n= number of moles of solute dissolved in 'V' litre of the solution.

Therefore, $\pi = \frac{n}{V} RT$ or

$$\pi V = nRT \quad (9.32)$$

If the solution is prepared by dissolving w_B g of nonvolatile solute in w_A g of solvent, then the number of moles 'n' is,

$$n = w_B / M_B$$

Since, M_B = molar mass of the solute

Substituting the 'n' in 9.32, we get,

$$\pi = \frac{w_B}{V} \frac{RT}{M_B}$$

$$M_B = \frac{w_B}{V} \frac{RT}{\pi} \qquad (9.33)$$

From the equation 9.33, molar mass of the solute can be calculated.

Significances of osmotic pressure over other colligative properties

Unlike elevation of boiling point (for 1 molal solution the elevation in boiling point is 0.512 ˚C for water) and the depression in freezing point (for 1 molal solution the depression in freezing point is 1.86 ˚C for water), the magnitude of osmotic pressure is large.

The osmotic pressure can be measured at room temperature enables to determine the molecular mass of biomolecules which are unstable at higher temperatures.

Even for a very dilute solution, the osmotic pressure is large.

Isotonic solutions

Two solutions having same osmotic pressure at a given temperature are called isotonic solutions. When such solutions are separated by a semipermeable membrane, solvent flow between one to the other on either direction is same, i.e. the net solvent flow between the two isotonic solutions is zero.

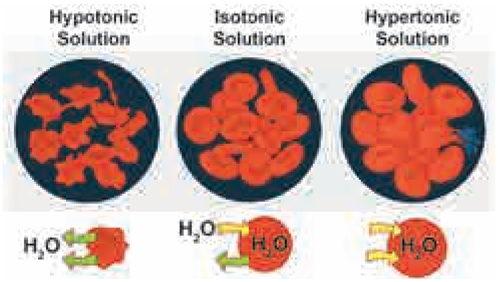


Figure 9.14 Isotonic solutions

The osmotic pressure of the blood cells is approximately equal to 7 atm at 37˚C. The intravenous injections should have same osmotic pressure as that of the blood (isotonic with blood). If the Intravenous solutions are too dilute that is hypotonic, the solvent from outside of the cells will flow into the cell to normalise the osmotic pressure and this process which is called hemolysis, causes the cells to burst. On the other hand, if the solution is too concentrated, that is hypertonic, the solvent molecules will flow out of the cells, which causes the cells to shrink and die. For this reason, the Intravenous fluids are prepared such they are isotonic to blood (0.9 % mass/volume sodium chloride solution).

9.10 Reverse osmosis (RO):

Let us consider the experimental setup (Figure 9.15) discussed in the osmosis. The pure water moves through the semipermeable membrane to the NaCl solution due to osmosis. This process can be reversed by applying pressure greater than the osmotic pressure to the solution side. Now the pure water moves from the solution side to the solvent side and this process is called reverse osmosis. It can be defined as a process in which a solvent passes through a semipermeable membrane in the opposite direction of osmosis, when subjected to a hydrostatic pressure greater than the osmotic pressure.

Application of Reverse osmosis in water purification:

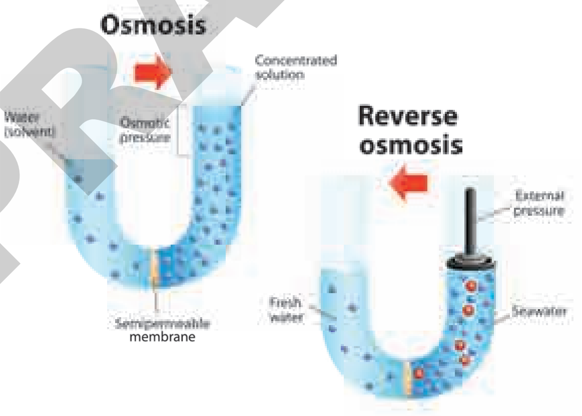


Figure 9.15 Osmosis & Reverse osmosis

Reverse osmosis is used in the desalination of sea water and also in the purification of drinking water. A simple set up used in both the process is shown in the figure 9.15. When a pressure higher than the osmotic pressure is applied on the solution sided (sea water) the water molecules moves from solution side to the solvent side through semipermeable membrane (Opposite to the Osmotic flow). The pure water can be collected. There are different types of semipermeable membranes used in this process. The membrane used for reverse osmosis has to withstand high pressures. Generally, cellulose acetate or polyamide membranes are commonly used in commercial systems. The selection of membrane used for reverse osmosis will be decided based on the nature of the input water.

Example Problem-6 :

At 400K 1.5 g of an unknown substance is dissolved in solvent and the solution is made to 1.5 L. Its osmotic pressure is found to be 0.3 bar. Calculate the molar mass of the unknown substance.

$$\text{Molar mass} = \frac{\text{mass of unknown solute} \times RT}{\text{osmotic pressure} \times \text{volume of solution}}$$

$$= \frac{1.5 \times 8.314 \times 10^{-2} \times 400}{0.3 \times 1.5}$$

$$= 110.85 \text{ gram mol}^{-1}$$

Evaluate Yourself

13) What is the mass of glucose ($C_6H_{12}O_6$) in it one litre solution which is isotonic with 6 g L^{-1} of urea (NH_2 CO NH_2) ?

9.11 Abnormal molar mass

The molar masses of the nonvolatile solutes can be calculated accurately using the experimentally determined colligative properties. In this method, we assume that the solution is very dilute and there is no dissociation or association of solute particles in the solution.

In a concentrated solution, the interaction between the solute and solvent becomes significant and reflected in the measured colligative properties. Similarly, the dissociation or association of solute molecules would alter the total number of particles present in the solution and hence affect the results of measured colligative properties. In such solutions, the value of the molar mass of the solute determined using colligative properties would be different from the actual molar mass, and it is called abnormal molar mass.

Association or dissociation of solute molecules:

Normally, the molar mass determination using measured colligative properties assumes that the solute does not dissociate or associate. In certain solvents, solute molecules associate to form a dimer or trimer etc… This reduces the total number of particles (molecules) formed in solution and as a result the calculated molar mass will be higher than the actual molar mass. Let us consider a solution of acetic acid in benzene. It is already established that acetic acid forms inter molecular hydrogen bonds as shown in the figure 9.9 and exists as a dimer in benzene.

$$2CH_3COOH \rightarrow (CH_3COOH)_2$$

The molar mass of acetic acid calculated using colligative properties is found to be around 120 g mol^{-1} is two times the actual molar mass (60 g mol^{-1}).

The electrolytes such as KCl or NaCl dissociates completely into its constitutent ions in their aqueous solution. This causes an increase in the total number of particles (ions) present in the solution. The calculated molar mass using colligative property measurement for this type of solutions will be lower than the actual molar mass. For example, the sodium chloride dissociates into Na^+ ions and Cl^- ions in aqueous solution, as shown below.

$$NaCl\,(s) \rightarrow Na^+\,(aq) + Cl^-\,(aq)$$

When we dissolve 1 mole of NaCl (58.4 g) in water, it dissociates and gives 1 mole of Na^+ and 1 mole of Cl^-. Hence, the solution will have 2 moles of particles. Thus, the colligative properties would be double the expected value.

van't Hoff factor

We have learnt that the dissociation or association of solute molecules in a solution will result in the increase or decrease in the calculated molar mass using the colligative property. This variation is proportional to the extent of association or dissociation. To quantify the extent of association or dissociation of solutes in solution, van't Hoff introduced a term 'i' which is now called van't Hoff factor. It is defined as the ratio of the actual molar mass to the abnormal (calculated) molar mass of the solute. Here, the abnormal molar mass is the molar mass calculated using the experimentally determined colligative property.

$$i = \frac{\text{Normal (actual) molar mass}}{\text{Observed (abnormal) molar mass}}$$

$$= \frac{\text{Observed colligative property}}{\text{Calculated colligative property}}$$

The estimated Van't Hoff factor for acetic acid solution in Benzene is 0.5 and that of sodium chloride solution in water is 2. The degree of dissociation or association can be related to Van't Hoff factor (i) using the following relationships

$$\alpha_{dissociation} = \frac{i-1}{n-1}$$

(Where n is number ions /species formed by the dissociation of a single molecule)

$$\alpha_{association} = \frac{(1-i)n}{n-1}$$

(here, n is the number of solute involved in association.

The equations relating the four colligative properties with the concentration of the solutes can be rewritten as follow by incorporating the van't Hoff factor

Relative lowering of vapour pressure,

$$= \frac{p^o_{solvent} - p_{solution}}{p^o_{solvent}} = i\frac{n_{solute}}{n_{solvent}}$$

Elevation of boiling point,

$$\Delta T_b = iK_b m$$

Depression in the freezing point,

$$\Delta T_f = iK_f m$$

Osmotic pressure,

$$\pi = i\frac{W_{solute}}{V}\frac{RT}{M_{solute}}$$

For a solute that does not dissociate or associate the van't Hoff factor is equal to 1 (i = 1) and the molar mass will be close to the actual molar mass.

For the solutes that associate to form higher oligomers in solution the van't Hoff factor will be less than one (i <1) and the observed molar mass will be greater than the actual molar mass.

For solutes that dissociates into their constituent ions the van't Hoff factor will be more than one (i > 1) and the observed molar mass will be less than the normal molar mass.

Example Problem - 7

The depression in freezing point is 0.24K obtained by dissolving 1g NaCl in 200g water. Calculate van't-Hoff factor. The molal depression constant is 1.86 K Kg mol^{-1}

Molar mass of solute

$$= \frac{1000 \times K_f \times \text{mass of NaCl}}{\Delta T_f \times \text{mass of solvent}}$$

$$= \frac{1000 \times 1.86 \times 1}{0.24 \times 200}$$

$$= 38.75 g\ mol^{-1}$$

$$= 38.75\ g\ mol^{-}$$

Theoretical molar mass of NaCl is =

$$i = \frac{\text{Theoretical molar mass}}{\text{Experimental molar mass}} = \frac{58.5}{38.75}$$

$$= 1.50$$

Evaluate Yourself

14. 0.2 m aqueous solution of KCl freezes at -0.68°C calculate van't Hoff factor. k_f for water is 1.86 K kg mol^{-1}.

SUMMARY

- A solution is a homogeneous mixture of two or more chemically non-reacting substances mixed uniformly. The proportion of component which is more in the solution is called solvent and the lesser component is called solute.

- The different concentration units used to prepare the solutions are formality, molality , normality, molarity, molefraction, %w/w solution, %w/v solution, %v/v solution. If the solute quantity is very minimum then ppm unit is used to express its concentration.

- The standard solutions are prepared and diluted to desired concentration (working standards). This helps in overcoming the error due to weighing and maintain efficiency and consistency in the preparation of solution.

- Solubility is defined as the amount of solute in a saturated solution per 100g of a solvent. Solubility of a solute in a solvent depends on the nature of the solute and solvent , temperature.

- The solubility of a gas in a liquid depends upon, the nature of the gas and the nature of the liquid, the temperature of the system, and the pressure of the gas.

- The effect of pressure on the solubility of a gas in a liquid is governed by Henry's Law. It states that the solubility of a gas in a liquid at a given temperature in directly proportional to the partial pressure of the gas.

- The vapour pressure of a liquid is the pressure exerted by its vapour when it is in dynamic equilibrium with its liquid, in a closed container. According to Raoults Law, the vapour pressure of a solution containing a non-volatile solute is directly proportional to the mole fraction of the solvent (XA). The proportionality constant being the vapour pressure of the pure solvent.

- The solution shows positive deviation from Raoult's Law if its vapour pressure is higher than that predicted by Raoult's Law for example ethyl alcohol and cyclohexane.

- The solution shows negative deviation if its vapour pressure is lower than that predicted by Raoult's Law for example acetone and chloroform.

- Colligative properties of solutions are those properties which depend only upon the number of solute particles in the solution and not on their nature. Such properties are

- (a) Relative lowering in vapour pressure: On addition of a non volatile solute it is observed that the vapour pressure of the solution is lesser than the solvent. According to Raolut's law relative lowering of vapour pressure is equal to the mole fraction of the solute.

- (b) Elevation of boiling pointΔTb: The solution boils at a higher temperature than the pure solvent. This is due to the decreased vapour pressure of solution and the temperature it reaches the atmospheric pressure on heating to boil is much higher than the solvent.

- (c) Depression of freezing point: The freezing point of the solution is much lower than the solvent as the temperature at which the solid and the liquid have the same vapour pressure is much lower than the solvent.
- (d) Osmotic pressure: The spontaneous flow of solvent molecules from a dilute solution into a concentrated solution when the two are separated by a perfect semipermeable membrane is called osmosis.
- Osmotic pressure (π) is the pressure which must be applied to the solution side (more concentrated solution) to just prevent the passage of pure solvent into it through a semipermeable membrane.
- Abnormal colligative properties
- If solutes undergo any association or dissociation in a solutiont, they exhibit abnormal colligative properties Van't Hoft factor explains quantitatively the extent of association or dissociation of soluts in solvent.

Evaluation

1. The molality of a solution containing 1.8g of glucose dissolved in 250g of water is

a) 0.2 M b) 0.01 M

c) 0.02 M d) 0.04 M

2. Which of the following concentration terms is / are independent of temperature

a) molality b) molarity

c) mole fraction d) (a) and (c)

3. Stomach acid, a dilute solution of HCl can be neutralised by reaction with Aluminium hydroxide

$Al(OH)_3 + 3HCl(aq) \longrightarrow AlCl_3 + 3H_2O$

How many millilitres of 0.1 M $Al(OH)_3$ solution are needed to neutralise 21 mL of 0.1 M HCl ?

a) 14 mL b) 7 mL

c) 21 mL d) none of these

4. The partial pressure of nitrogen in air is 0.76 atm and its Henry's law constant is 7.6×10^4 atm at 300K. What is the molefraction of nitrogen gas in the solution obtained when air is bubbled through water at 300K ?

a) 1×10^{-4} b) 1×10^{-6}

c) 2×10^{-5} d) 1×10^{-5}

5. The Henry's law constant for the solubility of Nitrogen gas in water at 350 K is 8×10^4 atm. The mole fraction of nitrogen in air is 0.5. The number of moles of Nitrogen from air dissolved in 10 moles of water at 350K and 4 atm pressure is

a) 4×10^{-4} b) 4×10^4

c) 2×10^{-2} d) 2.5×10^{-4}

6. Which one of the following is incorrect for ideal solution ?

a) $\Delta H_{mix} = 0$

b) $\Delta U_{mix} = 0$

c) $\Delta P = P_{observed} - P_{\text{Calculated by raoults law}} = 0$

d) $\Delta G_{mix} = 0$

7. Which one of the following gases has the lowest value of Henry's law constant ?

a) N_2 b) He

c) CO_2 d) H_2

8. P_1 and P_2 are the vapour pressures of pure liquid components, 1 and 2 respectively of an ideal binary solution if x_1 represents the mole fraction of component 1, the total pressure of the solution formed by 1 and 2 will be

a) $P_1 + x_1 (P_2 - P_1)$

b) $P_2 - x_1 (P_2 + P_1)$

c) $P_1 - x_2 (P_1 - P_2)$

d) $P_1 + x_2 (P_1 - P_2)$

9. Osometic pressure (π) of a solution is given by the relation

a) $\pi = nRT$ b) $\pi V = nRT$

c) $\pi RT = n$ d) none of these

10. Which one of the following binary liquid mixtures exhibits positive deviation from Raoults law ?

a) Acetone + chloroform

b) Water + nitric acid

c) HCl + water

d) ethanol + water

11. The Henry's law constants for two gases A and B are x and y respectively. The ratio of mole fractions of A to B is 0.2. The ratio of mole fraction of B and A dissolved in water will be

a) $\frac{2x}{y}$ b) $\frac{y}{0.2x}$

c) $\frac{0.2x}{y}$ d) $\frac{5x}{y}$

12. At 100°C the vapour pressure of a solution containing 6.5g a solute in 100g water is 732mm. If $K_b = 0.52$, the boiling point of this solution will be

a) 102°C b) 100°C

c) 101°C d) 100.52°C

13. According to Raoults law, the relative lowering of vapour pressure for a solution is equal to

a) mole fraction of solvent

b) mole fraction of solute

c) number of moles of solute

d) number of moles of solvent

14. At same temperature, which pair of the following solutions are isotonic ?

a) 0.2 M $BaCl_2$ and 0.2M urea

b) 0.1 M glucose and 0.2 M urea

c) 0.1 M NaCl and 0.1 M K_2SO_4

d) 0.1 M $Ba(NO_3)_2$ and 0.1 M Na_2SO_4

15. The empirical formula of a non-electrolyte(X) is CH_2O. A solution containing six gram of X exerts the same osmotic pressure as that of 0.025M glucose solution at the same temperature. The molecular formula of X is

a) $C_2H_4O_2$ b) $C_8H_{16}O_8$

c) $C_4H_8O_4$ d) CH_2O

16. The K_H for the solution of oxygen dissolved in water is 4×10^4 atm at a given temperature. If the partial pressure of oxygen in air is 0.4 atm, the mole fraction of oxygen in solution is

a) 4.6×10^3 b) 1.6×10^4

c) 1×10^{-5} d) 1×10^5

17. Normality of 1.25M sulphuric acid is

a) 1.25 N   b) 3.75 N

c) 2.5 N   d) 2.25 N

18. Two liquids X and Y on mixing gives a warm solution. The solution is

a) ideal

b) non-ideal and shows positive deviation from Raoults law

c) ideal and shows negative deviation from Raoults Law

d) non-ideal and shows negative deviation from Raoults Law

19. The relative lowering of vapour pressure of a sugar solution in water is 3.5×10^{-3}. The mole fraction of water in that solution is

a) 0.0035   b) 0.35
c) 0.0035 / 18   d) 0.9965

20. The mass of a non-voltaile solute (molar mass 80 g mol^{-1}) which should be dissolved in 92g of toluene to reduce its vapour pressure to 90%

a) 10g   b) 20g

c) 9.2 g   d) 8.89g

21. For a solution, the plot of osmotic pressure (π) verses the concentration (c in mol L^{-1}) gives a straight line with slope 310R where 'R' is the gas constant. The temperature at which osmotic pressure measured is

a) 310 × 0.082 K   b) 310°C

c) 37°C   d) $\frac{310}{0.082}$K

22. 200ml of an aqueous solution of a protein contains 1.26g of protein. At 300K, the osmotic pressure of this solution is found to be 2.52×10^{-3} bar. The molar mass of protein will be (R = 0.083 L bar mol^{-1} K^{-1})

a) 62.22 Kg mol–1   b) 12444g mol^{-1}
c) 300g mol^{-1} d) none of these

23. The Van't Hoff factor (i) for a dilute aqueous solution of the strong elecrolyte barium hydroxide is (NEET)

a) 0   b) 1

c) 2   d) 3

24. What is the molality of a 10% W/W aqueous sodium hydroxide solution ?

a) 2.778   b) 2.5

c) 10   d) 0.4

25. The correct equation for the degree of an associating solute, 'n' molecules of which undergoes association in solution, is

a) $\alpha = \frac{n(i-1)}{n-1}$ b) $\alpha^2 = \frac{n(1-i)}{(n-1)}$

c) $\alpha = \frac{n(i-1)}{1-n}$ d) $\alpha = \frac{n(1\text{-}i)}{n(1\text{-}i)}$

26. Which of the following aqueous solutions has the highest boiling point ?

a) 0.1 M KNO_3 b) 0.1 M Na_3PO_4
c) 0.1 M $BaCl_2$ d) 0.1 M K_2SO_4

27. The freezing point depression constant for water is 1.86° K $Kgmol^{-1}$. If 5g Na_2SO_4 is dissolved in 45g water, the depression in freezing point is 3.64°C. The Vant Hoff factor for Na_2SO_4 is

a) 2.50   b) 2.63

c) 3.64   d) 5.50

28. Equimolal aqueous solutions of NaCl and KCl are prepared. If the freezing point of NaCl is –2°C, the freezing point of KCl solution is expected to be

a) –2°C b) – 4°C

c) – 1°C d) 0°C

29. Phenol dimerises in benzene having van't Hoff factor 0.54. What is the degree of association ?

a) 0.46 b) 92

c) 46 d) 0.92

30. Assertion : An ideal solution obeys Raoults Law

Reason : In an ideal solution, solvent-solvent as well as solute-solute interactions are similar to solute-solvent interactions.

a) both assertion and reason are true and reason is the correct explanation of assertion

b) both assertion and reason are true but reason is not the correct explanation of assertion

c) assertion is true but reason is false

d) both assertion and reason are false

31. Define (i) molality (ii) Normality

32. What is a vapour pressure of liquid?

What is relative lowering of vapour pressure?

33. State and explain Henry's law

34. State Raoult law and obtain expression for lowering of vapour pressure when nonvolatile solute is dissolved in solvent.

35. What is molal depression constant? Does it depend on nature of the solute ?

36. What is osmosis?

37. Define the term 'isotonic solution'.

38. You are provided with a solid 'A' and three solutions of A dissolved in water - one saturated, one unsaturated, and one super saturated. How would you determine which solution is which ?

39. Explain the effect of pressure on the solubility.

40. A sample of 12 M Concentrated hydrochloric acid has a density 1.2 gL^{-1} Calculate the molality

41. A 0.25 M glucose solution at 370.28 K has approximately the pressure as blood does what is the osmotic pressure of blood ?

42. Calculate the molality of a solution containing 7.5 g of glycine (NH_2-CH_2 -COOH) dissolved in 500 g of water.

43. Which solution has the lower freening point?10 g of methanol (CH_3OH) in 100g of water (or) 20 g of ethanol (C_2H_5OH) in 200 g of water.

44. How many moles of solute particles are present in one litre of 10^{-4} M potassium sulphate?

45. Henry's law constant for solubility of methane in benzene is $4.2x10^{-5}$ mm Hg at a particular constant temperature At this temperature. Calculate the solubility of methane at i) 750 mm Hg ii) 840 mm Hg

46. The observed depression in freezing point of water for a particular solution is 0.093°C. Calculate the concentration of the solution in molality. Given that molal depression constant for water is 1.86 KKg mol^{-1}

47. The vapour pressure of pure benzene (C_6H_6) at a given temperature is 640 mm Hg. 2.2 g of non-volatile solute is added to 40 g of benzene. The vapour pressure of the solution is 600 mm Hg. Calculate the molar mass of the solute?

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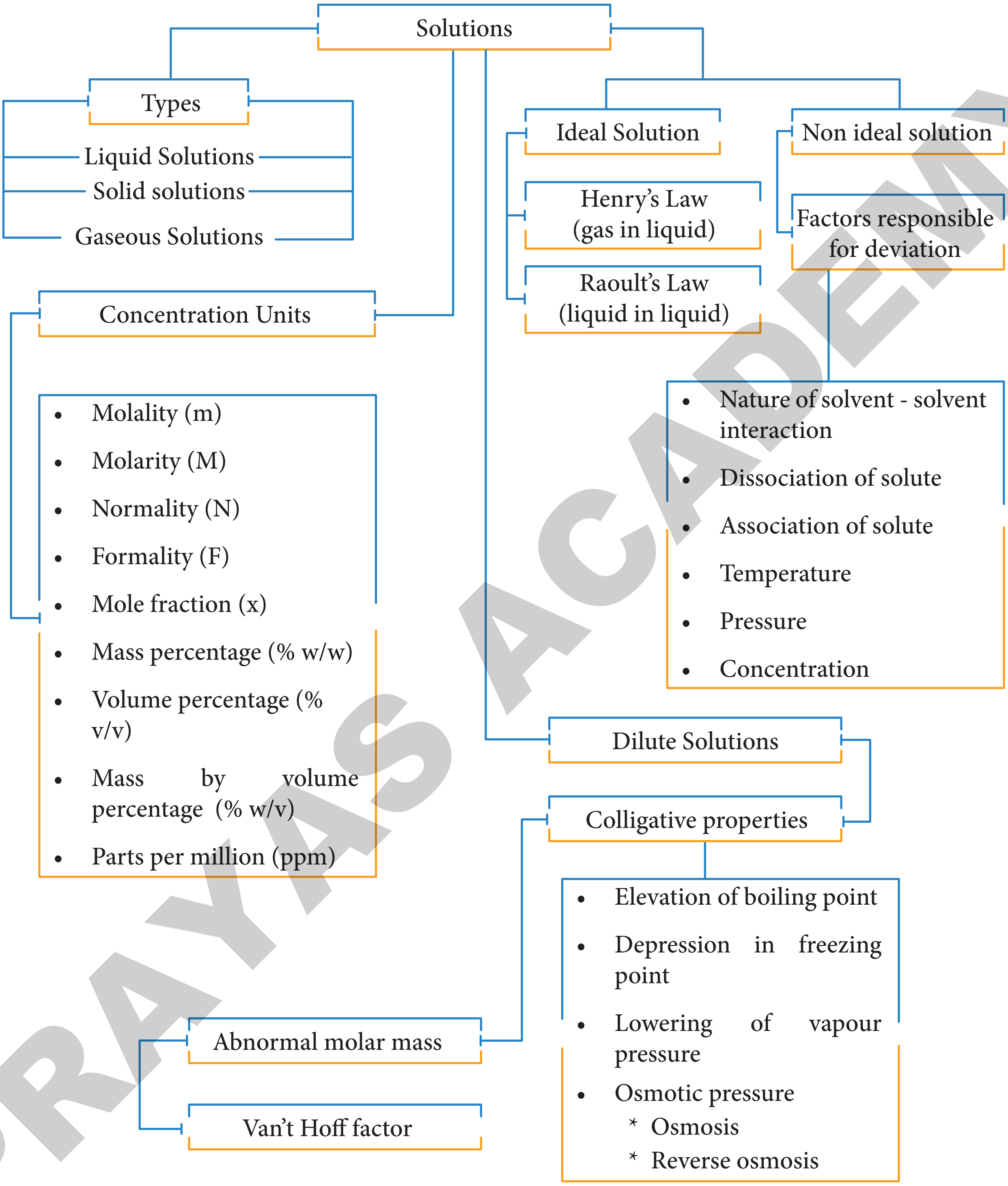


BZ1RE5

Unit 10 Chemical bonding

Linus Carl Pauling was an American chemist, biochemist, peace activist, author and educator. In addition to his contribution to chemistry and he also worked with many biologists.

He received the Nobel Prize in Chemistry in 1954 for his research into the nature of the chemical bond and its application to the elucidation of the structure of complex substances.

Learning Objectives

After studying this unit students will be able to

- describe Kossel – Lewis approach to chemical bonding
- explain the octet rule
- sketch the Lewis structures of simple molecules
- describe the formation of different types of bonds and bond parameters
- sketch the resonance structures for simple molecules
- apply the concept of electronegativity to explain the polarity of covalent bonds
- describe VSEPR theory and predict the shapes of simple molecules
- explain the valence bond approach for the formation of covalent bonds
- explain the different types of hybridisation involving s, p & d orbitals and sketch shapes of simple covalent molecules
- explain the molecular orbital theory, calculate the bond order and explain the magnetic properties of H_2, O_2, N_2 CO and NO
- describe metallic bonding briefly.

10.1 Introduction

Diamond is very hard while its allotrope graphite is very soft. Gases like hydrogen and oxygen are diatomic while the inert gases are monoatomic.

Carbon combines with chlorine to form carbon tetrachloride, which is a liquid and insoluble (immiscible) in water. Sodium combines with chlorine atom to form sodium chloride, a hard and brittle compound that readily dissolves in water. The possible reason for these observations lies in the type of interaction that exists between the atoms of these molecules and these interactions are responsible for holding the atoms/ions together. The interatomic attractive forces which hold the constituent atoms/ions together in a molecule are called chemical bonds.

Why do atoms combine only in certain combinations to form molecules? For example oxygen combines with hydrogen to give water (H_2O) and with carbon it gives carbon dioxide (CO_2). The structure of water is 'V' shaped while that of the carbon dioxide is linear. Such questions can be answered using the principles of chemical bonding. In this unit we will analyse the various theories and their principles, which were developed over the years to explain the nature of chemical bonding.

10.1.1 Kossel – Lewis approach to chemical bonding

A logical explanation for chemical bonding was provided by Kossel and Lewis in 1916. Their approach to chemical bonding is based on the inertness of the noble gases which have little or no tendency to combine with other atoms. They proposed that the noble gases are stable due to their completely filled outer shell electronic configuration. Elements other than noble gases, try to attain the completely filled electronic configurations by losing, gaining or sharing one or more electrons from their outer shell. For example, sodium loses one electron to form Na^+ ion and chlorine accepts that electron to give chloride ion (Cl^-), enabling both atoms to attain the nearest noble gas configuration. The resultant ions, Na^+ and Cl^- are held together by electrostatic attractive forces and the attractive force is called a chemical bond, more specifically an electrovalent bond.

$$\begin{array}{lcl} \text{Na} & \longrightarrow & \text{Na}^+ + e^- \\ \textbf{[Ne] 3s}^{\mathbf{1}} & & \textbf{[Ne]} \\ \text{Cl} \quad + \; e^- & \longrightarrow & \text{Cl}^- \\ \textbf{[Ne] 3s}^{\mathbf{2}}\,\textbf{3p}^{\mathbf{5}} & & \textbf{[Ar]} \\ \text{Na}^+ + \text{Cl}^- & \longrightarrow & \text{NaCl} \end{array}$$

G. N. Lewis proposed that the attainment of stable electronic configuration in molecules such as diatomic nitrogen, oxygen etc… is achieved by mutual sharing of the electrons. He introduced a simple scheme to represent the chemical bond and the electrons present in the outer shell of an atom, called Lewis dot structure. In this scheme, the valence electrons (outer shell electrons) of an element are represented as small dots around the symbol of the element. The first four valence electrons are denoted as single dots around the four sides of the atomic symbol and then the fifth onwards, the electrons are denoted as pairs. For example, the electronic configuration of nitrogen is $1s^2$, $\mathbf{2s^2, 2p^3}$. It has 5 electrons in its outer shell (valence shell). The Lewis structure of nitrogen is as follows.

Fig 10.1 Lewis Structure of Nitrogen atom

Similarly, Lewis dot structure of carbon, oxygen can be drawn as shown below.

Fig 10.2 Lewis Structures of C & O atoms

Only exception to this is helium which has only two electrons in its valence shell which is represented as a pair of dots (duet).

Fig 10.3 Lewis Structures of He atoms

Octet rule

The idea of Kossel – Lewis approach to chemical bond lead to the octet rule, which states that "***the atoms transfer or share electrons so that all atoms involved in chemical bonding obtain 8 electrons in their outer shell (valence shell)***".

10.2 Types of chemical bonds

The chemical bonds can be classified based on the nature of the interaction between the bonded atoms. Two major types of chemical bonds are covalent bonds and ionic bonds. Generally metals reacts with non-metals to form ionic compounds, and the covalent bonds are present in the compounds formed by nonmetals.

10.2.1 Covalent bonds:

Do you know all elements (except noble gases) occurs either as compounds or as polyatomic molecules? Let us consider hydrogen gas in which two hydrogen atoms bind to give a dihydrogen molecule. Each hydrogen atom has one electron and it requires one more electron to attain the electronic configuration of the nearest noble gas helium. Lewis suggested that both hydrogen atoms will attain the stable configuration by mutually sharing the electrons available with them. Similarly, in the case of oxygen molecule, both the oxygen atoms share two electron pairs between them and in nitrogen molecule three electron pairs are shared between two nitrogen atoms. ***This type of mutual sharing of one or more pairs of electrons between two combining atoms results in the formation of a chemical bond called a covalent bond***. If two atoms share just one pair of electron a single covalent bond is formed as in the case of hydrogen molecule. If two or three electron pairs are shared between the two combining atoms, then the covalent bond is called a double bond or a triple bond, respectively.

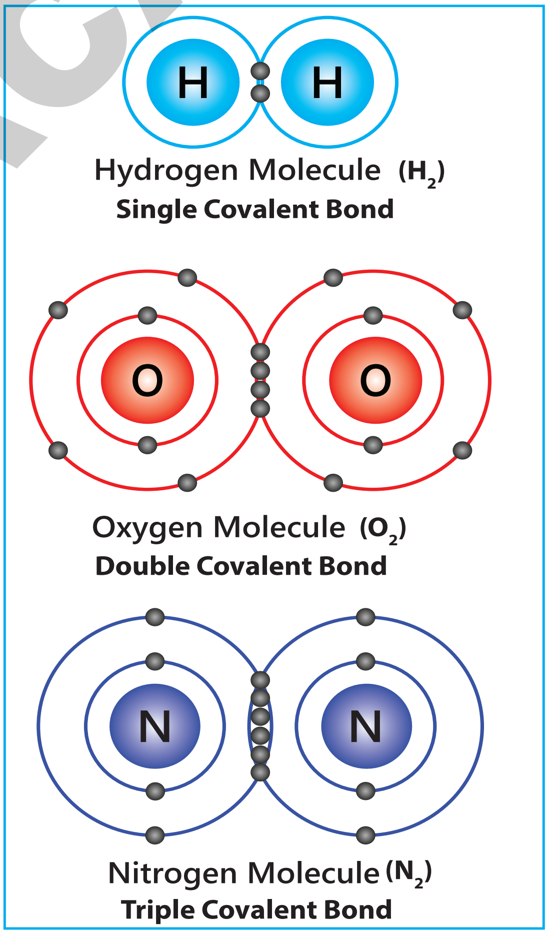


Fig 10. 4 Representation of Lewis Structures of covalent bonds

10.2.2 Representing a covalent bond - Lewis structure (Lewis dot structure)

Lewis structure (Lewis dot structure) is a pictorial representation of covalent bonding between the combining atoms. In this structure the shared valence electrons are represented as a pair of dots between the combining atoms and the unshared electrons of the atoms are represented as a pair of dots (lone pair) on the respective individual atoms.

The Lewis dot structure for a given compound can be written by following the steps given below. Let us understand these steps by writing the Lewis structure for water.

1. **Draw the skeletal structure of the molecule**. In general, the most electronegative atom is placed at the centre. Hydrogen and fluorine atoms should be placed at the terminal positions. For water, the skeletal structure is

   H O H

2. **Calculate the total number of valence electrons of all the atoms in the molecule**. In case of polyatomic ions the charge on ion should also be considered during the calculation of the total number of valence electrons. In case of anions the number of negative charges should be added to the number of valence electrons. For positive ions the total number of positive charges should be subtracted from the total number of valence electrons.

   In water, total number of valence electron =[2×1 (valence electron of hydrogen)] + [1 × 6 (valence electrons of oxygen)] = 2 + 6 = 8.

3. **Draw a single bond between the atoms in the skeletal structure of the molecule**. Each bond will account for two valence electrons (a bond pair). For water, we can draw two bonds accounting for four valence electrons as follows.

   H — O — H

4. **Distribute the remaining valence electrons as pairs (lone pair), giving octet (only duet for hydrogen) to the atoms in the molecule**. The distribution of lone pairs starts with the most electronegative atoms followed by other atoms.

   In case of water, the remaining four electrons (two lone pairs) are placed on the most electronegative central oxygen, giving octet.

$$H - \ddot{\underset{\cdot\cdot}{O}} - H$$

5. **Verify weather all the atoms satisfy the octet rule (for hydrogen duet).** If not, use the lone pairs of electrons to form additional bond to satisfy the octet rule.

   In case of water, oxygen has octet and the hydrogens have duets, hence there is no need for shifting the lone pairs. The Lewis structure of water is as follows

$$H - \ddot{\underset{\cdot\cdot}{O}} - H$$

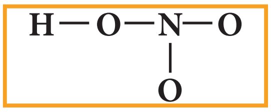
Fig 10. 5 Lewis structure of water

Let us draw the Lewis structure for nitric acid.

1. Skeletal structure

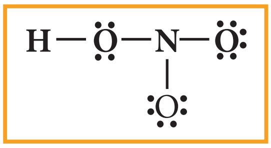
$$\begin{array}{cccc} \mathrm{H} & \mathrm{O} & \mathrm{N} & \mathrm{O} \\ & & \mathrm{O} & \end{array}$$

2. Total number of valence electrons in HNO_3
   = [1 × 1(hydrogen)] + [1 × 5(nitrogen)] + [3× 6(oxygen)] = 1+ 5 + 18 = 24
3. Draw single bonds between atoms. Four bonds can be drawn as shown in the figure for HNO_3 which account for eight electrons (4 bond pairs).



$$\begin{array}{ccccccc} \mathrm{H} & - & \mathrm{O} & - & \mathrm{N} & - & \mathrm{O} \\ & & & & | & & \\ & & & & \mathrm{O} & & \end{array}$$

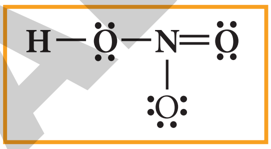
4. Distribute the remaining sixteen (24 - 8= 16) electrons as eight lone pairs starting from most electronegative atom, the oxygen. Six lone pairs are distributed to the two terminal oxygens (three each) to satisfy their octet and two pairs are distributed to the oxygen that is connected to hydrogen to satisfy its octet.



$$\begin{array}{ccccccc} \mathrm{H} & - & \ddot{\underset{\cdot\cdot}{\mathrm{O}}} & - & \mathrm{N} & - & :\ddot{\underset{\cdot\cdot}{\mathrm{O}}}: \\ & & & & | & & \\ & & & & :\underset{\cdot\cdot}{\mathrm{O}}: & & \end{array}$$

5. Verify weather all the atoms have octet configuration. In the above distribution, the nitrogen has one pair short for octet. Therefore, move one of the lone pair from the terminal oxygen to form another bond with nitrogen.

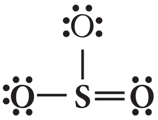
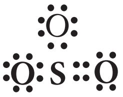
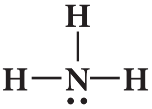
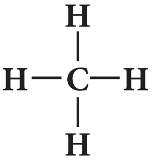
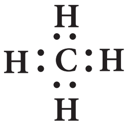
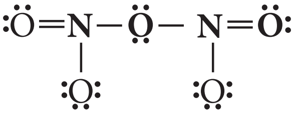
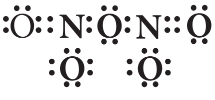
The Lewis structure of nitric acid is given as



$$\begin{array}{ccccccc} \mathrm{H} & - & \ddot{\underset{\cdot\cdot}{\mathrm{O}}} & - & \mathrm{N} & = & \ddot{\underset{\cdot\cdot}{\mathrm{O}}} \\ & & & & | & & \\ & & & & :\underset{\cdot\cdot}{\mathrm{O}}: & & \end{array}$$

Fig 10. 6 Lewis structure of Nitric acid

Table 10.1 : The Lewis dot structures for some molecules

S. No	Molecule	Lewis Structure	
1.	Sulphur trioxide (SO_3)		
2.	Ammonia (NH_3)		
3.	Methane		
4.	Dinitrogen Pentoxide (N_2O_5)		

Note

It is to be noted that nearly in all their compounds, certain elements form a fixed number of bonds. For example, Fluorine forms only one bond. Hydrogen, oxygen, nitrogen and carbon atoms form one, two, three and four bonds, respectively.

Evaluate Yourself

1) Draw the lewis structures for
   - i) Nitrous acid (HNO_2)
   - ii) Phosphoric acid
   - iii) Sulphur troxide (SO_3)

10.2.3 Formal charge:

Let us draw the Lewis structure for carbon dioxide.

1. Skeletal structure

O C O

2. Total number of valence electrons in CO_2

   = [1 x 4(carbon)] +[2 x 6(oxygen)] = 4+ 12 = 16

3. Draw single bonds between atoms. Two bonds can be drawn as shown in the figure for CO_2 which accounts for four electrons (2 bond pairs).

O—C—O

4. Distribute the remaining twelve electrons (16 - 4= 12) as six lone pairs starting from most electronegative atom, the oxygen. Six lone pairs are distributed to the two terminal oxygens (three each) to satisfy their octet.

5. Verify weather all the atoms have octet configuration. In the above distribution, the central carbon has two pair short for octet. Therefore, to satisfy the octet rule two lone pairs from one oxygen or one pair from each oxygen can be moved to form multiple bonds, leading the formation of two possible structures for carbon dioxide as shown below

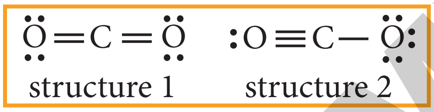


Fig 10. 7 (a) two possible structures for carbon dioxide

Similarly, the Lewis structure for many molecules drawn using the above steps gives more than one acceptable structure. Let us consider the above mentioned two structures of carbon dioxide.

Which one the above forms represents the best distribution of electrons in the molecule. To find an answer, we need to know the formal charge of each atom in the Lewis structures. Formal charge of an atom in a molecule, is the electrical charge difference between the valence electron in an isolated atom and the number of electrons assigned to that atom in the Lewis structure.

$$\text{Formal charge of an atom} = N_v - \left(N_l + \frac{N_b}{2} \right)$$

Where,

N_v - Number of valence electron of atom in its isolated state.

N_l - Number of electrons present as lone pairs around the atom in the Lewis structure

N_b - Number of electrons present in bonds around the atom (bond pairs) in the

Lewis structure]

Now let us calculate the formal charge on all atoms in both structures,

For Structure 1,

$$\text{Formal charge on carbon} = N_v - \left(N_l + \frac{N_b}{2}\right)$$

$$= 4 - \left(0 + \frac{8}{2}\right) = 0$$

$$\text{Formal charge on oxygen} = 6 - \left(4 + \frac{4}{2}\right)$$

$$= 0 \text{ (for both oxygens)}$$

For structure 2

Formal charge on carbon

$$= N_v - \left(N_l + \frac{N_b}{2}\right)$$

$$= 4 - \left(0 + \frac{8}{2}\right) = 0$$

Formal charge on singly bonded oxygen

$$= 6 - \left(6 + \frac{2}{2}\right) = -1$$

Formal charge on triply bonded oxygen

$$= 6 - \left(2 + \frac{6}{2}\right) = +1$$

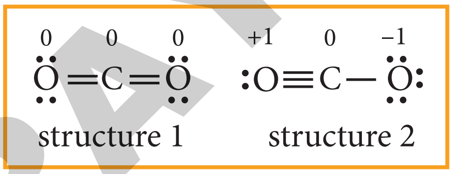


Fig 10. 7 (b) two possible structures for carbon dioxide (with formal charges)

After calculating the formal charges, the best representation of Lewis structure can be selected by using following guidelines.

1. A structure in which all formal charges are zero preferred over the one with charges.
2. A structure with small formal charges is preferred over the one with higher formal charges.
3. A structure in which negative formal charges are placed on the most electronegative atom is preferred.

In case of CO_2 structures, the structure one is preferred over the structure 2 as it has zero formal charges for all atoms.

10.2.4 Lewis structures for exceptions to octet rule

The octet rule is useful for writing Lewis structures for molecules with second period element as central atoms. In some molecules, the central atoms have less than eight electrons around them while some others have more than eight electrons. Exception to the octet rule can be categorized into following three types.

1. Molecules with electron deficient central atoms
2. Molecules containing odd electrons
3. Molecules with expanded valence shells

Molecules with electron deficient central atoms

Let us consider boron trifluoride, as an example. The central atom boron has three valence electron and each fluorine has seven valence electrons. The Lewis structure is

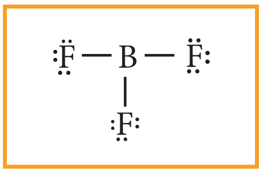


Fig 10. 8 (a) Lewis structure of BF_3

In the above structure, only six

electrons around boron atom. Moving a lone pair from one of the fluorine to form additional bond as shown below.

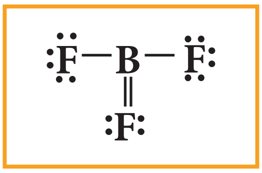


Fig 10. 8 (b) Lewis structure of BF_3

However, the above structure is unfavourable as the most electronegative atom fluorine shows positive formal charge and hence the structure with incomplete octet is the favourable one. Molecules such as BCl_3, $BeCl_2$, etc... also have incomplete octets.

Molecules containing odd electrons

Few molecules have a central atom with an odd number of valence electrons. For example, in nitrogen dioxide and nitric oxide all the atoms does not have octet configuration. The lewis structure of the above molecules are shown in the figure.

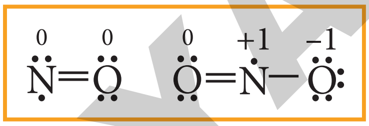


Fig 10. 9 Lewis structures of Nitric oxide and Nitrogen dioxide (with formal charges)

Molecules with expanded valence shells

In molecules such as sulphur hexafluoride (SF_6), phosphorous pentachloride (PCl_5) the central atom has more than eight valence electrons around them. Here the central atom can accommodate additional electron pairs by using outer vacant d orbitals. In SF_6 the central atom sulphur is surrounded by six bonding pair of electrons or twelve electrons.

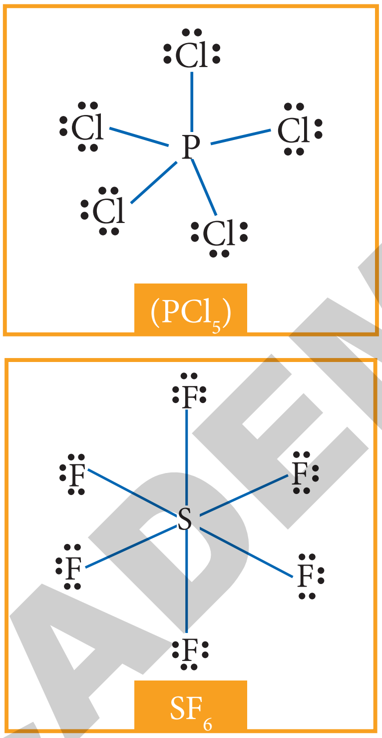


Fig 10. 10 Lewis structures for SF_6 and PCl_5

Evaluate Yourself

2) Calculate the formal charge on each atom of carbonyl chloride ($COCl_2$)

10.3 Ionic or electrovalent bond

When the electronegativity difference between the two combining atoms is large, the least electronegative atom completely transfers one or more of its valence electrons to the other combining atom so that both atoms can attain the nearest inert gas electronic configuration. The complete transfer of electron leads to the formation of a cation and an anion. Both these ions are held together by the electrostatic attractive force which is known as ionic bond.

Let us consider the formation potassium chloride. The electronic configuration of potassium and chlorine are

Potassium (K) : [Ar] $4s^1$

Chlorine (Cl) : [Ne]$3s^2$, $3p^5$

Potassium has one electron in its valence shell and chlorine has seven electron in its valence shell. By loosing one electron potassium attains the inert gas electronic configuration of argon and becomes a unipositive cation (K^+) and chlorine accepts this electron to become uninegative chloride ion (Cl^-) there by attaining the stable electronic configuration of argon. These two ions combine to form an ionic crystal in which they are held together by electrostatic attractive force. The energy required for the formation of one mole of K^+ is 418.81 kJ (ionization energy) and the energy released during the formation of one mole of Cl^- is -348.56 kJ (electron gain enthalpy). The sum of these two energies is positive (70.25 kJ) However, during the formation of one mole potassium chloride crystal from its constituent ions, 718 kJ energy is released. This favours the formation of KCl and its stabilises.

Evaluate Yourself

3) Explain the ionic bond formation in MgO and CaF_2

10.4 Coordinate covalent bond

In the formation of a covalent bond, both the combining atoms contribute one electron each and the these electrons are mutually shared among them. However, in certain bond formation, one of the combining atoms donates a pair of electrons i.e. two electrons which are necessary for the covalent bond formation, and these electrons are shared by both the combining atoms. These type of bonds are called coordinate covalent bond or coordinate bond. The combining atom which donates the pair of electron is called a donor atom and the other atom an acceptor atom. This bond is denoted by an arrow starting from the donor atom pointing towards the acceptor atom. (Later in coordination compound, we will refer the donor atom as ligand and the acceptor atom as central-metal atom/ion.

For Example, in ferrocynide ion $[Fe(CN)_6]^{4-}$, each cyanide ion (CN^-) donates a pair of electrons to form a coordinate bond with iron (Fe^{2+}) and these electrons are shared by Fe^{2+} and CN^-.

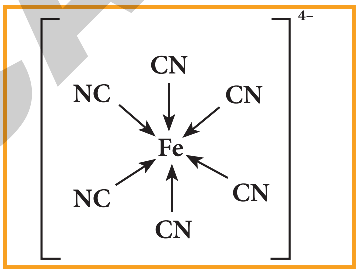


Fig 10. 11 Structure of Ferrocyanide ion

In certain cases, molecules having a lone pair of electrons such as ammonia donates its pair to an electron deficient molecules such as BF_3. to form a coordinate

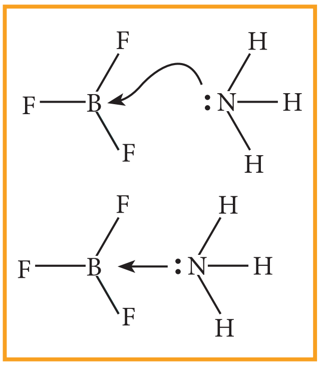


Fig 10. 12 Structure of $BF_3 \rightarrow NH_3$

10.5 Bond parameters

A covalent bond is characterised by parameters such as bond length, bond angle, bond order etc... A brief description of some of the bond parameters is given below.

10.5.1 Bond length

The distance between the nuclei of the two covalently bonded atoms is called bond length. Consider a covalent molecule A-B. The bond length is given by the sum of the radii of the bonded atoms ($r_A + r_B$). The length of a bond can be determined by spectroscopic, x-ray diffraction and electron-diffraction techniques The bond length depends on the size of the atom and the number of bonds (multiplicity) between the combining atoms.

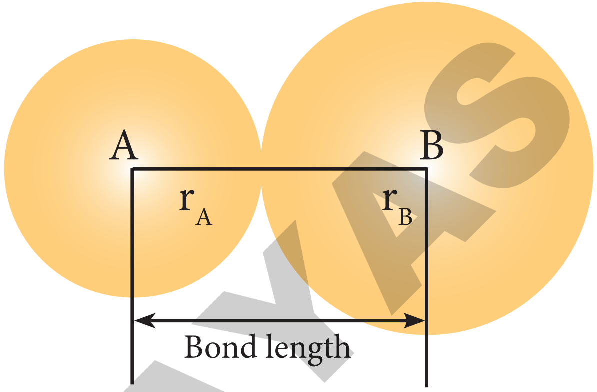


Fig 10. 13 Bond length of covalent molecule A–B

Greater the size of the atom, greater will be the bond length. For example, carbon-carbon single bond length (1.54 Å) is longer than the carbon-nitrogen single bond length (1.43 Å).

Increase in the number of bonds between the two atoms decreases the bond length. For example, the carbon-carbon single bond is longer than the carbon-carbon double bond (1.33 Å) and the carbon-carbon triple bond (1.20 Å).

10.5.2 Bond order

The number of bonds formed between the two bonded atoms in a molecule is called the bond order. In Lewis theory, the bond order is equal to the number of shared pair of electrons between the two bonded atoms. For example in hydrogen molecules, there is only one shared pair of electrons and hence, the bond order is one. Similarly, in H_2O, HCl, Methane, etc the central atom forms single bonds with bond order of one.

Table 10.2 Bond order of some common bonds:

S. No.	Molecule	Bonded atoms	Bond order (No. of shared pair of electrons between bonded atoms)
1	H_2	H-H	1
2	O_2	O=O	2
3	N_2	N≡N	3
4	HCN	C≡N	3
5	HCHO	C=O	2
6	CH_4	C–H	1
7	C_2H_4	C=C	2

10.5.3 Bond angle

Covalent bonds are directional in nature and are oriented in specific directions in space. This directional nature creates a fixed angle between two covalent bonds in a molecule and this angle is termed as bond angle. It is usually expressed in degrees. The bond angle can be determined by spectroscopic methods and it can give some idea about the shape of the molecule.

Table 10.3 Bond angles for some common molecules

S. No.	Molecule	Atoms defining the angle	Bond angle (^{0})
1	CH_4	H-C-H	109^0 28'
2	NH_3	H-N-H	107^0 18'
3	H_2O	H-O-H	104^0 35'

10.5.4 Bond enthalpy

The bond enthalpy is defined as the minimum amount of energy required to break one mole of a particular bond in molecules in their gaseous state. The unit of bond enthalpy is kJ mol^{-1}. Larger the bond enthalpy, stronger will be the bond. The bond energy value depends on the size of the atoms and the number of bonds between the bonded atoms. Larger the size of the atom involved in the bond, lesser is the bond enthalpy.

In case of polyatomic molecules with, two or more same bond types, in the term average bond enthalpy is used. For such bonds, the arithmetic mean of the bond energy values of the same type of bonds is considered as average bond enthalpy. For example in water, there are two OH bonds present and the energy needed to break them are not same.

$$H_2O(g) \rightarrow H(g) + OH(g) \quad \Delta H_1 = 502 \text{ kJ mol}^{-1}$$

$$OH(g) \rightarrow H(g) + O(g) \quad \Delta H_2 = 427 \text{ kJ mol}^{-1}$$

The average bond enthalpy of OH bond in water $= \dfrac{502+427}{2} = 464.5 \text{ kJ mol}^{-1}$

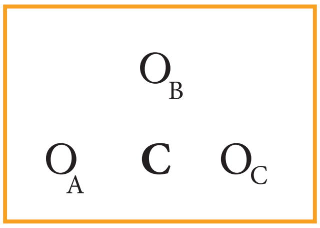
Table 10.4 Bond lengths and bond enthalpies of some common bonds:

S. No.	Bond type	Bond Enthalpy (kJ mol^{-1})	Bond Length (Å)
1	H-H	432	0.74
2	H-F	565	0.92
3	H-Cl	427	1.27
4	H-Br	363	1.41
5	H-I	295	1.61
6	C-H	413	1.09
7	C-C	347	1.54
8	C-Si	301	1.86
9	C-N	305	1.47
10	C-O	358	1.43
11	C-P	264	1.87
12	C-S	259	1.81
13	C-F	453	1.33
14	C-Cl	339	1.77
15	C-Br	276	1.94
16	C-I	216	2.13

10.5.5 Resonance

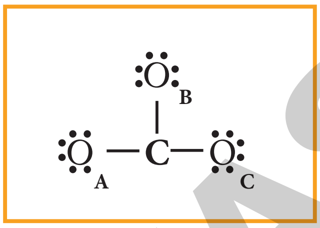
When we write Lewis structures for a molecule, more than one valid Lewis structures are possible in certain cases. For example let us consider the Lewis structure of carbonate ion $[CO_3]^{2-}$.

The skeletal structure of carbonate ion (The oxygen atoms are denoted as O_A, O_B & O_C



Total number of valence electrons = [1 x 4(carbon)] + [3 x 6 (oxygen)] + [2 (charge)] = 24 electrons.

Distribution of these valence electrons gives us the following structure.



Complete the octet for carbon by moving a lone pair from one of the oxygens (O_A) and write the charge of the ion (2-) on the upper right side as shown in the figure.

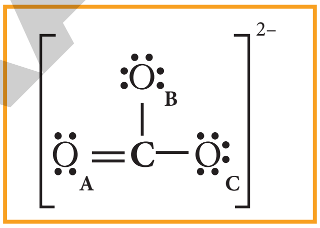


Fig 10. 14 (a) Lewis Structure of CO_3^{2-}

In this case, we can draw two additional Lewis structures by moving the lone pairs from the other two oxygens (O_B and O_C) thus creating three similar structures as shown below in which the relative position of the atoms are same. They only differ in the position of bonding and lone pair of electrons. Such structures are called resonance structures (canonical structures) and this phenomenon is called resonance.

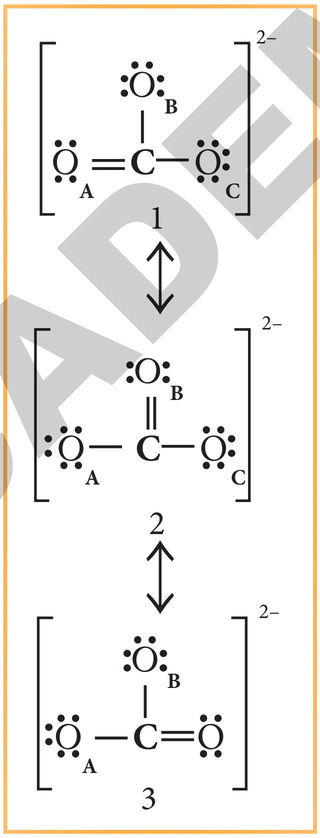


Fig 10. 14 (b) Resonance structures of CO_3^{2-}

It is evident from the experimental results that all carbon-oxygen bonds in carbonate ion are equivalent. The actual structure of the molecules is said to be the resonance hybrid, an average of these three resonance forms. It is important to note that carbonate ion does not change from one structure to another and vice versa. It is not possible to picturise the resonance hybrid by drawing a single Lewis structure. However, the following structure gives a qualitative idea about the correct structure.

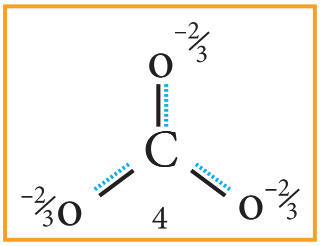


Fig 10. 14 (c) Resonance Hybrid structures of CO_3^{2-}

It is found that the energy of the resonance hybrid (structure 4) is lower than that of all possible canonical structures (Structure 1, 2 & 3). The difference in energy between structure 1 or 2 or 3, (most stable canonical structure) and structure 4 (resonance hybrid) is called resonance energy.

Evaluate Yourself

4) Write the resonance structures for

i) Ozone molecule ii) N_2O

10.5.6 Polarity of Bonds

Partial ionic character in covalent bond:

When a covalent bond is formed between two identical atoms (as in the case of H_2, O_2, Cl_2 etc...) both atoms have equal tendency to attract the shared pair of electrons and hence the shared pair of electrons lies exactly in the middle of the nuclei of two atoms. However, in the case of covalent bond formed between atoms having different electronegativities, the atom with higher electronegativity will have greater tendency to attract the shared pair of electrons more towards itself than the other atom. As a result the cloud of shared electron pair gets distorted.

Let us consider the covalent bond between hydrogen and fluorine in hydrogen fluoride. The electronegativities of hydrogen and fluorine on Pauling's scale are 2.1 and 4 respectively. It means that fluorine attracts the shared pair of electrons approximately twice as much as the hydrogen which leads to partial negative charge on fluorine and partial positive charge on hydrogen. Hence, the H-F bond is said to be polar covalent bond.

Here, a very small, equal and opposite charges are separated by a small distance (91 pm) and is referred to as a dipole.

Dipole moment:

The polarity of a covalent bond can be measured in terms of dipole moment which is defined as

$$\mu = q \times 2d$$

Where μ is the dipole moment, q is the charge and 2d is the distance between the two charges. The dipole moment is a vector and the direction of the dipole moment vector points from the negative charge to positive charge.

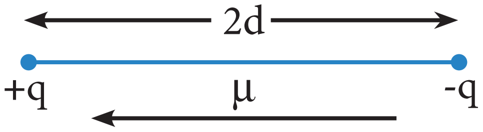


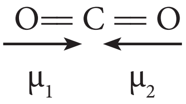
Fig 10. 15 Representation of Dipole

The unit for dipole moment is columb meter (C m). It is usually expressed in Debye unit (D). The conversion factor is 1 Debye = 3.336 x 10^{-30} C m

Diatomic molecules such as H_2, O_2, F_2 etc... have zero dipole moment and are called non polar molecules and molecules such as HF, HCl, CO, NO etc... have non zero dipole moments and are called polar molecules.

Molecules having polar bonds will not necessarily have a dipole moment. For example, the linear form of carbon dioxide has zero dipole moment, even though it has two polar bonds. In CO_2, the dipole moments of two polar bonds (CO) are equal in magnitude but have opposite direction. Hence, the net dipole moment of the CO_2 is,

$$\mu = \mu_1 + \mu_2 = \mu_1 + (-\mu_1) = 0$$



In this case $\mu = \vec{\mu_1} + \vec{\mu_2}$

$= \vec{\mu_1} + (\vec{-\mu_1}) = 0$

Incase of water net dipole moment is the vector sum of $\mu_1 + \mu_2$ as shown.

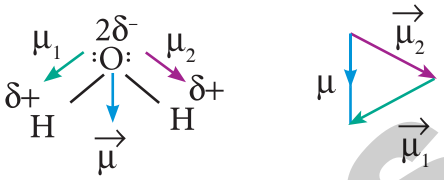


Fig 10. 16 Dipole moment in water

Dipole moment in water is found to be 1.85D

Table 10. 5 Dipole moments of common molecules

S. No.	Molecule	Dipole moment (in D)
1	HF	1.91
2	HCl	1.03
3	H_2O	1.85
4	NH_3	1.47
5	$CHCl_3$	1.04

The extent of ionic character in a covalent bond can be related to the electro negativity difference to the bonded atoms. In a typical polar molecule, $A^{\delta-}$-$B^{\delta+}$, the electronegativity difference (χ_A- χ_B) can be used to predict the percentage of ionic character as follows.

If the electronegativity difference (χ_A- χ_B), is

equal to 1.7, then the bond A-B has 50% ionic character

if it is greater than 1.7, then the bond A-B has more than 50% ionic character,

and if it is lesser than 1.7, then the bond A-B has less than 50% ionic character.

Evaluate Yourself

5) Of the two molecules OCS and CS_2 which one has higher dipole moment value? why?

Partial covalent character in ionic bonds:

Like the partial ionic character in covalent compounds, ionic compounds show partial covalent character. For example, the ionic compound, lithium chloride shows covalent character and is soluble in organic solvents such as ethanol.

The partial covalent character in ionic compounds can be explained on the basis of a phenomenon called polarisation. We know that in an ionic compound, there is an electrostatic attractive force between the cation and anion. The positively charged cation attracts the valence electrons of anion while repelling the nucleus. This causes a distortion in the electron cloud of the anion and its electron density drifts towards the cation, which results in some sharing of the valence electrons between these ions. Thus, a partial covalent character is developed between them. This phenomenon is called polarisation.

The ability of a cation to polarise an anion is called its polarising ability and the tendency of an anion to get polarised is called its polarisability. The extent of polarisation in an ionic compound is given by the Fajans rules

Fajans Rules

(i) To show greater covalent character, both the cation and anion should have high charge on them. Higher the positive charge on the cation, greater will be the attraction on the electron cloud of the anion. Similarly higher the magnitude of negative charge on the anion, greater is its polarisability. Hence, the increase in charge on cation or in anion increases the covalent character

Let us consider three ionic compounds aluminum chloride, magnesium chloride and sodium chloride. Since the charge of the cation increase in the order $Na^+ < Mg^{2+} < Al^{3+}$, the covalent character also follows the same order $NaCl < MgCl_2 < AlCl_3$.

(ii) The smaller cation and larger anion show greater covalent character due to the greater extent of polarisation.

Lithium chloride is more covalent than sodium chloride. The size of Li^+ is smaller than Na^+ and hence the polarising power of Li^+ is more. Lithium iodide is more covalent than lithium chloride as the size of I^- is larger than the Cl^-. Hence I^- will be more polarised than Cl^- by the cation, Li^+ .

(iii) Cations having ns^2 np^6 nd^{10} configuration show greater polarising power than the cations with ns^2 np^6 configuration. Hence, they show greater covalent character.

CuCl is more covalent than NaCl. Compared to Na^+ (1.13 Å) . Cu^+ (0.6 Å) is small and have $3s^2$ $3p^6$ $3d^{10}$ configuration.

Electronic configuration of Cu^+

[Ar] $3s^2, 3p^6, 3d^{10}$

Electronic Configuration of Na^+

[He] $2s^2, 2p^6$

10.6 Valence Shell Electron Pair Repulsion (VSEPR) theory

Lewis concept of structure of molecules deals with the relative position of atoms in the molecules and sharing of electron pairs between them. However, we cannot predict the shape of the molecule using Lewis concept. Lewis theory in combination with VSEPR theory will be useful in predicting the shape of molecules.

Important principles of VSEPR Theory are as follows:

1. The shape of the molecules depends on the number of valence shell electron pair around the central atom.

2. There are two types of electron pairs namely bond pairs and lone pairs. The bond pair of electrons are those shared between two atoms, while the lone pairs are the valence electron pairs that are not involved in bonding.

3. Each pair of valence electrons around the central atom repels each other and hence, they are located as far away as possible in three dimensional space to minimize the repulsion between them.

4. The repulsive interaction between the different types of electron pairs is in the following order.

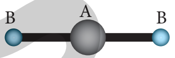
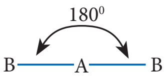
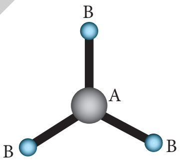
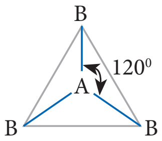
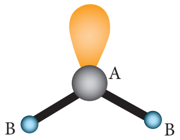
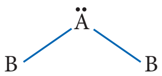
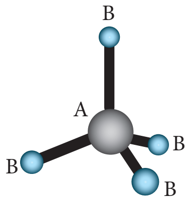
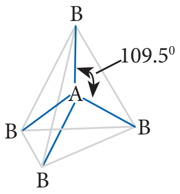
lp - lp > lp - bp> bp-bp

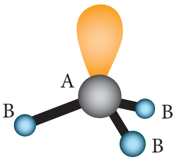
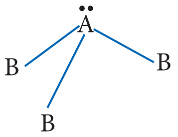
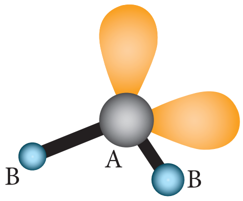
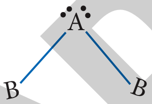
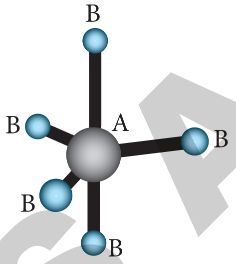
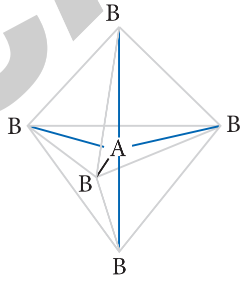
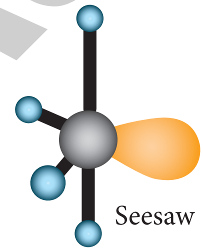
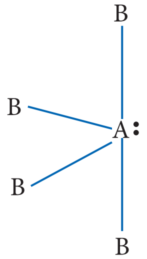
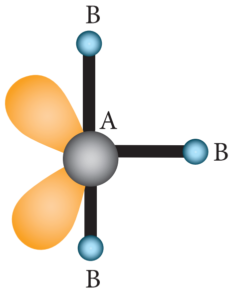
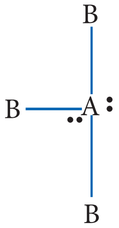
lp- lone pair ; bp- bond pair

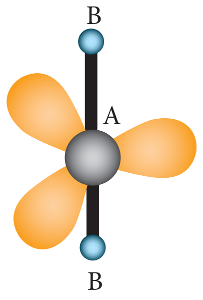
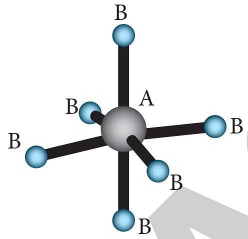
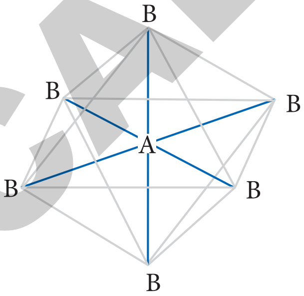
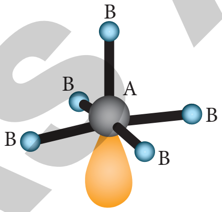
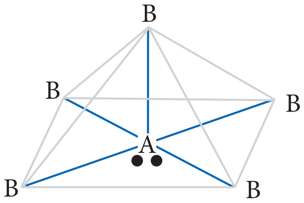
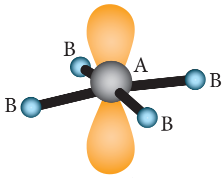
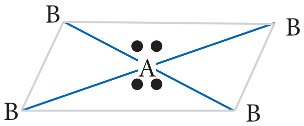
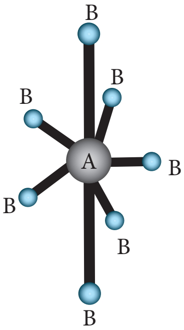
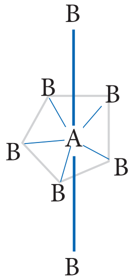
The lone pair of electrons are localised only on the central atom and interacts with only one nucleus whereas the bond pairs are shared between two atoms and they interact with two nuclei. Because of this the lone pairs occupy more space and have greater repulsive power than the bond pairs in a molecule.

The following Table illustrates the shapes of molecules predicted by VSEPR theory. Consider a molecule AB_x where A is the central atom and x represents the number of atoms of B covalently bonded to the central atom A. The lone pairs present in the atoms are denoted as L.

Table 10. 6 Shapes of molecules predicted by VSEPR theory.

Number of electron Pairs	Molecule	No.of bond pairs	No.of. lone pairs	Shape	Molecular geometry	Examples
2	AB_2	2	-	 Linear	 Linear	$BeCl_2$, $HgCl_2$, CO_2, CS_2, HCN, BeF_2
3	AB_3	3	-	 Trigonal planar	 Trigonal planar	BF_3, BCl_3, NO_3^-, BF_3, CO_3^{2-}
	AB_2L	2	1	 Bent or V - Shape	 Bent or V - Shape	HCHO, SO_2, O_3, $PbCl_2$, $SnBr_2$
4	AB_4	4	-	 Tetrahedral	 Tetrahedral	CH_4, CCl_4, CCl_2F_2, SO_4^{2-}, ClO_4^-, NH_4^+

Number of electron Pairs	Molecule	No.of bond pairs	No.of. lone pairs	Shape	Molecular geometry	Examples
	AB_3L	3	1	 pyramidal	 pyramidal	NH_3, PF_3, ClO_3^-, H_3O^+,
	AB_2L_2	2	2	 Bent (V Shaped)	 Bent (V Shaped)	H_2O, OF_2, SCl_2
5	AB_5	5	-	 Trigonal bipyramidal	 Trigonal bipyramidal	PCl_5, ASF_5, SOF_4
	AB_4L	4	1	 Seesaw	 Seesaw	SF_4, XeO_2F_2, IF_4^+, $IO_2F_2^-$
	AB_3L_2	3	2	 T shaped	 T Shaped	BrF_3, ClF_3,

Number of electron Pairs	Molecule	No.of bond pairs	No.of. lone pairs	Shape	Molecular geometry	Examples
	AB_2L_3	2	3	 Linear	 Linear	XeF_2, I_3^-, IF_2^-
6	AB_6	6	-	 Octathedral		SF_6, IOF_5,
	AB_5L	5	1	 Square pyramidal	 Square pyramidal	BrF_5, IF_5, TeF_5^-, $XeOF_4$,
	AB_4L_2	4	2	 Square planar	 Square Planar	XeF_4, ICl_4^-
7	AB_7	7	-		 pentagonal bi-pyramidal	IF_7

Evaluate Yourself

6) Arrange the following in the decreasing order of Bond angle

i) CH_4, H_2O, NH_3 ii) C_2H_2, BF_3, CCl_4

10.7 Valence Bond Theory

Heitler and London gave a theoretical treatment to explain the formation of covalent bond in hydrogen molecule on the basis of wave mechanics of electrons. It was further developed by Pauling and Slater. The wave mechanical treatment of VB theory is beyond the scope of this textbook. A simple qualitative treatment of VB theory for the formation of hydrogen molecule is discussed below.

Consider a situation wherein two hydrogen atoms (H_a and H_b) are separated by infinite distance. At this stage there is no interaction between these two atoms and the potential energy of this system is arbitrarily taken as zero. As these two atoms approach each other, in addition to the electrostatic attractive force between the nucleus and its own electron (purple arrows), the following new forces begins to operate.

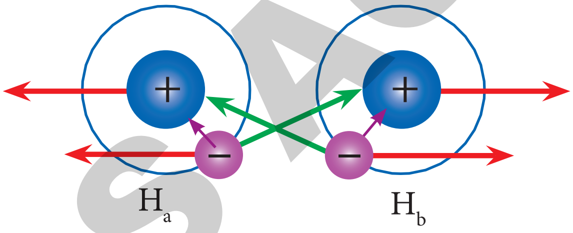


Fig 10. 17 (a) VB theory for the formation of hydrogen molecule

The new attractive forces (green arrows) arise between

(i) nucleus of H_a and valence electron of H_b

(ii) nucleus of H_b and the valence electron of $H_{a.}$

The new repulsive forces (red arrows) arise between

(i) the nucleus of H_a and H_b

(ii) valence electrons of H_a and H_b.

The attractive forces tend to bring H_a and H_b together whereas the repulsive forces tends to push them apart. At the initial stage, as the two hydrogen atoms approach each other, the attractive forces are stronger than the repulsive forces and the potential energy decreases. A stage is reached where the net attractive forces are exactly balanced by repulsive forces and the potential energy of the system acquires a minimum energy.

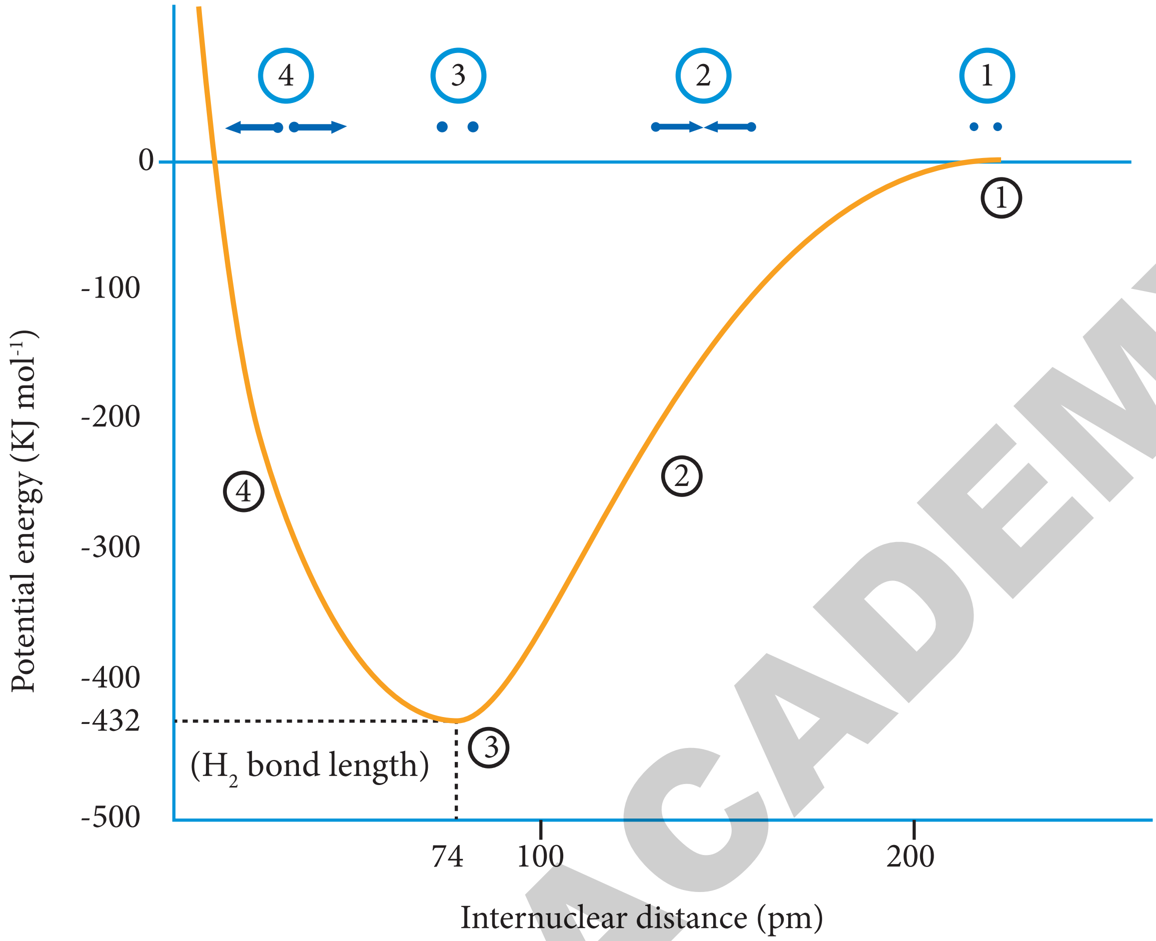


Fig 10. 17 (b) VB theory for the formation of hydrogen molecule

At this stage, there is a maximum overlap between the atomic orbitals of H_a and H_b, and the atoms H_a and H_b are now said to be bonded together by a covalent bond. The internuclear distance at this stage gives the H-H bond length and is equal to 74 pm. The liberated energy is 436 kJ mol^{-1} and is known as bond energy. Since the energy is released during the bond formation, the resultant molecule is more stable. If the distance between the two atoms is decreased further, the repulsive forces dominate the attractive forces and the potential energy of the system sharply increases

10.7.1 Salient features of VB Theory:

(i) When half filled orbitals of two atoms overlap, a covalent bond will be formed between them.

(ii) The resultant overlapping orbital is occupied by the two electrons with opposite spins. For example, when H_2 is formed, the two 1s electrons of two hydrogen atoms get paired up and occupy the overlapped orbital.

(iii) The strength of a covalent bond depends upon the extent of overlap of atomic orbitals. Greater the overlap, larger is the energy released and stronger will be the bond formed.

(iv) Each atomic orbital has a specific direction (except s-orbital which is spherical) and hence orbital overlap takes place in the direction that maximizes overlap

Let us explain the covalent bond formation in hydrogen, fluorine and hydrogen fluoride using VB theory.

10.8 Orbital Overlap

When atoms combines to form a covalent molecule, the atomic orbitals of the combining atoms overlap to form a covalent bond. The bond pair of electrons will occupy the overlapped region of the orbitals. Depending upon the nature of overlap we can classify the covalent bonding between the two atoms as sigma (σ) and pi (π) bonds.

10.8.1 Sigma and Pi bonds

When two atomic orbitals overlap linearly along the axis, the resultant bond is called a sigma (σ) bond. This overlap is also called 'head-on overlap' or 'axial overlap'. Overlap involves an s orbital (s-s and s-p overlaps) will always result in a sigma bond as the s orbital is spherical. Overlap between two p orbitals along the molecular axis will also result in sigma bond formation. When we consider x-axis as molecular axis, the p_x-p_x overlap will result in σ-bond.

When two atomic orbitals overlaps sideways, the resultant covalent bond is called a pi (π)bond. When we consider x-axis as molecular axis, the p_y-p_y and p_z-p_z overlaps will result in the formation of a π-bond.

Following examples will be useful to understand the overlap:

10.8.2 Formation of hydrogen (H_2) Molecule

Electronic configuration of hydrogen atom is $1s^1$

During the formation of H_2 molecule, the 1s orbitals of two hydrogen atoms containing one unpaired electron with opposite spin overlap with each other along the internuclear axis. This overlap is called s-s overlap. Such axial overlap results in the formation of a σ-covalent bond.

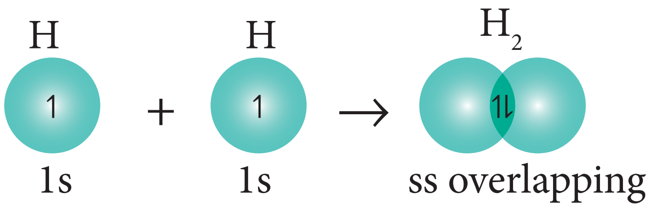


Fig 10. 18 Formation of hydrogen molecule

Formation of fluorine molecule (F_2):

Valence shell electronic configuration of fluorine atom : $2s^2\ 2p_x^{\,2}, 2p_y^{\,2}, 2p_z^{\,1}$

When the half filled p_z orbitals of two fluorine overlaps along the z-axis, a σ-covalent bond is formed between them.

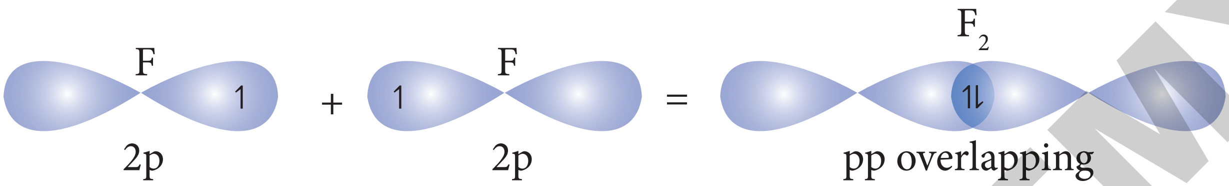


Fig 10. 19 Formation of F_2 Molecule

Formation of HF molecule:

Electronic configuration of hydrogen atom is $1s^1$

Valence shell electronic configuration of fluorine atom : $2s^2\ 2p_x^{\,2}, 2p_y^{\,2}, 2p_z^{\,1}$

When half filled 1s orbital of hydrogen linearly overlaps with a half filled $2p_z$ orbital of fluorine, a σ-covalent bond is formed between hydrogen and fluorine.

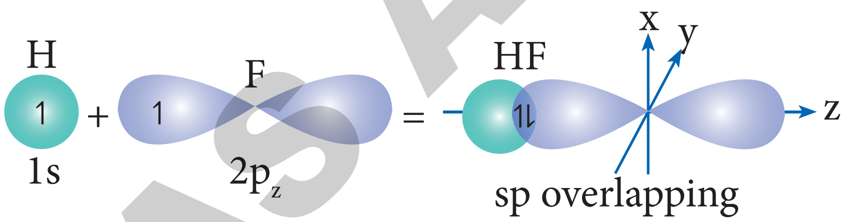
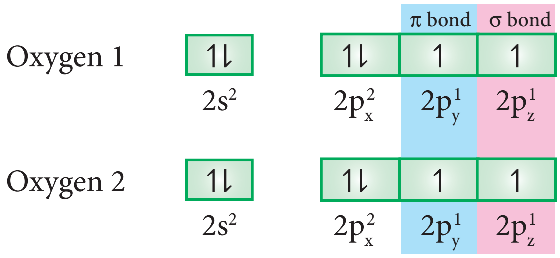


Fig 10.20 Formation of HF Molecule

Formation of oxygen molecule (O_2):

Valence shell electronic configuration of oxygen atom : $2s^2\ 2p_x^{\,2}, 2p_y^{\,1}, 2p_z^{\,1}$



When the half filled p_z orbitals of two oxygen overlaps along the z-axis (considering molecular axis as z axis), a σ-covalent bond is formed between them. Other two half filled p_y orbitals of two oxygen atoms overlap laterally (sideways) to form a π-covalent bond between the oxygen atoms. Thus, in oxygen molecule, two oxygen atoms are connected by two covalent bonds (double bond). The other two pair of electrons present in the 2s and $2p_x$ orbital do not involve in bonding and remains as lone pairs on the respective oxygen.

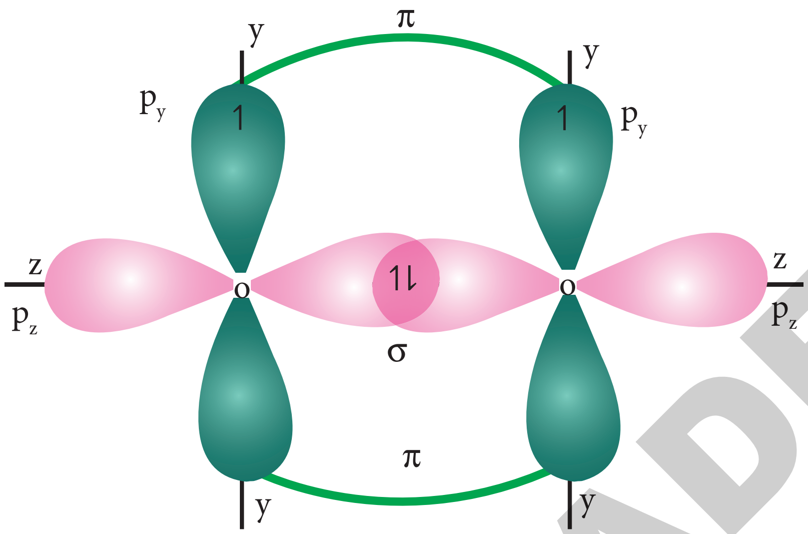


Fig 10. 21 Formation of π bond in O_2 Molecule

Evaluate Yourself

7) Bond angle in PH_4^+ is higher than in PH_3 why?

10.9 Hybridisation

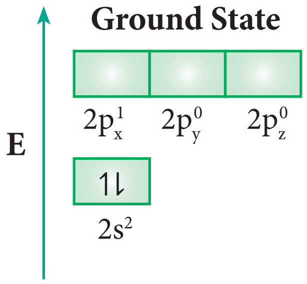
Bonding in simple molecules such as hydrogen and fluorine can easily be explained on the basis of overlap of the respective atomic orbitals of the combining atoms. But the observed properties of polyatomic molecules such as methane, ammonia, beryllium chloride etc... cannot be explained on the basis of simple overlap of atomic orbitals. For example, it was experimentally proved that methane has a tetrahedral structure and the four C-H bonds are equivalent. This fact cannot be explained on the basis of overlap of atomic orbitals of hydrogen (1s) and the atomic orbitals of carbon with different energies ($2s^2\ 2p_x^2\ 2p_y\ 2p_z$).

In order to explain these observed facts, Linus Pauling proposed that the valence atomic orbitals in the molecules are different from those in isolated atom and he introduced the concept of hybridisation. Hybridisation is the process of mixing of atomic orbitals of the same atom with comparable energy to form equal number of new equivalent orbitals with same energy. The resultant orbitals are called hybridised orbitals and they posses maximum symmetry and definite orientation in space so as to minimize the force of repulsion between their electrons .

10.9.1 Types of hybridisation and geometry of molecules

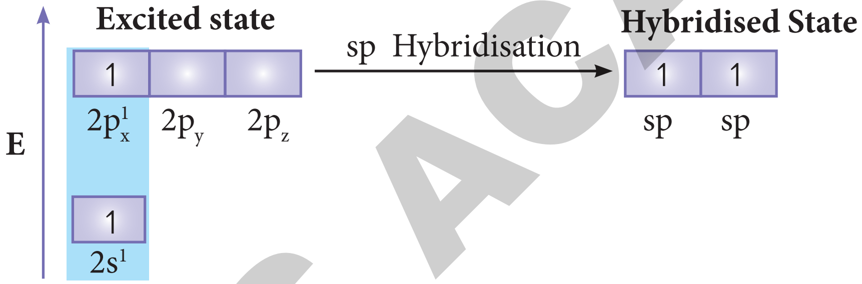
sp Hybridisation:

Let us consider the bond formation in beryllium chloride. The valence shell electronic configuration of beryllium in the ground state is shown in the figure.



In $BeCl_2$ both the Be-Cl bonds are equivalent and it was observed that the molecule is linear. VB theory explain this observed behaviour by sp hybridisation. One of the paired electrons in the 2s orbital gets excited to 2p orbital and the electronic configuration at the excited state is shown.

Now, the 2s and 2p orbitals hybridise and produce two equivalent sp hybridised orbitals which have 50 % s-character and 50 % p-character. These sp hybridised orbitals are oriented in opposite direction as shown in the figure.



Overlap with orbital of chlorine

Each of the sp hybridized orbitals linearly overlap with p_z orbital of the chlorine to form a covalent bond between Be and Cl as shown in the Figure.

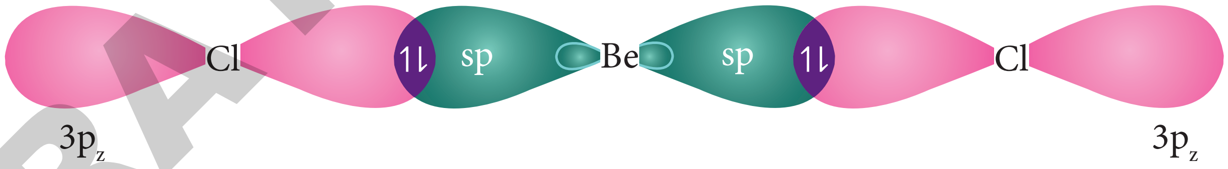
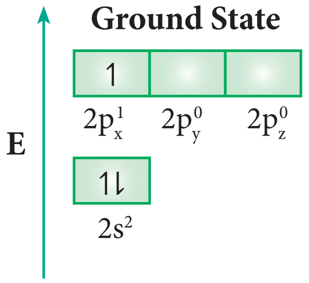


Fig 10.22 sp Hybridisation : $BeCl_2$

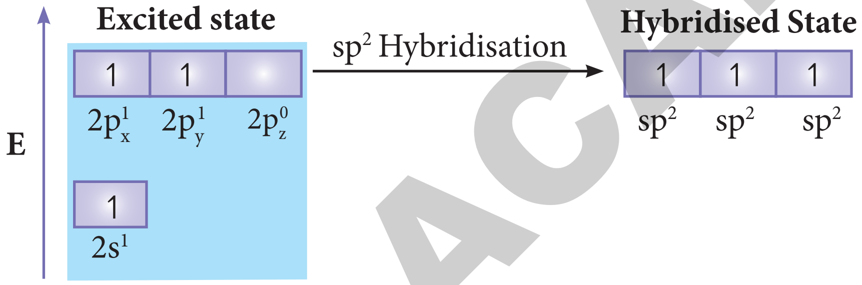
sp2 Hybridisation:

Consider boron trifluoride molecule. The valence shell electronic configuration of boron atom is [He]$2s^2\ 2p^1$.



In the ground state boron has only one unpaired electron in the valence shell. In order to form three covalent bonds with fluorine atoms, three unpaired electrons are required. To achieve this, one of the paired electrons in the 2s orbital is promoted to the $2p_y$ orbital in the excite state.

In boron, the s orbital and two p orbitals (p_x and p_y) in the valence shell hybridses, to generate three equivalent sp^2 orbitals as shown in the Figure. These three orbitals lie in the same xy plane and the angle between any two orbitals is equal to 120^0



Overlap with 2pz orbitals of fluorine:

The three sp^2 hybridised orbitals of boron now overlap with the $2p_z$ orbitals of fluorine (3 atoms). This overlap takes place along the axis as shown below.

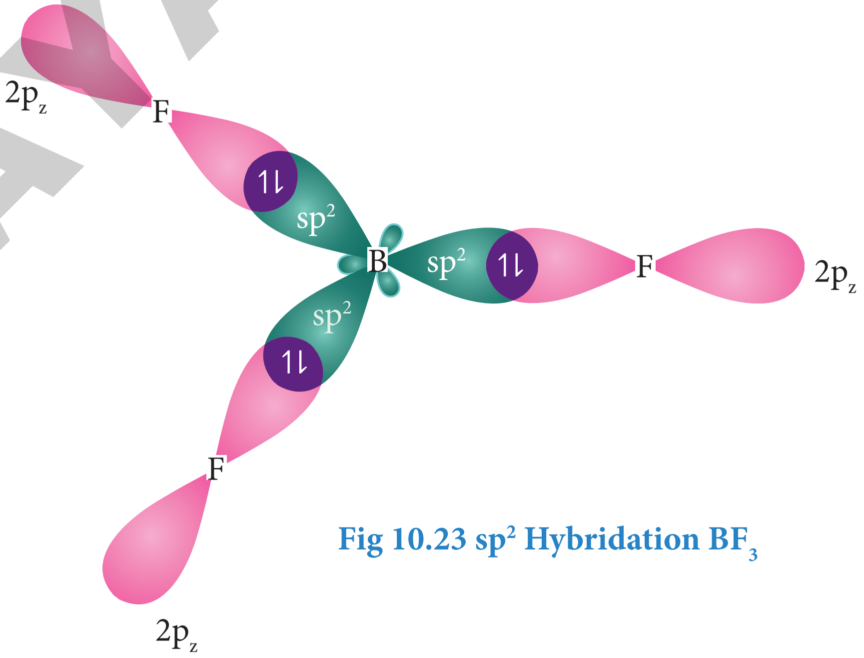
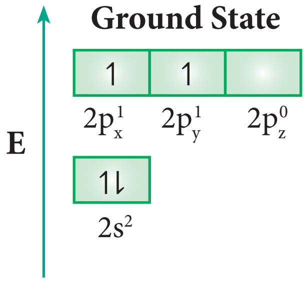


Fig 10.23 sp^2 Hybridation BF_3

sp3 Hybridisation:

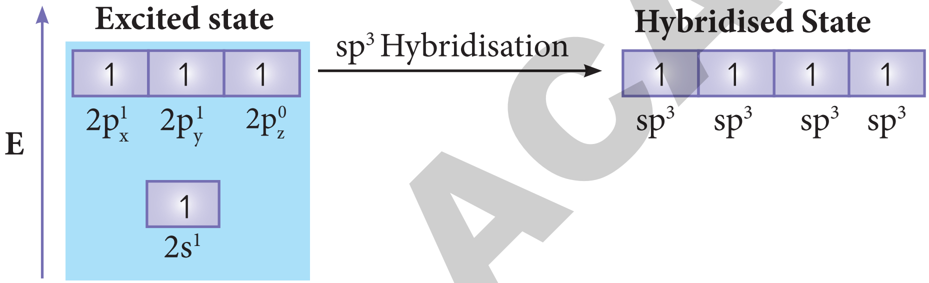
sp^3 hybridisation can be explained by considering methane as an example. In methane molecule the central carbon atom bound to four hydrogen atoms. The ground state valence shell electronic configuration of carbon is $[He]2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^0$.



In order to form four covalent bonds with the four hydrogen atoms, one of the paired electrons in the 2s orbital of carbon is promoted to its $2p_z$ orbital in the excite state. The one 2s orbital and the three 2p orbitals of carbon mixes to give four equivalent sp^3 hybridised orbitals. The angle between any two sp^3 hybridised orbitals is $109^0\ 28'$

Overlap with 1s orbitals of hydrogen:

The 1s orbitals of the four hydrogen atoms overlap linearly with the four sp^3 hybridised orbitals of carbon to form four C-H σ-bonds in the methane molecule, as shown below.



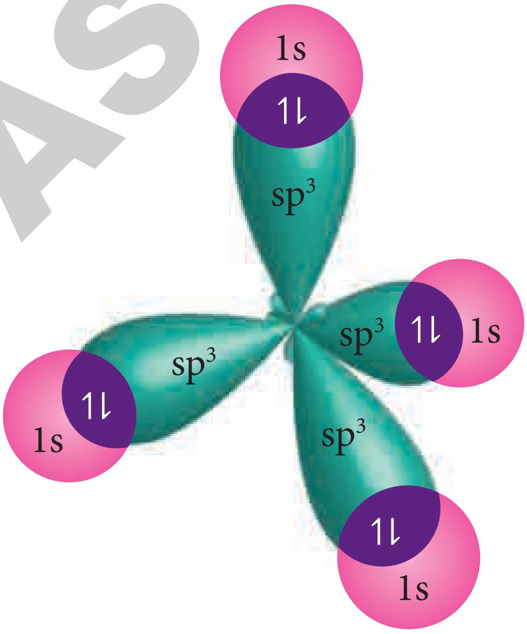
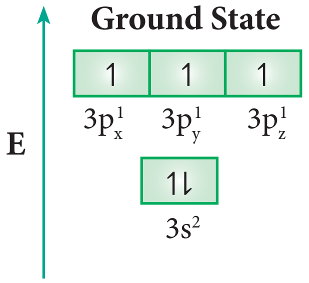


Fig 10.24 sp^3 Hybridisation CH_4

sp^3d Hybridisation:

In the molecules such as PCl_5, the central atom phosphorus is covalently bound to five chlorine atoms. Here the atomic orbitals of phosphorous undergoes sp^3d hybridisation which involves its one 3s orbital, three 3p orbitals and one vacant 3d orbital (d_{z^2}). The ground state electronic configuration of phosphorous is $[Ne]3s^2\ 3p_x^1\ 3p_y^1\ 3p_z^1$ as shown below.



One of the paired electrons in the 3s orbital of phosphorous is promoted to one of its vacant 3d orbital (d_{z^2}) in the excite state. One 3s orbital, three 3p orbitals and one $3d_{z^2}$ orbital of phosphorus atom mixes to give five equivalent sp^3d hybridised orbitals. The orbital geometry of sp^3d hybridised orbitals is trigonal bi-pyramidal as shown in the figure 10. x.

Overlap with $3p_z$ orbitals of chlorine:

The $3p_z$ orbitals of the five chlorine atoms linearly overlap along the axis with the five sp^3d hybridised orbitals of phosphorous to form the five P-Cl σ-bonds, as shown below.

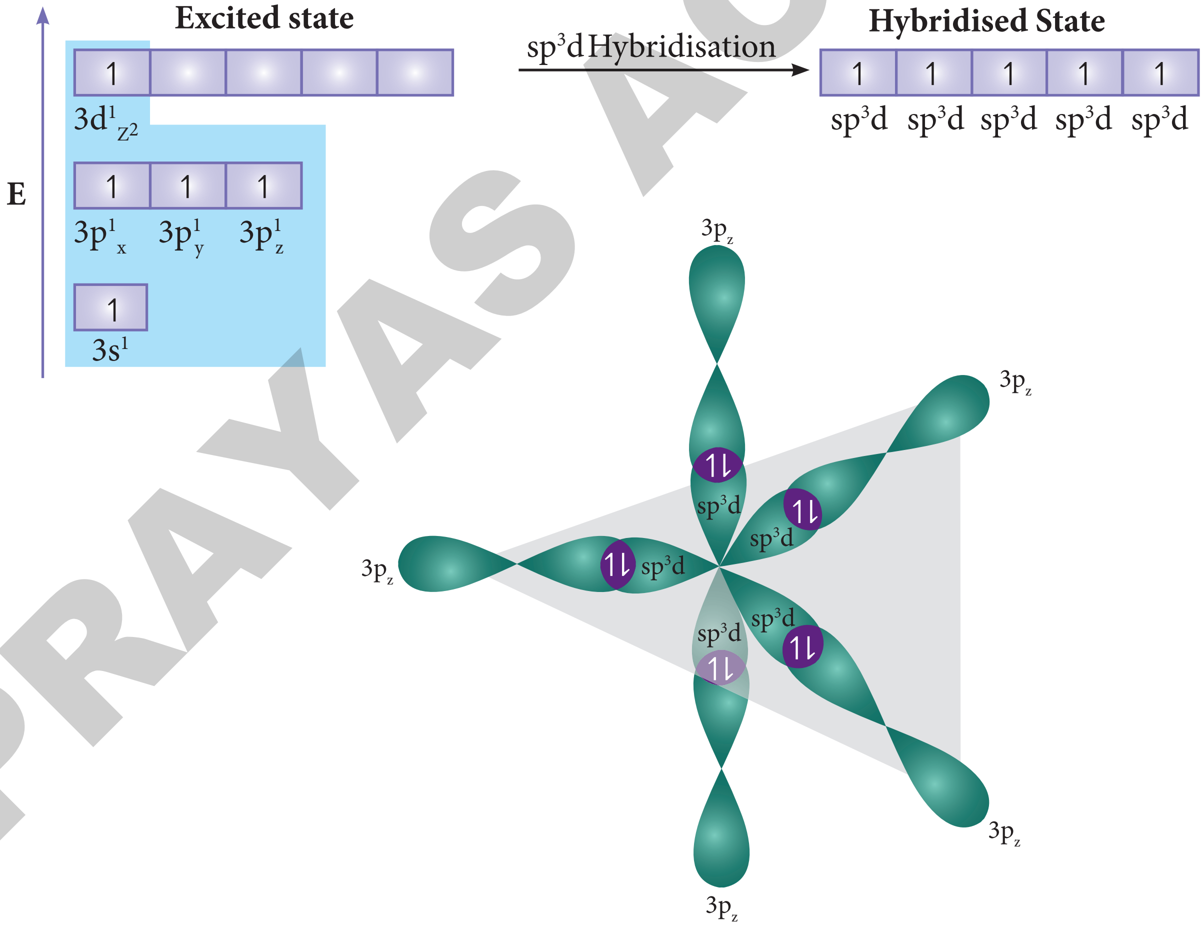
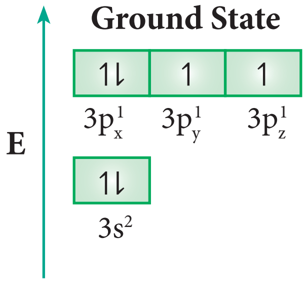


Fig 10.25 sp^3d Hybridisation PCl_5

sp^3d^2 Hybridisation:

In sulphur hexafluoride (SF_6) the central atom sulphur extend its octet to undergo sp^3d^2 hybridisation to generate six sp^3d^2 hybridised orbitals which accounts for six equivalent S-F bonds. The ground state electronic configuration of sulphur is $[Ne]3s^2\ 3p_x^1\ 3p_y^1\ 3p_z^1$.



One electron each from 3s orbital and 3p orbital of sulphur is promoted to its two vacant 3d orbitals (d_{z^2} and $d_{x^2-y^2}$) in the excite state. A total of six valence orbitals from sulphur (one 3s orbital, three 3p orbitals and two 3d orbitals) mixes to give six equivalent sp^3d^2 hybridised orbitals. The orbital geometry is octahedral as shown in the figure.

Overlap with 2pz orbitals of fluorine:

The six sp^3d^2 hybridised orbitals of sulphur overlaps linearly with $2p_z$ orbitals of six fluorine atoms to form the six S-F bonds in the sulphur hexafluoride molecule.

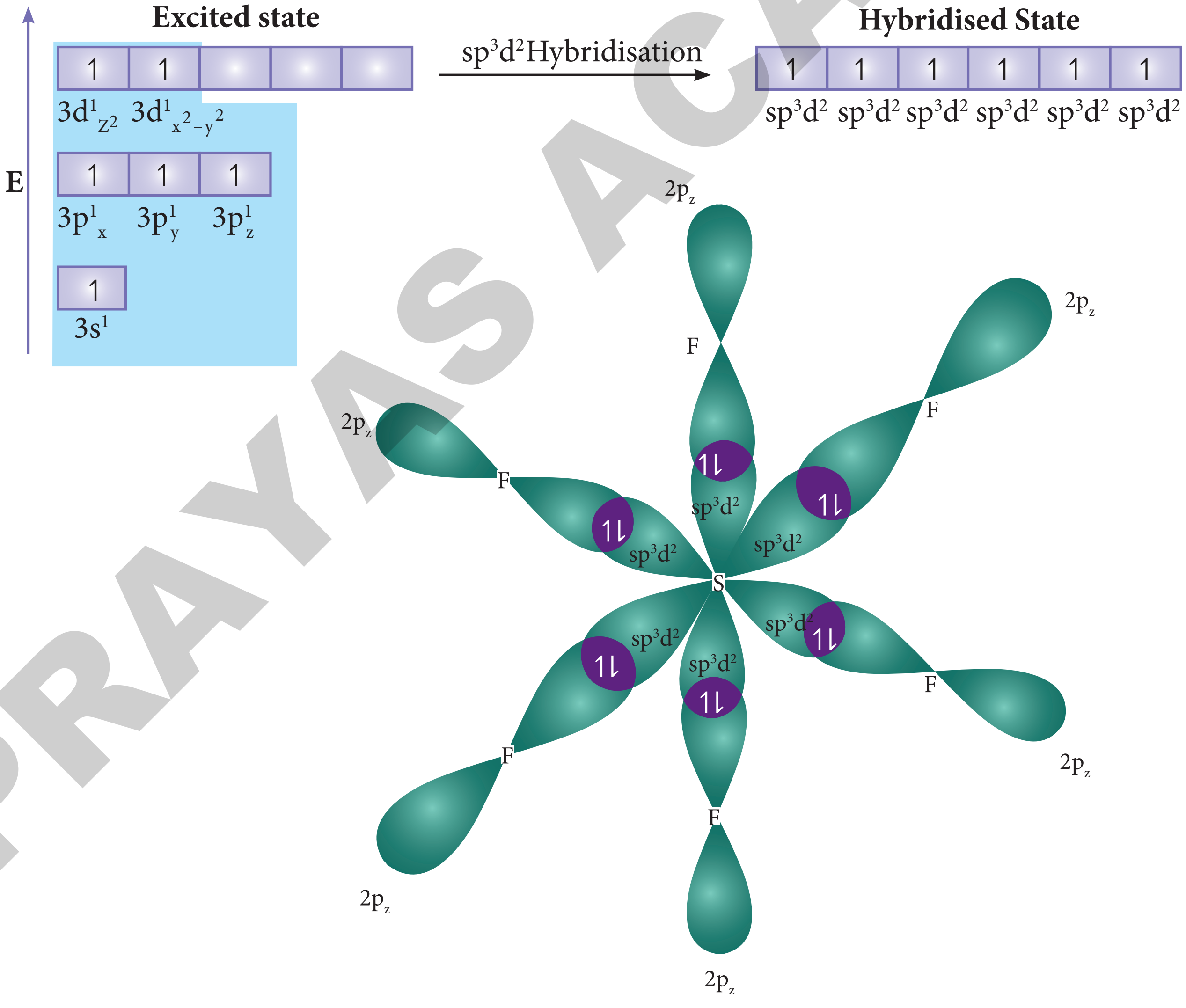
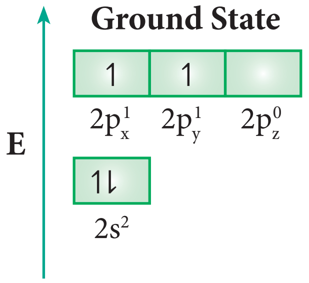


Fig 10.26 sp^3d^2 Hybridisation : SF_6

Bonding in ethylene:

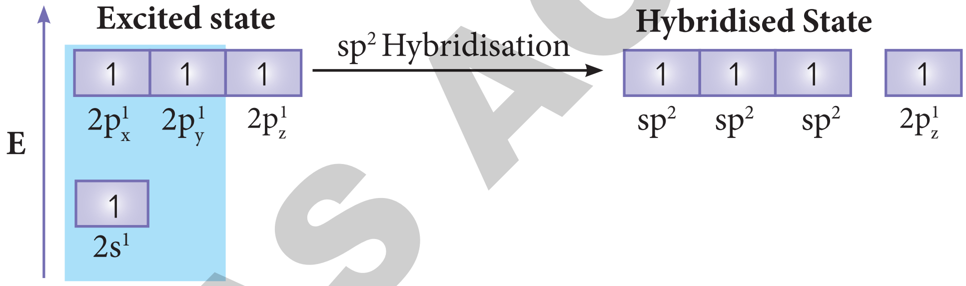
The bonding in ethylene can be explained using hybridisation concept. The molecular formula of ethylene is C_2H_4. The valency of carbon is 4. The electronic configuration of valence shell of carbon in ground state is $[He]2s^2\,2p_x^1\,2p_y^1\,2p_z^0$. To satisfy the valency of carbon promote an electron from 2s orbital to $2p_z$ orbital in the excited state.



In ethylene both the carbon atoms undergoes sp^2 hybridisation involving 2s, $2p_x$ and $2p_y$ orbitals, resulting in three equivalent sp^2 hybridised orbitals lying in the xy plane at an angle of 120^0 to each other. The unhybridised $2p_z$ orbital lies perpendicular to the xy plane.

Formation of sigma bond:

One of the sp^2 hybridised orbitals of each carbon lying on the molecular axis (x-axis) linearly overlaps with each other resulting in the formation a C-C sigma bond. Other two sp^2 hybridised orbitals of both carbons linearly overlap with the four 1s orbitals of four hydrogen atoms leading to the formation of two C-H sigma bonds on each carbon.



Formation of pi bond:

The unhybridised $2p_z$ orbital of both carbon atoms can overlap only sideways as they are not in the molecular axis. This lateral overlap results in the formation a pi bond between the two carbon atoms as shown in the figure.

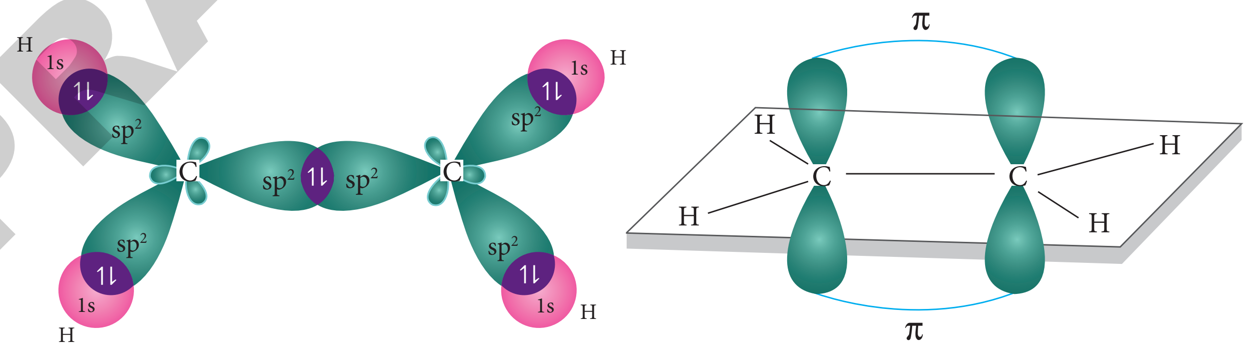


Fig 10.27 sp^2 Hybridisation : C_2H_4

Bonding in acetylene:

Similar to ethylene, the bonding in acetylene can also be explained using hybridisation concept. The molecular formula of acetylene is C_2H_2. The electronic configuration of valence shell of carbon in ground state is $[He]2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^0$. To satisfy the valency of carbon promote an electron from 2s orbital to $2p_z$ orbital in the excited state.

In acetylene molecule, both the carbon atoms are in sp hybridised state. The 2s and $2p_x$ orbitals, resulting in two equivalent sp hybridised orbitals lying in a straight line along the molecular axis (x-axis). The unhybridised $2p_y$ and $2p_z$ orbitals lie perpendicular to the molecular axis.

Formation of sigma bond:

One of the two sp hybridised orbitals of each carbon linearly overlaps with each other resulting in the formation a C-C sigma bond. The other sp hybridised orbital of both carbons linearly overlap with the two 1s orbitals of two hydrogen atoms leading to the formation of one C-H sigma bonds on each carbon.

Formation of pi bond:

The unhybridised $2p_y$ and $2p_z$ orbitals of each carbon overlap sideways. This lateral overlap results in the formation of two pi bonds (p_y-p_y and p_z-p_z) between the two carbon atoms as shown in the figure.

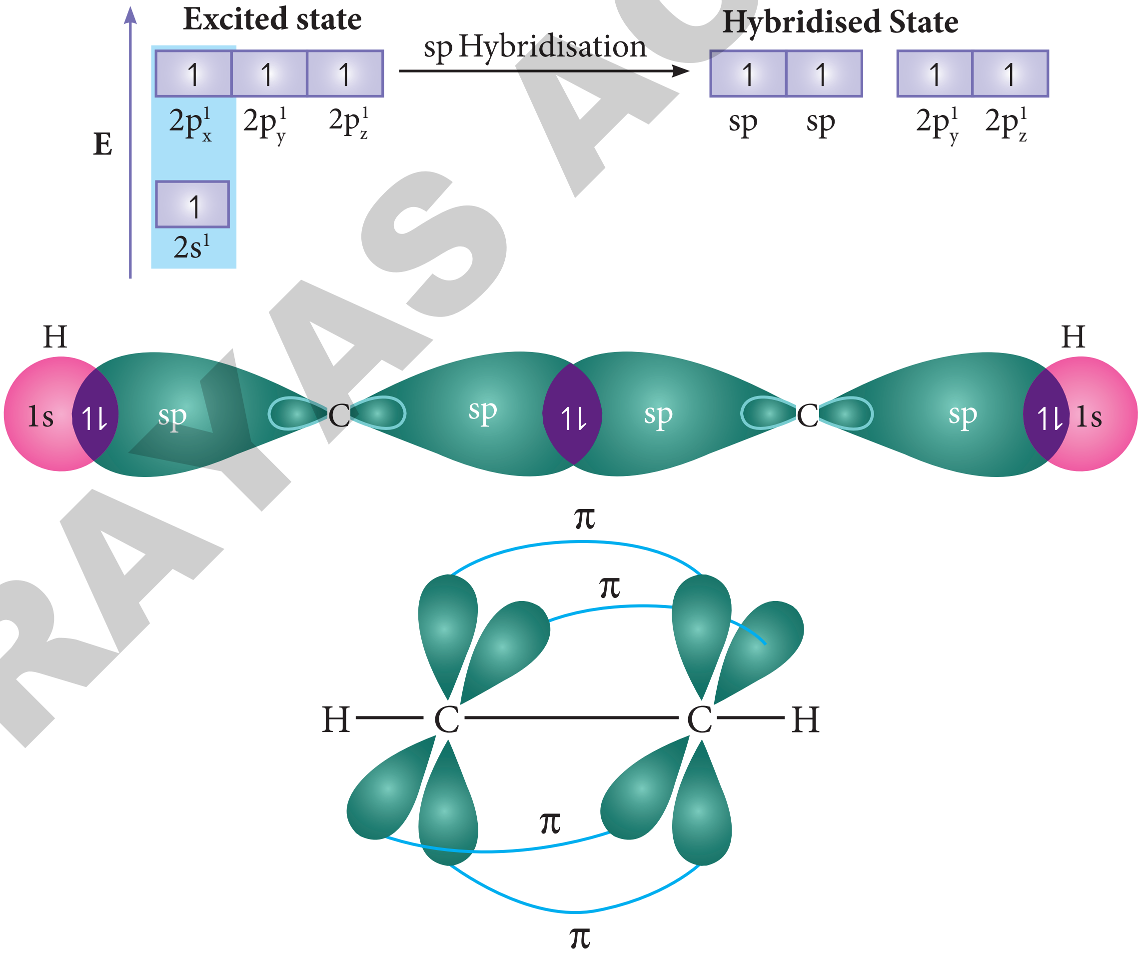


Fig 10.28 sp Hybridisation in acetylene

Evaluate Yourself

8) Explain the bond formation in SF_4 and CCl_4 using hybridisation concept.

Evaluate Yourself

9) The observed bond length of N_2^+ is larger than N_2 while the bond length in NO^+ is less than in NO. Why?

10.10 Molecular orbital theory

Lewis concept and valence bond theory qualitatively explains the chemical bonding and molecular structure. Both approaches are inadequate to describe some of the observed properties of molecules. For example, these theories predict that oxygen is diamagnetic. However, it was observed that oxygen in liquid form was attracted towards the poles of strong magnet, indicating that oxygen is paramagnetic. As both these theories treated the bond formation in terms of electron pairs and hence they fail to explain the bonding nature of paramagnetic molecules. F. Hund and Robert. S. Mulliken developed a bonding theory called molecular orbital theory which explains the magnetic behaviour of molecules.

The salient features of this theory are as follows.

1. When atoms combines to form molecules, their individual atomic orbitals lose their identity and forms new orbitals called molecular orbitals.

2. The shapes of molecular orbitals depend upon the shapes of combining atomic orbitals.

3. The number of molecular orbitals formed is the same as the number of combining atomic orbitals. Half the number of molecular orbitals formed will have lower energy than the corresponding atomic orbital, while the remaining molecular orbitals will have higher energy. The molecular orbital with lower energy is called bonding molecular orbital and the one with higher energy is called anti-bonding molecular orbital. The bonding molecular orbitals are represented as σ (Sigma), π (pi), δ (delta) and the corresponding antibonding orbitals are denoted as σ^*, π^* and δ^*.

4. The electrons in a molecule are accommodated in the newly formed molecular orbitals. The filling of electrons in these orbitals follows Aufbau's principle, Pauli's exclusion principle and Hund's rule as in the case of filling of electrons in atomic orbitals.

5. Bond order gives the number of covalent bonds between the two combining atoms. The bond order of a molecule can be calculated using the following equation

$$\text{Bond order} = \frac{N_b - N_a}{2}$$

Where, N_b = Total number of electrons present in the bonding molecular orbitals

N_a = Total number of electrons present in the antibonding molecular orbitals and

A bond order of zero value indicates that the molecule doesn't exist.

10.10.1 Linear combination of atomic orbitals

The wave functions for the molecular orbitals can be obtained by solving Schrödinger wave equation for the molecule. Since solving the Schrödinger equation is too complex, approximation methods are used to obtain the wave function for molecular orbitals. The most common method is the linear combination of atomic orbitals (LCAO).

We know that the atomic orbitals are represented by the wave function Ψ. Let us consider two atomic orbitals represented by the wave function ψ_A and ψ_B with comparable energy, combines to form two molecular orbitals. One is bonding molecular orbital($\psi_{bonding}$) and the other is antibonding molecular orbital($\psi_{antibonding}$). The wave functions for these two molecular orbitals can be obtained by the linear combination of the atomic orbitals ψ_A and ψ_B as below.

$$\psi_{bonding} = \psi_A + \psi_B$$

$$\psi_{antibonding} = \psi_A - \psi_B$$

The formation of bonding molecular orbital can be considered as the result of constructive interference of the atomic orbitals and the formation of anti-bonding molecular orbital can be the result of the destructive interference of the atomic orbitals. The formation of the two molecular orbitals from two 1s orbitals is shown below.

Constructive interaction: The two 1s orbitals are in phase and have the same sign.

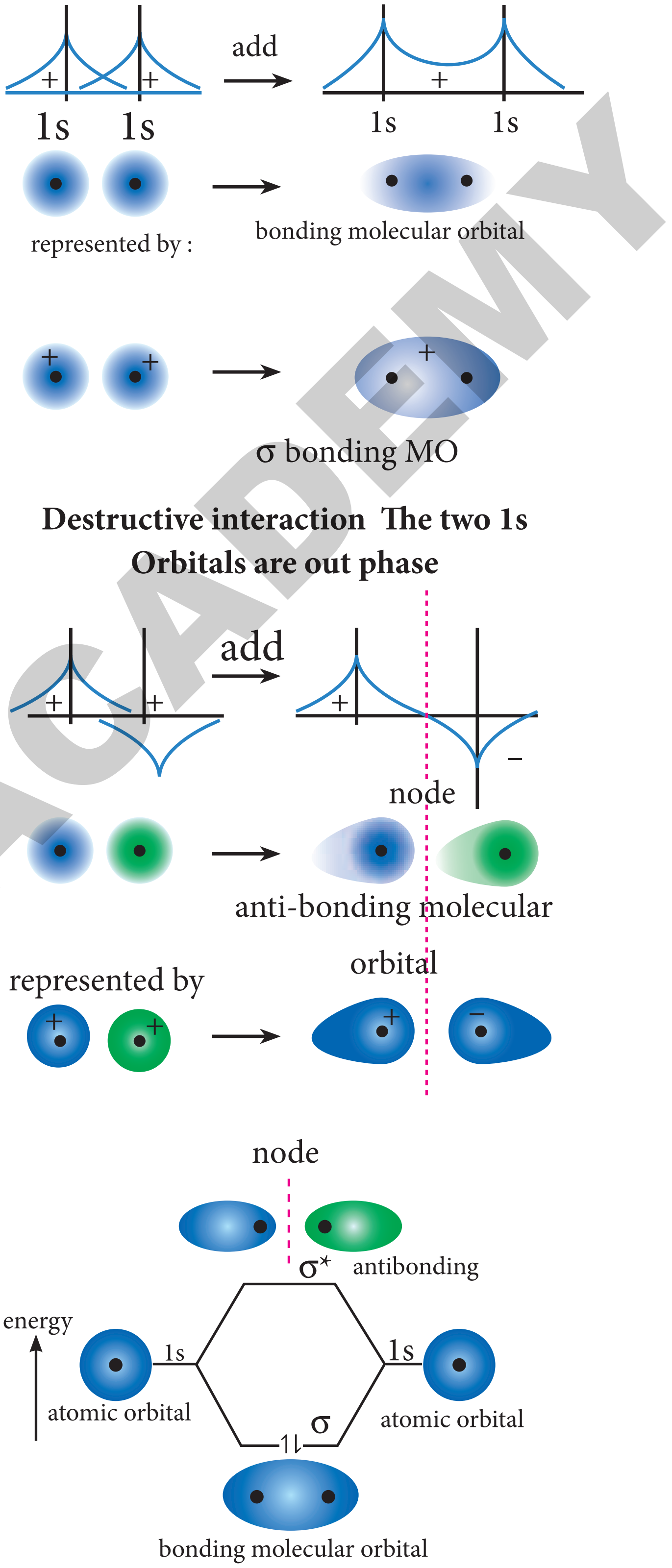
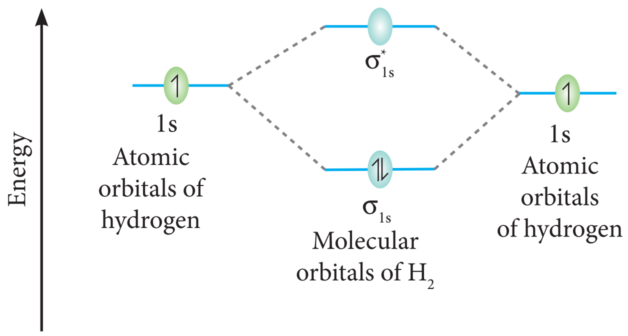


Fig 10.29 Linear Combination of atomic orbitals

10.10.2 Bonding in some Homonuclear di-atomic molecules:



Molecular orbital diagram of hydrogen molecule (H_2)

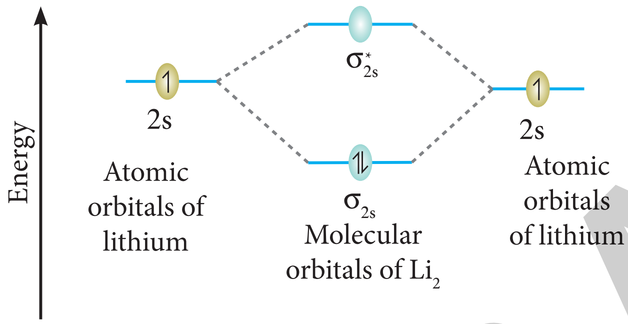
Electronic configuration of H atom $1s^1$

Electronic configuration of H_2 molecule σ_{1s}^2

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{2-0}{2} = 1$$

Molecule has no unpaired electrons hence it is diamagnetic.

Fig 10.30 MO Diagram for H_2 molecule



Molecular orbital diagram of lithium molecule (Li_2)

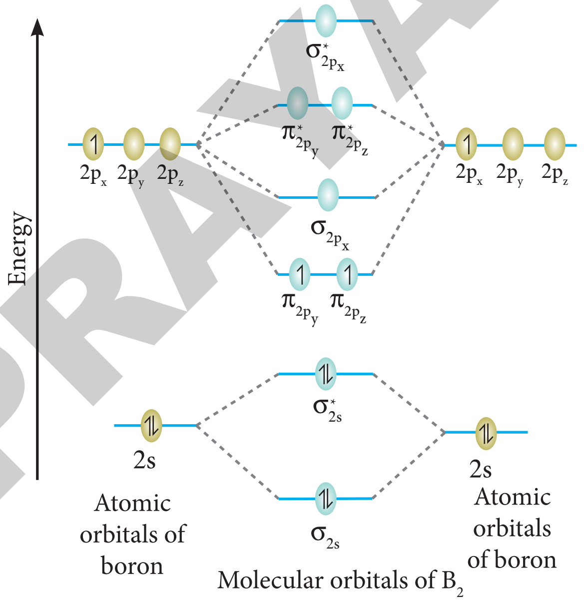
Electronic configuration of Li atom $1s^2$ $2s^1$

Electronic configuration of Li_2 molecule $\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{4-2}{2} = 1$$

Molecule has no unpaired electrons hence it is diamagnetic.

Fig 10.31 MO Diagram for Li_2 molecule



Molecular orbital diagram of boron molecule (B_2)

Electronic configuration of B atom $1s^2\,2s^2$ $2p^1$

Electronic configuration of B_2 molecule $\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \pi^1_{2p_y}, \pi^1_{2p_z}$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{6-4}{2} = 1$$

Molecule has two unpaired electrons hence it is paramagnetic.

Fig 10.32 MO Diagram for B_2 molecule

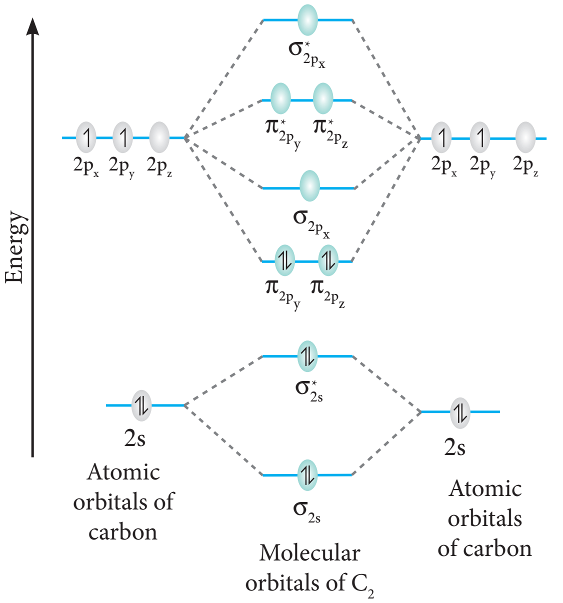


Fig 10.33 MO Diagram for C_2 molecule

Molecular orbital diagram of carbon molecule (C_2)

Electronic configuration of C atom $1s^2\,2s^2\,2p^2$

Electronic configuration of C_2 molecule $\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \pi^2_{2p_y}, \pi^2_{2p_z}$

Bond order $= \dfrac{N_b - N_a}{2} = \dfrac{8-4}{2} = 2$

Molecule has no unpaired electrons hence it is diamagnetic.

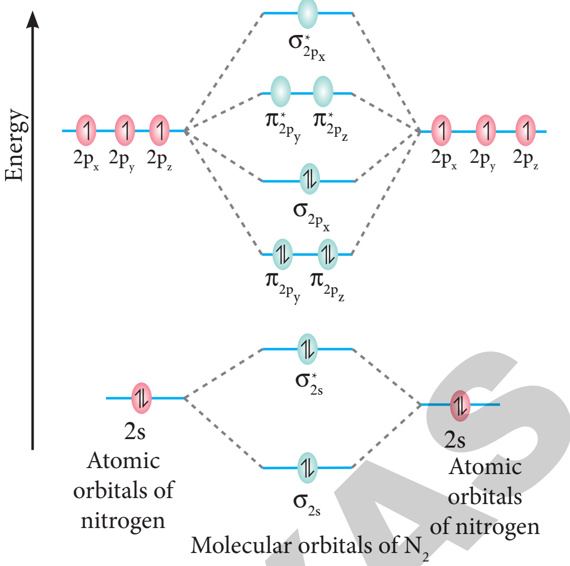


Fig 10.34 MO Diagram for N_2 molecule

Molecular orbital diagram of nitrogen molecule (N_2)

Electronic configuration of N atom $1s^2\,2s^2\,2p^3$

Electronic configuration of N_2 molecule $\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \pi^2_{2p_y}, \pi^2_{2p_z}\, \sigma_2{}^2px$

Bond order $= \dfrac{N_b - N_a}{2} = \dfrac{10-4}{2} = 3$

Molecule has no unpaired electrons hence it is diamagnetic.

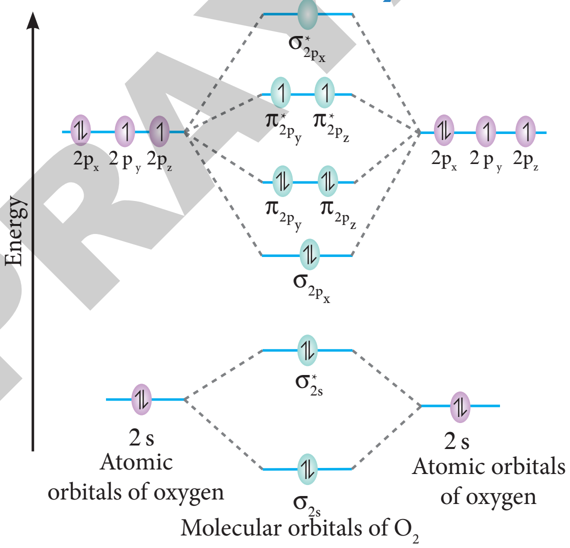


Fig 10.35 MO Diagram for O_2 molecule

Molecular orbital diagram of oxygen molecule (O_2)

Electronic configuration of O atom $1s^2\,2s^2\,2p^4$

Electronic configuration of O_2 molecule $\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \sigma_{2p_x}^2, \pi^2_{2p_y}, \pi^2_{2p_z}, \pi^{*1}_{2p_y}, \pi^{*1}_{2p_z},$

Bond order $= \dfrac{N_b - N_a}{2} = \dfrac{10-6}{2} = 2$

Molecule has two unpaired electrons hence it is paramagnetic.

Bonding in some heteronuclear di-atomic molecules

Molecular orbital diagram of Carbon monoxide molecule (CO)

Electronic configuration of C atom $1s^2\ 2s^2\ 2p^2$

Electronic configuration of O atom $1s^2\ 2s^2\ 2p^4$

Electronic configuration of CO molecule $\sigma_{1s}^{2}, \sigma_{1s}^{*2}, \sigma_{2s}^{2}, \sigma_{2s}^{*2}, \pi^{2}_{2p_y}, \pi^{2}_{2p_z}, \sigma^{2}_{2p_x}$

Bond order $= \dfrac{N_b - N_a}{2} = \dfrac{10-4}{2} = 3$

Molecule has no unpaired electrons hence it is diamagnetic.

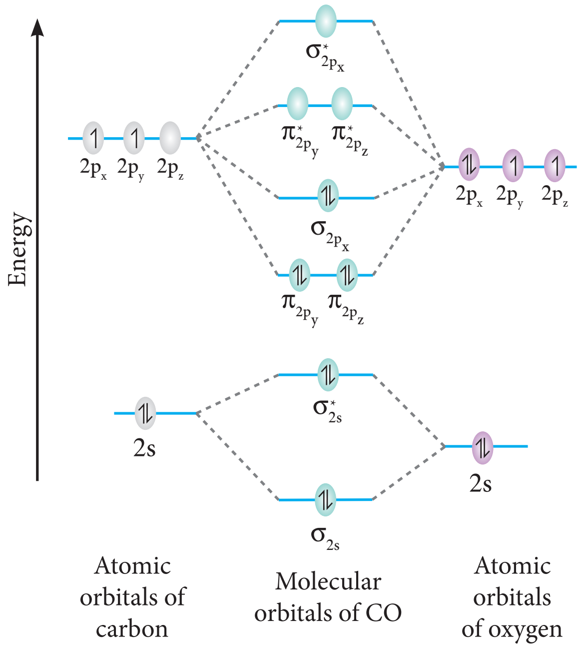


Fig 10.36 MO Diagram for CO molecule

Molecular orbital diagram of Nitric oxide molecule (NO)

Electronic configuration of N atom $1s^2\ 2s^2\ 2p^3$

Electronic configuration of CO molecule $\sigma_{1s}^{2}, \sigma_{1s}^{*2}, \sigma_{2s}^{2}, \sigma_{2s}^{*2}, \pi^{2}_{2p_y}, \pi^{2}_{2p_z}, \sigma_{2}p^{2}_{x}\ \pi^{*1}_{2p_y}$

Bond order $= \dfrac{N_b - N_a}{2} = \dfrac{10-5}{2} = 2.5$

Molecule has one unpaired electron hence it is paramagnetic.

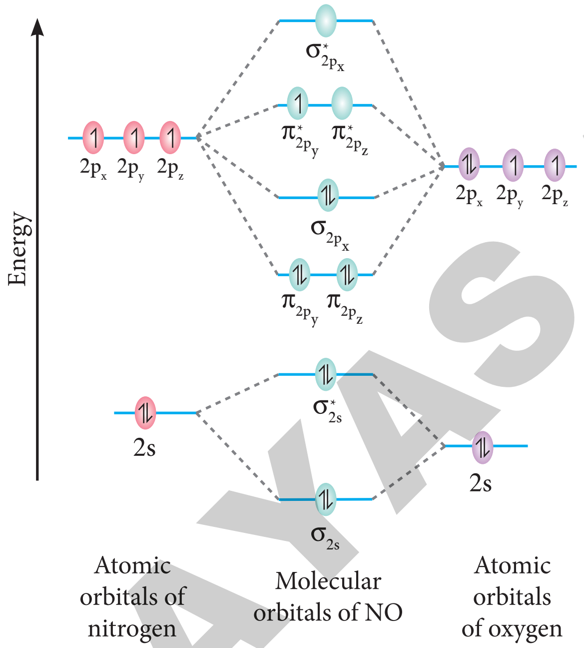


Fig 10.36 MO Diagram for NO molecule

Evaluate Yourself

10) Draw the MO diagram for acetylide ion C_2^{2-} and calculate its bond order.

Metallic bonding

Metals have some special properties of lustre, high density, high electrical and thermal conductivity, malleability and ductility, and high melting and boiling points. The forces that keep the atoms of the metal so closely in a metallic crystal constitute what is generally known as the metallic bond. The metallic bond is not just an electrovalent bond(ionic bond), as the latter is formed between atoms of different electro negativities. Similarly, the metallic bond is not a covalent bond,as the metal atoms do not have sufficient number of valence electrons for mutual sharing with 8 or 12 neighboring metal atoms in a crystal. So, we have to search for a new theory to explain metallic bond. The first successful theory is due to Drude and Lorentz, which regards metallic crystal as an assemblage of positive ions immersed in a gas of free electrons. The free electrons are due to ionization of the valence electrons of the atoms of the metal. As the valence electrons of the atoms are freely shared by all the ions in the crystal, the metallic bonding is also referred to as electronic bonding. As the free electrons repel each other, they are uniformly distributed around the metal ions. Many physical properties of the metals can be explained by this theory, nevertheless there are exceptions.

The electrostatic attraction between the metal ions and the free electrons yields a three-dimensional close packed crystal with a large number of nearest metal ions. So, metals have high density. As the close packed structure contains many slip planes along which movement can occur during mechanical loading, the metal acquires ductility. Pure metals can undergo 40 to 60% elongation prior to rupturing under mechanical loading. As each metal ion is surrounded by electron cloud in all directions, the metallic bonding has no directional properties.

As the electrons are free to move around the positive ions, the metals exhibit high electrical and thermal conductivity. The metallic luster is due to reflection of light by the electron cloud. As the metallic bond is strong enough, the metal atoms are reluctant to break apart into a liquid or gas, so the metals have high melting and boiling points.

The bonding in metal is better treated by Molecular orbital theory. As per this theory, the atomic orbitals of large number of atoms in a crystal overlap to form numerous bonding and antibonding molecular orbitals without any band gap. The bonding molecular orbitals are completely filled with an electron pair in each, and the antibonding molecular orbitals are empty. Absence of band gap accounts for high electrical conductivity of metals. High thermal conductivity is due to thermal excitation of many electrons from the valence band to the conductance band. With an increase in temperature, the electrical conductivity decreases due to vigorous thermal motion of lattice ions that disrupts the uniform lattice structure, that is required for free motion of electrons within the crystal. Most metals are black except copper, silver and gold. It is due to absorption of light of all wavelengths. Absorption of light of all wavelengths is due to absence of bandgap in metals.

SUMMARY

In molecules, atoms are held together by attractive forces, called chemical bonds. Kossel and Lewis are the first people to provide a logical explanation for chemical bonding. They proposed that atoms try to attain the nearest noble gas electronic configuration by losing, gaining or sharing one or more electrons during the bond formation. The noble gases contain eight electrons in their valance shell which is considered to be stable electronic configuration. The idea of Kossel – Lewis approach to chemical bond lead to the octet rule, which states that "the atoms transfer or share electrons so that all atoms involved in chemical bonding obtain 8 electrons in their outer shell (valance shell)".

There are different types of chemical bonds. In compounds such as sodium chloride, the sodium atom loses an electron which is accepted by the chlorine atom resulting in the formation of Na+ and Cl- ions. These two ions are held together by the electrostatic attractive forces. This type of chemical bond is known as ionic bonds or electrovalent bonds. In certain compounds, instead of the complete transfer of electrons, the electrons are shared by both the bonding atoms. The two combining atoms are held together by their mutual attraction towards the shared electrons. This type of bond is called covalent bonding. In addition, there also another bond type known as coordinate covalent bonds, where the shared electrons of a covalent bond are provided by only one of the combining atoms. Metallic bonding is another type of bonding which is observed in metals.

Lewis theory in combination with VSEPR theory will be useful in predicting the shape of molecules. According to this theory, the shape of the molecules depends on the number of valance shell electron pair (lone pairs and bond pairs) around the central atom. Each pair of valance electrons around the central atom repels each other and hence, they are located as far away as possible in three-dimensional space to minimise the repulsion between them.

Heitler and London gave a theoretical treatment to explain the formation of covalent bond in hydrogen molecule on the basis of wave mechanics of electrons. It was further developed by Pauling and Slater. According to this theory when half-filled orbitals of two atoms overlap, a covalent bond will be formed between them. Linus Pauling introduced the concept of hybridisation. Hybridisation is the process of mixing of atomic orbitals of the same atom with comparable energy to form equal number of new equivalent orbitals with same energy. There are different types of hybridization such as sp, sp2, sp3, sp3d2 etc..

F. Hund and Robert. S. Mulliken developed a bonding theory called molecular orbital theory. According to this theory, when atoms combines to form molecules, their individual atomic orbitals lose their identity and forms new orbitals called molecular orbitals. The filling of electrons in these orbitals follows Aufbau's principle, Pauli's exclusion principle and Hund's rule as in the case of filling of electrons in atomic orbitals.

Evaluation

1. In which of the following Compounds does the central atom obey the octet rule?

   a) XeF_4 b) $AlCl_3$

   c) SF_6 d) SCl_2

2. In the molecule $O_A = C = O_B$, the formal charge on O_A, C and O_B are respectively.

   a) -1, 0, + 1 b) +1, 0,-1

   c) -2,0,+2 d) 0,0,0

3. Which of the following is electron deficient?

   a) PH_3 b) $(CH_3)_2$

   c) BH_3 d) NH_3

4. Which of the following molecule contain no π bond?

   a) SO_2 b) NO_2

   c) CO_2 d) H_2O

5. The ratio of number of sigma (σ) and pi (π) bonds in 2- butynal is

   a) 8/3 b) 5/3

   c) 8/2 d) 9/2

6. Which one of the following is the likely bond angles of sulphur tetrafluoride molecule?

   a) $120^0, 80^0$ b) $109^0.28$

   c) 90^0 d) $89^0, 117^0$

7. **Assertion:** Oxygen molecule is paramagnetic.

   Reason : It has two unpaired electron in its bonding molecular orbital

   a) both assertion and reason are true and reason is the correct explanation of assertion

   b) both assertion and reason are true but reason is not the correct explanation of assertion

   c) assertion is true but reason is false

   d) Both assertion and reason are false

8. According to Valence bond theory, a bond between two atoms is formed when

   a) fully filled atomic orbitals overlap

   b) half filled atomic orbitals overlap

   c) non- bonding atomic orbitals overlap

   d) empty atomic orbitals overlap

9. In ClF_3 ,NF_3 and BF_3 molecules the chlorine, nitrogen and boron atoms are

   a) sp^3 hybridised

   b) sp^3 ,sp^3 and sp^2 respectively

   c) sp^2 hybridised

   d) sp^3d, sp^3 and sp hybridised respectively

10. When one s and three p orbitals hybridise,

    a) four equivalent orbitals at 90^0 to each other will be formed

    b) four equivalent orbitals at 109^0

28' to each other will be formed.

c) four equivalent orbitals, that are lying the same plane will be formed

d) none of these

11. Which of these represents the correct order of their increasing bond order.

a) $C_2 < C_2^{2-} < O_2^{2-} < O_2$

b) $C_2^{2-} < C_2^{+} < O_2 < O_2^{2-}$

c) $O_2^{2-} < O_2 < C_2^{2-} < C_2^{+}$

d) $O_2^{2-} < C_2^{+} < O_2 < C_2^{2-}$

12. Hybridisation of central atom in PCl_5 involves the mixing of orbitals.

a) s, p_x, p_y, d_{x2} , d_{x2-y2}

b) s, p_x . p_y, p_{xy} . d_{x2-y2}

c) s, p_x , p_y , p_z , d_{x2-y2}

d)s, p_x , p_y , d_{xy} , d_{x2-y2}

13. The correct order of O-O bond length in hydrogen peroxide, ozone and oxygen is

a) $H_2O_2 > O_3 > O_2$

b) $O_2 > O_3 > H_2O_2$

c) $O_2 > H_2O_2 > O_3$

d) $O_3 > O_2 > H_2O_2$

14. Which one of the following is diamagnetic.?

a) O_2 b) O_2^{2-}

c) O_2^{+} d) None of these

15. Bond order of a species is 2.5 and the number of electons in its bonding molecular orbital is formd to be 8 The no. of electons in its antibonding molecular orbital is

a) three b) four

c) Zero d) can not be calculated form the given unformation.

16. Shape and hybridisation of IF_5 are

a) Trigonal bipyramidal, Sp^3d^2

b) Trigonal bipyramidal, Sp^3d

c) Square pyramidal, Sp^3d^2

d) Octahedral, Sp^3d^2

17. Pick out the incorrect statement from the following

a) Sp^3 hybrid orbitals are equivalent and are at an angle of 109^0 28' with eachother

b) dsp^2 hybrid orbitals are equivalent and bond angle between any two of them is 90^0

c) All five sp^3d hybrid orbitals are not equivalent out of these five sp^3d hybrid orbitals, three are at an angle of 120^0, remainir two are perpendicular to the plane containing the other three

d) none of these

18. The molecules having same hybridisation, shape and number of lone pairs of electons are

a) SeF_4, XeO_2F_2 b) SF_4, XeF_2

c) $XeOF_4$, TeF_4 d) $SeCl_4$, XeF_4

19. In which of the following molecules / ions BF_3, NO_2^-, H_2O the central atom is sp^2 hybridised?

a) NH_2^- and H_2O

b) NO_2- and H_2O

c) BF_3 and NO_2-

d) BF_3 and NH_2^-

20. Some of the following properties of two species, NO_3^- and H_3O^+ are described below. which one of them is correct?

a) dissimilar in hybridisation for the central atom with different structure.

b) isostructural with same hybridisation for the Central atom.

c) different hybridiration for the central atom with same structure

d) none of these

21. The types of hybridiration on the five carbon atom from right to left in the, 2,3 pentadiene.

a) sp^3, sp^2, sp, sp^2, sp^3

b) sp^3, sp, sp, sp, sp^3

c) sp^2, sp, sp^2,sp^2, sp^3

d) sp^3, sp^3, sp^2, sp^3, sp^3

22. Xe F_2 is isostructural with

a) $SbCl_2$ b) $BaCl_2$

c) TeF_2 d) ICl_2^-

23. The percentage of s-character of the hybrid orbitals in methane, ethane, ethene and ethyne are respectively

a) 25, 25,33.3,50

b) 50,50,33.3,25

c) 50,25,33.3,50

d) 50,25,25,50

24. Of the following molecules, which have shape similar to carbondixide?

a) $SnCl_2$ b) NO_2

c) C_2 H_2 d) All of these.

25. According to VSEPR theory, the repulsion between different parts of electrons obey the order.

a) l.p – l.p > b.p–b.p> l.p–b.p

b) b.p–b.p> b.p–l.p> l.p–b.p

c) l.p–l.p> b.p–l.p > b.p–b.p

d) b.p–b.p> l.p–l.p> b.p–l.p

26. Shape of ClF_3 is

a) Planar triangular

b) Pyramidal

c) 'T' Shaped

d) none of these

27. Non- Zero dipole moment is shown by

a) CO_2

b) p-dichlorobenzene

c) carbontetrachloride

d) water.

28. Which of the following conditions is not correct for resonating structures?

a) the contributing structure must have the same number of unpaired electrons

b) the contributing structures should have similar energies

c) the resonance hybrid should have higher energy than any of the contributing structure.

d) none of these

29. Among the following, the compound that contains, ionic, covalent and Co-ordinate linkage is

a) NH_4Cl b) NH_3

c) NaCl d) none of these

30. CaO and NaCl have the same crystal structure and approximately the same radii. It U is the lattice energy of NaCl, the approximate lattice energy of CaO is

a) U b) 2U

c) U/2 d) 4U

31. Define the following

i) Bond order

ii) Hybridisation

iii) σ- bond

32. What is a pi bond?

33. In CH_4, NH_3 and H_2O, the central atom undergoes sp^3 hybridisation - yet their bond angles are different. why?

34. Explain Sp^2 hybridisation in BF_3

35. Draw the M.O diagram for oxygen molecule calculate its bond order and show that O_2 is paramagnetic.

36. Draw MO diagram of CO and calculate its bond order.

37. What do you understand by Linear combination of atomic orbitals in MO theory.

38. Discuss the formation of N_2 molecule using MO Theory

39. What is dipolment?

40. Linear form of carbondioxide molecule has two polar bonds. yet the molecule has Zero dipolement why?

41. Draw the Lewis structures for the following species.

i) NO_3^- ii) SO_4^{2-} iii) HNO_3
iv) O_3

42. Explain the bond formation in $BeCl_2$ and $MgCl_2$.

43. Which bond is stronger σ or π? Why?

44. Define bond energy.

45. Hydrogen gas is diatomic where as inert gases are monoatomic – explain on the basis of MO theory.

46. What is Polar Covalent bond? explain with example.

47. Considering x- axis as molecular axis, which out of the following will form a sigma bond.

i) 1s and $2p_y$ ii) $2P_x$ and $2P_x$
iii) $2p_x$ and $2p_z$ iv) 1s and $2p_z$

48. Explain resonance with reference to carbonate ion?

49. Explain the bond formation in ethylene and acetylene.

50. What type of hybridisations are possible in the following geometeries?

a) octahedral

b) tetrahedral

c) square planer.

51. Explain VSEPR theory. Applying this theory to predict the shapes of IF_7, and SF_6

52. CO_2 and H_2O both are triatomic molecule but their dipole moment values are different. Why?

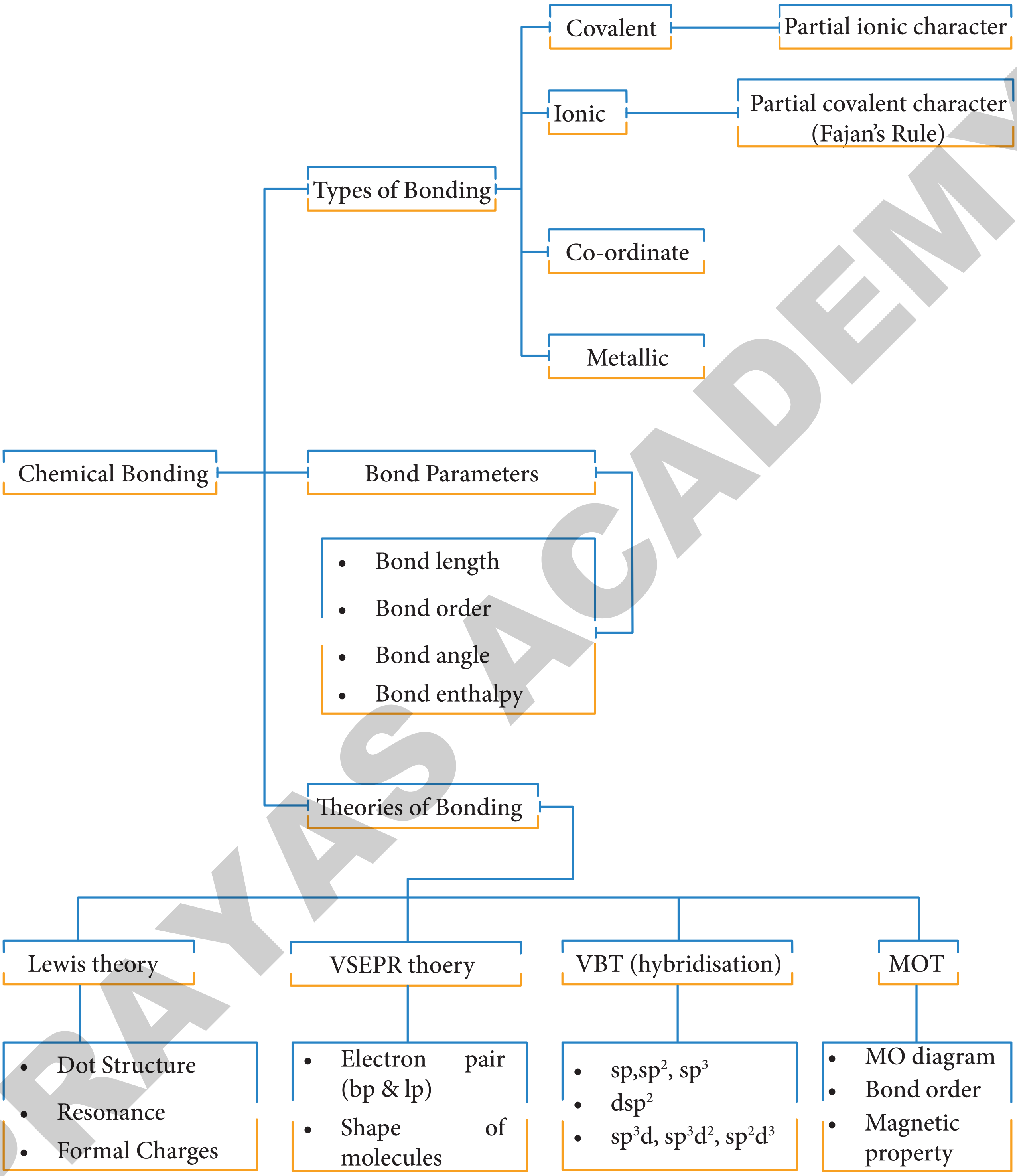
53. Which one of the following has highest bond order?

N_2, N_2^+ or N_2^-

54. Explain the covalent character in ionic bond.

55. Describe fajan's rule.

CONCEPT MAP



- Chemical Bonding
  - Types of Bonding
    - Covalent
      - Partial ionic character
    - Ionic
      - Partial covalent character (Fajan's Rule)
    - Co-ordinate
    - Metallic
  - Bond Parameters
    - Bond length
    - Bond order
    - Bond angle
    - Bond enthalpy
  - Theories of Bonding
    - Lewis theory
      - Dot Structure
      - Resonance
      - Formal Charges
    - VSEPR thoery
      - Electron pair (bp & lp)
      - Shape of molecules
    - VBT (hybridisation)
      - sp,sp^2, sp^3
      - dsp^2
      - sp^{3}d, sp^{3}d^2, sp^{2}d^3
    - MOT
      - MO diagram
      - Bond order
      - Magnetic property

Unit 11

Fundamentals of Organic Chemistry

Friedrich Wöhler, was a German pioneer in organic chemistry. He is best known for his synthesis of urea an the organic compound from the inorganic compound, ammonium cyanate. This finding went against the mainstream theory of that time called *vitalism* which stated that organic matter possessed a special force or vital force inherent to all living things. He is also the first to isolate several chemical elements. He is the discoverer of the element aluminum and also the co-discoverer of yttrium, beryllium, and titanium.

Learning Objectives

After studying this unit students will be able to

- understand the reason for the tetra valency of carbon and shapes of organic molecules
- classify the organic compounds
- name the organic compounds according to IUPAC nomenclature and derive the structure from the IUPAC name
- describe various types of isomerism
- explain the principles of detection and estimation of elements in organic compounds
- describe various techniques used in the purification of organic compounds

Introduction

Organic chemistry is the study of compounds of carbon. Carbon has a tendency to form more compounds with itself and other atoms (H, O, N, S and halogens) than any other elements. The tendency of an atom to form a chain of bonds with the atoms of the same element is called catenation. The high strength of C-C bond is responsible for its catenation property.

The word 'organic' means 'derived from living organisms'. Organic compounds were thought to be found only in living things. Cell the basic unit of living things, consumes, creates and consists of mainly organic compounds. DNA, the genetic material, the lipids, that forms our cell membrane and the glycogen the energy reserve stored in our liver are all organic compounds. Except few inorganic compounds like salt, water etc... all others such as food, medicine, clothing, cosmetics, fuel etc... are compounds of carbon. All the essential biochemical reactions are also organic in nature leading to the fomation various essential bioorganic molecules such as lipoproteins, phospolipids, glycolipids etc...

Synthesis of acetic acid by kolbe and methane by Berthlot, confirmed that organic compounds can be synthesized in laboratory. Since then, millions of organic compounds were synthesised and characterised. The field of organic chemistry is very vast and its principles find applications in many industries including food, textile, pertrochemical, pharmaceutical, dye, polymers, fetiliser, cosmetics etc... Discussing the importance of organic chemistry is just like describing a drop of water in a mighty ocean.

The knowledge of chemical bonding and molecular structure will help in understanding the properties of organic compounds. We know that, the carbon has four valance electrons and its ground state electronic configuration is $1s^2\ 2s^2\ 2p^2$. An atom can attain noble gas electronic configuration either by transferring or sharing of electrons. It is not possible for the carbon to form either C^{4+} or C^{4-} ions to attain the nearest noble gas configuration, as it requires large amount of energy. This implies that carbon cannot form ionic bond. Almost in all compounds of carbon, it forms four covalent bonds.

The formation of four covalent bonds can be explained as below. During bond formation, one of the electrons from 2s orbital is promoted to $2p_z$ orbital. The formation of four sigma bonds by carbon can be explained on the basis of sp^3 hybridisation of carbon. Carbon forms multiple (double and triple) bonds in certain compounds. These can be explained by sp^2 and sp hybridisation of carbon. The carbon forms relatively short bonds which enable the lateral overlap of unhybridised 2p orbitals of sp^2 and sp hybridised carbon to form one and two pi bonds respectively.

Molecular stucture can be derived from the type of hybridisation. An sp^3 hybridised carbon will have a tetrahedral geometry, a sp^2 hybridised carbon will have trigonal planar geometry. and sp hybridised carbon will have a linear geometry.

Characteristics of organic compounds:

All organic compounds have the following characteristic properties.

1. They are covalent compounds of carbon and generally insoluble in water and readily soluble in organic solvent such as benzene, toluene, ether, chloroform etc...

2. Many of the organic compounds are inflammable (except CCl_4).They possess low boiling and melting points due to their covalent nature

3. Organic compounds are characterised by functional groups. A functional group is an atom or a specific combination of bonded atoms that

react in a characteristic way, irrespective of the organic molecule in which it is present. In almost all the cases, the reaction of an organic compound takes place at the functional group. They exhibit isomerism which is a unique phenomenon.

4. **Homologous series:** A series of organic compounds each containing a characteric functional group and the successive members differ from each other in molecular formula by a CH_2 group is called homologous series. Eg.

   Alkanes: Methane (CH_4), Ethane (C_2H_6), Propane (C_3H_8) etc..

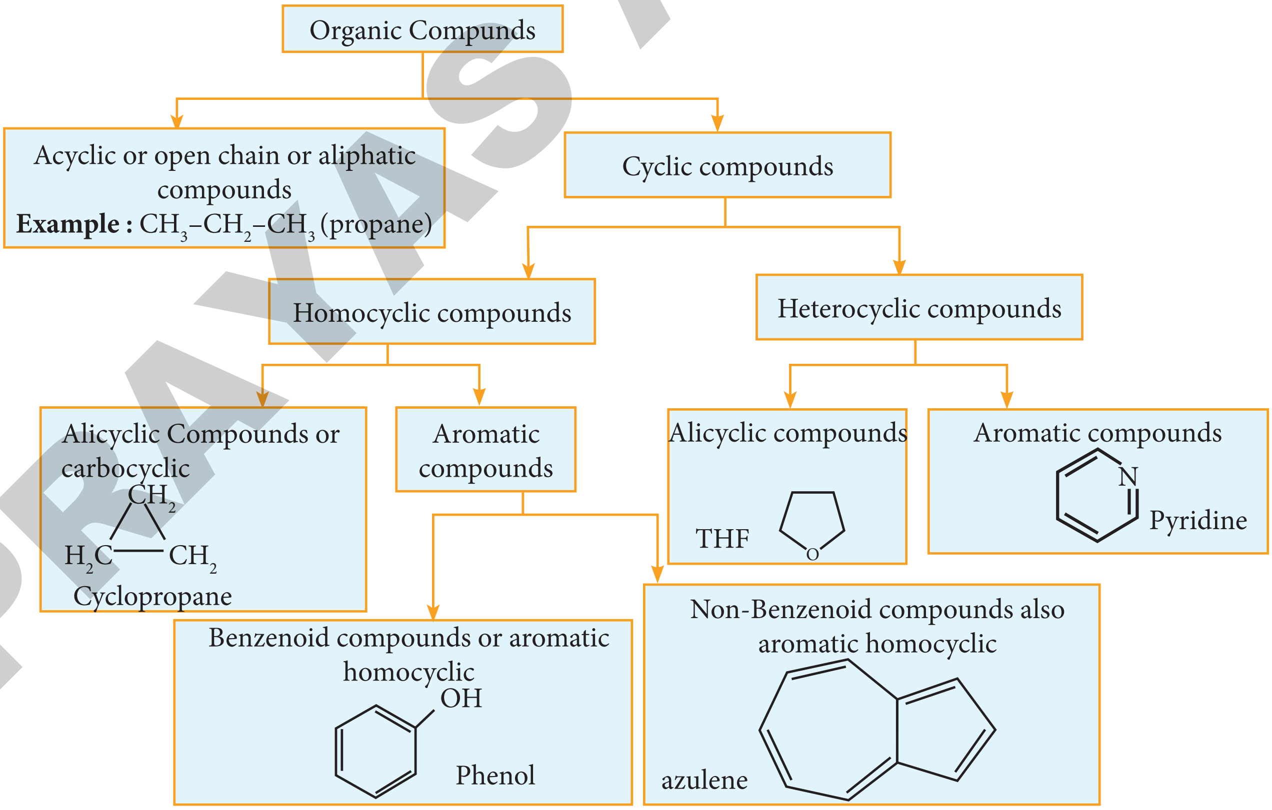
   Alcohols: Methanol (CH_3OH), Ethanol (C_2H_5OH) Propanol (C_3H_7OH) etc..)

   Compounds of the homologous series are represented by a general formula Alkanes C_nH_{2n+2}, Alkenes C_nH_{2n}, Alkynes C_nH_{2n-2} and can be prepared by general methods. They show regular gradation in physical properties but have almost similar chemical property.

11.2 Classification of organic compounds

The existing large number of organic compounds and ever-increasing number have made it necessary to classify them. They may be classified based on their structure or the functional group.

11.2.1 Classification based on the structure:

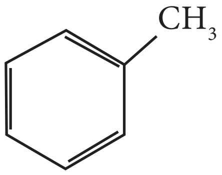


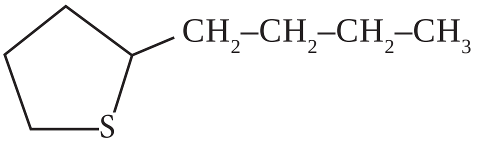
Based on the above classification let us classify the following compounds.

1. Classify the following compounds based on the structure

i) $CH \equiv C- CH_2-C \equiv CH$

ii) $CH_3 - CH_2 - CH_2 - CH_2- CH_3$

iii) 

iv) 

Solutions:

(i) Unsaturated open chain compound

(ii) saturated open chain compound

(iii) aromatic benzenoid compound

(iv) alicyclic compound

Evaluate Yourself

1) Give two examples for each of the following type of organic compounds.

(i) non-benzonoid aromatic,

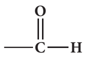
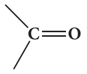
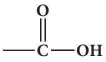
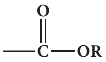
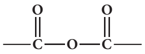
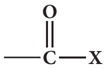
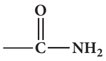
(ii) aromatic heterocyclic,

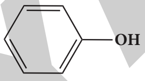
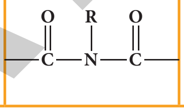
(iii) alicyclic and

(iv) aliphatic open chain.

11.2.2 Classification based on functional groups:

Table 11.1 Class of compounds and their functional group

S. No.	Class of compounds	Functional group	General formula (R - Alkyl group)
1	Alkene	–	C_nH_{2n}
2	Alkyne	–	C_nH_{2n-2}
3	Alkyl halide	—F, —Cl, —Br, —I	R- X
4	Alcohol	—OH	R-OH
5	Ether	—O—	R-O-R'
6	Aldehyde	 $-\overset{O}{\overset{\|}{C}}-H$	R-CHO
7	Ketone		R-CO-R'
8	Carboxylic acid	 $-\overset{O}{\overset{\|}{C}}-OH$	R-COOH
9	Ester	 $-\overset{O}{\overset{\|}{C}}-OR$	RCOOR'
10	Acid anhydride	 $-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-$	R-CO-O-CO-R'
11	Acyl chloride	 $-\overset{O}{\overset{\|}{C}}-X$	R-COX
12	Sulphonic acid	$—SO_3H$	$R\text{-}SO_3H$
13	Nitro alkane	$—NO_2$	$R\text{-}NO_2$
14	Amine	$—NH_2$	$R\text{-}NH_2$
15	Amide	 $-\overset{O}{\overset{\|}{C}}-NH_2$	$R\text{-}CO\text{-}NH_2$

S. No.	Class of compounds	Functional group	General formula (R - Alkyl group)
16	Cyanide (Nitrile)	—C≡N	R-CN
17	Isocyanide	**—NC**	R-NC
18	Cyanate	**—OCN**	R-OCN
19	Isocyanate	**—NCO**	R-NCO
20	Thiocyanate	**—SCN**	R-SCN
21	Isothiocyanate	**—NCS**	R-NCS
23	Thioalcohols or thiols	**—SH**	R-SH
24	Thioethers	**—S—R**	R-S-R'
25	Imines	**=NH**	R-CH=NH
26	Nitroso compounds	**—NO**	R-NO
27	Hydrazines	**—NH—NH₂**	$R-NH-NH_2$
28	Hydrazo compounds	**—NH—NH—**	R-NH-NH-R
29	Phenols		C_6H_5OH
30	Imide	 $-\overset{O}{\overset{\parallel}{C}}-\overset{R}{\overset{\mid}{N}}-\overset{O}{\overset{\parallel}{C}}-$	RCON(R') | COR''

11.3 Nomenclature of organic compounds:

The International Union of Pure and Applied Chemistry (IUPAC) is the world authority on chemical nomenclature and terminology, naming of new elements in the periodic table standardized methods for measurement; atomic weights, and many other critically-evaluated data. According to IUPAC recommendations to name any organic compound, it is considered as a derivative of its parent saturated hydrocarbon. The IUPAC name of an organic compound consists of three parts.

prefix + root word + suffix

Root word denotes the number of carbon atoms in the longest continiuous chain in molecules. Prefix denotes the group(s) attached to the main chain which is placed before the root. Suffix denotes the funtional group and is paced after the root word.

Table 11.2 Number of carbons in parent chain and the corresponding root words

Chain length(or) no. of carbon atoms	Root word	Chain length(or) no. of carbon atom	Root word
C_1	Meth-	C_{17}	Heptadec-
C_2	Eth-	C_{18}	Octadec-
C_3	Prop-	C_{19}	Nonadec-
C_4	But-	C_{20}	Eicos-
C_5	Pent-	C_{21}	Henecos
C_6	Hex-	C_{22}	Docos
C_7	Hept-	C_{30}	Triacont-
C_8	Oct-	C_{31}	Hentriacont
C_9	Non-	C_{32}	Ditriacont
C_{10}	Dec-	C_{40}	Tetracont-
C_{11}	Undec-	C_{50}	Pentacont-

Chain length(or) no. of carbon atoms	Root word	Chain length(or) no. of carbon atom	Root word
C_{12}	Dodec-	C_{60}	Hexacont-
C_{13}	Tridec -	C_{70}	Heptacont-
C_{14}	Tetradec-	C_{80}	Octacont-
C_{15}	Pentadec-	C_{90}	Nonacont-
C_{16}	Hexadec-	C_{100}	Hect-

Suffix: There are two types of suffix. They are primary suffix and secondary suffix

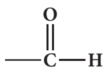
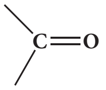
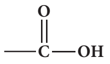
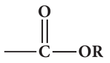
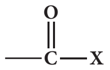
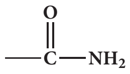
Primary suffix: It denotes the saturation/ unsaturation of organic compounds. It is added immediately after the root word. Primary suffix for various saturated and unsaturated carbon chains are as follows:

Table 11.3 Primary suffix for various saturated and unsaturated carbon chains

Name & type of carbon chain	Primary suffix
Saturated, C-C	ane
Unsaturated carbon chain	
one $C=C$ bond	ene
Two $C=C$ bonds	diene
Three $C=C$ bonds	triene
One $C\equiv C$ bond	yne
Two $C\equiv C$ bonds	diyne

Secondary suffix: It is used to denote the nature of functional group present in the organic compound. It is added to the primary suffix by removig its terminal 'e'. Secondary suffix names for some functional groups is listed below in table 11.4

Table 11.4 Secondary sufix and prefixes for some functional groups:

Class of organic compounds	Functional group	Prefix	Secondary suffix
Alcohols	$-OH$	hydroxy-	-ol
Thioalcohols	$-SH$	mercapto	-thiol
Aldehydes	 $-\overset{O}{\overset{\|}{C}}-H$	formyl-	-al
Ketones		oxo-	-one
Carboxylic acid	 $-\overset{O}{\overset{\|}{C}}-OH$	carboxy-	-oic acid
Esters	 $-\overset{O}{\overset{\|}{C}}-OR$	Alkoxy–Carbonyl	-oate
Acid chlorids	 $-\overset{O}{\overset{\|}{C}}-X$	chlorocarbonyl	-oyl chloride
Acid amines	 $-\overset{O}{\overset{\|}{C}}-NH_2$	Carbamoyl	-amide
Amines	$-NH_2$	amino-	-amine
Nitriles	$-C\equiv N$	cyano-	-nitrile
Sulphonic acid	$-SO_3H$	sulpho-	-sulphonic acid

Prefix: Substituents that are attached to the parent carbon chain are denoted by adding prefix names before the root word. The prefix names for some common substituents are listed below. If the functional groups are not part of the parent chain, they are considered as substituents. In such cases its prefix name is added before the root word. Prefix names for some functional groups mentioned along with their secondary prefix are listed in table 11.4

Table 11.5 List of substitutents and their Prefix names

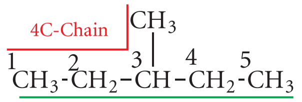
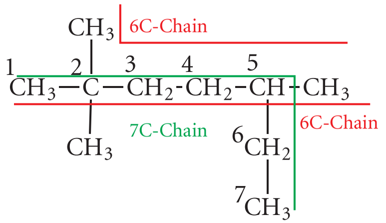
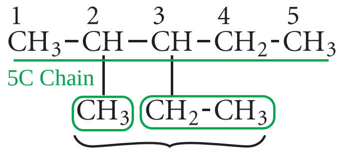
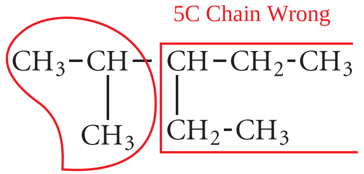
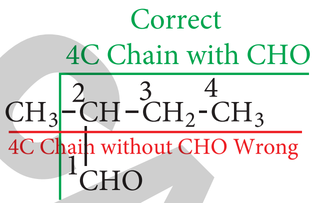
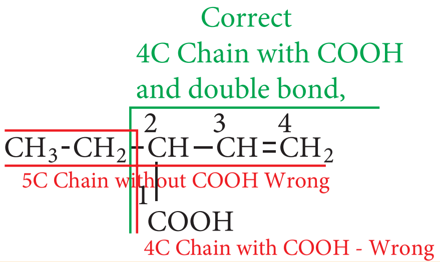
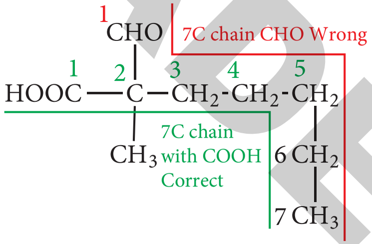
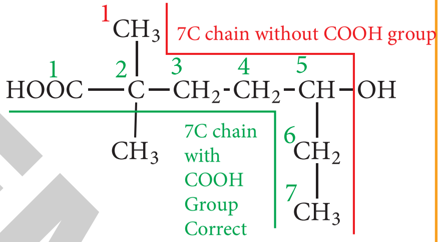
Substituent group	Prefix
-F	Fluoro
-Cl	Chloro
-Br	Bromo
-I	Iodo
$-NO_2$	Nitro
-NO	Nitroso
$-\overset{+}{N}=N$	Diazo
-OR	Alkoxy
$-OCH_3$ (or) -OMe	Methoxy
$-OC_2H_5$ (or) -OEt	Ethoxy
$-CH_3$ (or) –Me	Methyl
$-C_2H_5$ (or) -Et	Ethyl
$-CH_2-CH_2-CH_3$	1- propyl (n propyl)
$-CH(CH_3)_2$	2-propyl (iso-propyl)
$-CH_2-CH_2-CH_2-CH_3$	1-butyl (n-butyl)
$-CH_2-CH(CH_3)-CH_3$	2-methyl propyl (iso propyl)
$-C(CH_3)_3$	1,1-dimethy lethyl (tert-butyl)
$-CH_2-CH_2-CH_2-CH_2-CH_3$	1-pentyl (n-pentyl)
$-CH_2-CH(CH_3)-CH_2-CH_3$	2-methyl butyl
$CH_2-CH(CH_3)_3$	2,2-dimethyl propyl (neopentyl)

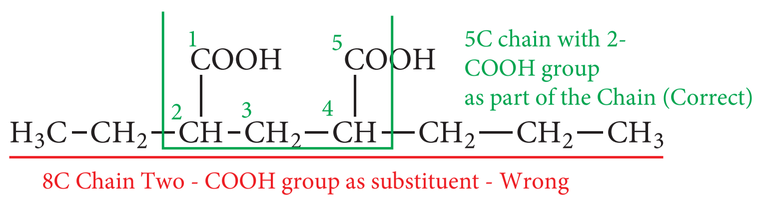
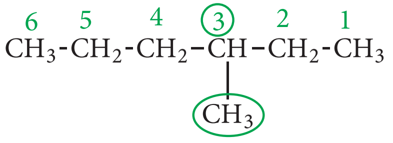
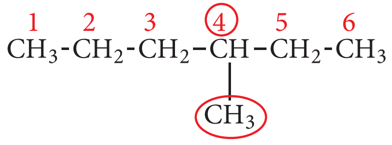
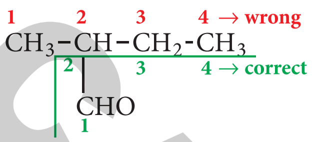
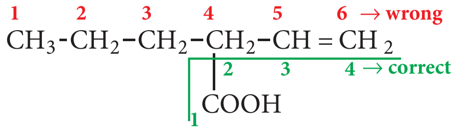
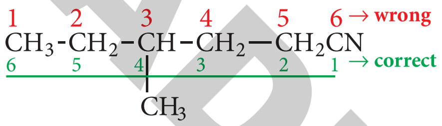
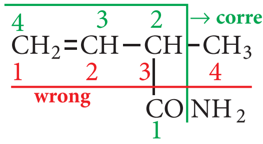
11.3.1 IUPAC rules for nomenclature of organic compounds

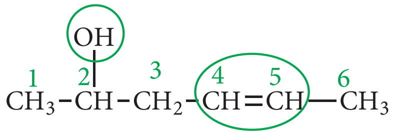
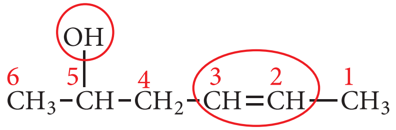
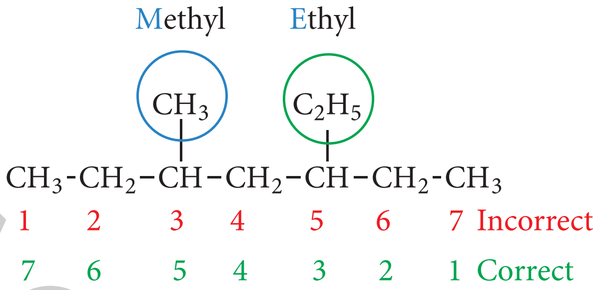
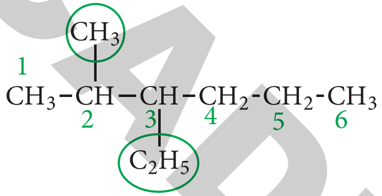
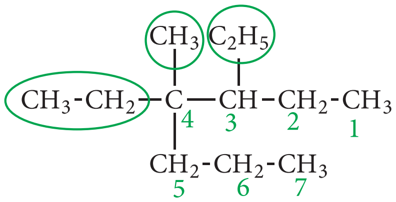
The following steps should be followed for naming an organic compound as per IUPAC nomenclature.

1. Choose the longest carbon chain. (Root word). Consider all the other groups attached to this chain as substitutents.
2. Numbering of the longest carbon chain
3. Naming of the substituents (prefixes or suffixes)
4. Arrange the substitutents in the alphabetical order
5. Write the name of the compound as below

"prefix + root word + primary suffix + secondary suffix"

Step No.	Conditions	Rule	Illustrations
Choose the longest carbon chain (parent chain)			 longest chain of 5 C atom  longest chain of 7 C atom
	Two chains of equal lengths.	Choose the chain with maximum number of substituents	 Two Subtituent Correct  One Subtituent
	Compound contains functional group or multiple bond or both	i) If any of the fucntional groups (-OH, -CHO, -COOH, -CN, -COOR, $CONH_2$, $-NH_2$, COR, COX, $-SO_3H$, -SH, -SR) are present, choose the longest carbon chain in such a way that it contains functional groups.	 
		ii) If more than one functional group is present, the one with highest precedence should be part of the parent chain. Order of precedence of functional group is -COOH > $-SO_3H$ > -COOR, -COX > $CONH_2$ > -CN > -CHO > -CO- > -OH > -SH $-NH_2$ > -C=C- > -C=C-> C-C > -O- > -X > $-NO_2$	 

Step No.	Conditions	Rule	Illustrations
		iii) If the same functional group is present more than once, choose the very longest carbon chain in such a way that it contains maximum number of that functional group	
Numbering the parent chain from one end to another substitutents	Presence of substituents (All other atoms or groups attached to the parent chain are considered as substitutents)	Numbering should be done in such a way that it gives the lowest possible number to the carbon atom carrying the substituent Numbering should start from terminal functional groups such as -CHO, -COOH, -COOR, -CONH$_2$, -CN etc.. (if present)	 Correct  Wrong
	More number of substitutents/ functional group present	Numbering should be done in such a way that the sum of **the number which indicates the position of the subtituents/functional group (Locant)** gives the lowest number	   

<table>
<tr><th>Step No.</th><th>Conditions</th><th>Rule</th><th>Illustrations</th></tr>
<tr><td></td><td>When more than one functional group have same locant the following order of priority should be followed.</td><td>Order of precedence of functional group is
-COOH > -SO$_3$H > -COOR, -COX > CONH$_2$ > -CN > -CHO > -CO- > -OH > -SH -NH$_2$ > -C=C- > -C=C- > C-C > -O- > -X > -NO2 .</td><td>
$CH_3-CH(OH)-CH_2-CH=CH-CH_3$
OH group > C=C Correct

$CH_3-CH(OH)-CH_2-CH=CH-CH_3$
Incorrect numbering</td></tr>
<tr><td></td><td>Two substituents are present on identical position with respect to the parent chain end.</td><td>Assign the lowest number according to the alphabetical order of the name of the substituent.</td><td>
$CH_3-CH_2-CH(CH_3)-CH_2-CH(C_2H_5)-CH_2-CH_3$
 </td></tr>
<tr><td colspan="4">Naming the substituents / functional group / side chain using the prefixes / suffixes given in table 11.3 primary suffix for various saturated and unsaturated carbon chains, Table 11.4 Secondary suffix and prefixes for some functional groups and table 11.5 prefix name for some substituents.</td></tr>
<tr><td>4. Arrange the substitutents in the alphabetical order</td><td>Two or more substituents are present on the parent chain,</td><td>These substituent prefixed with their position number are arranged in alphabetical order (irrespective of the position number) before root word (The prefixes di-, tri-, etc. are not taken into consideration for grouping alphabetically)</td><td>
$CH_3-CH(CH_3)-CH(C_2H_5)-CH_2-CH_2-CH_3$
3-Ethyl-2-methyl-

$CH_3-CH_2-C(CH_3)(CH_2-CH_2-CH_3)-CH(C_2H_5)-CH_2-CH_3$
3,4- Diethyl-4-methyl-</td></tr>
</table>

The following are guide lines for writing IUPAC of the organic compound.

1. The IUPAC names are always written as single word, with notable exception of organic salts, acids and acid derivatives.

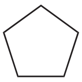
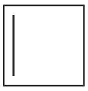
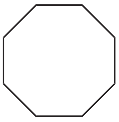
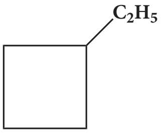
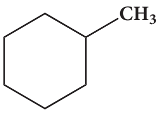
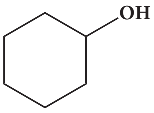
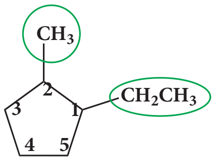
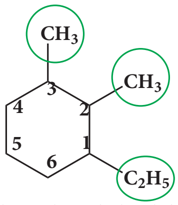
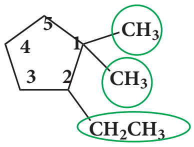
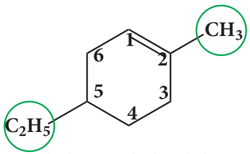
2. Commas are used between two adjacent number or letter symbols, and hypens are used to separate numbers and letter symbol in names **Eg: 2,2-Dimethyl-3-hexene N,N-Dimethyl methanamide**

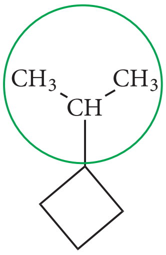
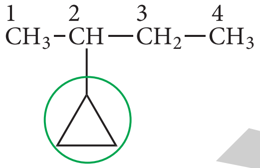
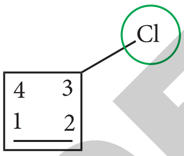
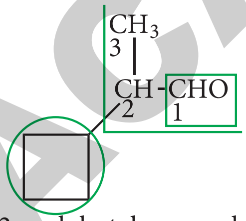
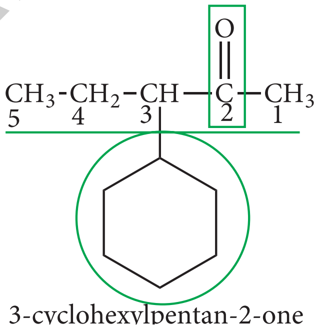
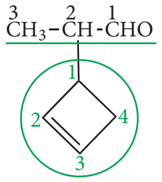
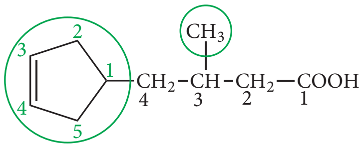
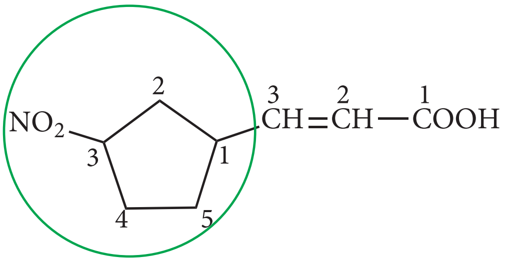
3. Structural prefix such as, meso-, cis-, trans-, are italicised and joined to the name by a hypen. These prefixes are omitted in alphabetising compound names or in capitalising names at the beginning of a sentence.**Eg:*trans*-2-Butene**

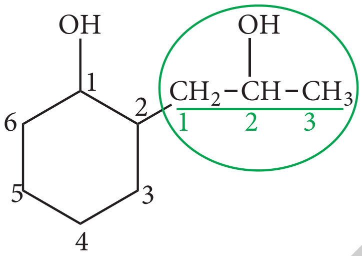
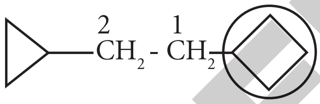
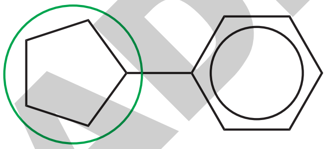
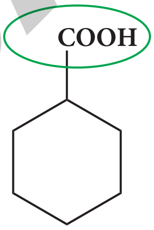
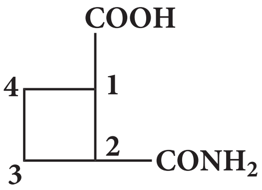
4 .Structural prefixes such as di, tri, tetra are treated as a part of the basic name and therefore are neither italicised nor separated by a hypen. These prefixes are not taken into account in alphabetising compound names **eg: 4- Ethyl -2,2-dimethyl hexane.**

5 To name alicyclic compounds , the additional rules should be followed as illustrated in the table 11.x

Table 11.6 Rules for naming of alicyclic compounds:

Rule	Illustration
In the naming of such compounds a prefix cyclo is added to the word root	 cyclobutane  cyclopentane  cyclobutene  cyclooctane
If only one substituent is present on the ring, then it is not required to give its position	 ethylcyclobutane  methylcyclohexane  cyclohexanol
If two or more substituents are present on the ring, the numbering of ring is done according to lowest set of locant rule. Alicyclic compounds also follow the numbering rules of acyclic compounds	 1-ethyl-2-methylcyclopentane  1-ethyl-2,3-dimethylcyclohexane  2-ethyl-1,1-dimethylcyclopentane  5-ethyl-2-methylcyclohex-1-ene

Rule	Illustration
If the ring contains lesser number of carbon atoms than that of alkyl group attached to it, the compound is named as derivative of alkane and the ring is considered as a substituent group to the alkane, otherwise it is named as derivative of cycloalkane	 2-Propylcyclobutane (derivative of cycloalkane)  2-Cyclopropylbutane (derivative of alkane)  ·Chlorocyclobut-1-ene ouble bond get prefernce over substituent-Cl for numbering)
If the side chain contains a multiple bond or a functional group, then the alicyclic ring is treated as the substituent irrespective of the size of the ring	 2-cyclobutylpropanal  3-cyclohexylpentan-2-one
If the alicyclic ring contains a multiple bond and the side chain contains a functional group the compound is named as derivative of the side chain and the ring is treated as substituent	 2-(cyclobut-2-en-1-yl)-propanal  4-(cyclopent-3-en-1-yl)-3-methylbutanoic acid
If both ring as well as the side chain contain the functional group, then parent hydrocarbon is decided on the basis of principal group which is further based on preferential order of functional groups	 3-(3-nitrocyclopentyl) - prop-2-enoicacid

Rule	Illustration
If both alicyclic ring and the side chain contain same functional group, the parent hydrocarbon is selected on the basis of number of carbon-atoms in the ring and side chain	 2-(2-hydroxypropyl)cyclohexan-1-ol
If more than one alicyclic rings are attached to the single chain of carbon atoms, the compound is named as a derivative of alkane and alicyclic rings are treated as substituent irrespective of the number of atom in the ring or chain	 1-(cyclobutyl)- 2- (cyclopropyl) - ethane
If the alicyclic ring is directly attached to the benzene ring the compound is named as a derivative of benzene	 **cyclopentylbenzene**
If the alicyclic ring has a functional group along with some substituent on the ring, then the appropriate prefixes and suffixes are used to represent such groups, and numbering is done in such a way that the functional group is not counted for word root rather appropriate suffixes are used to represent such groups	 **cyclohexanecarboxylic acid**  **2-carbamoylcyclobutane-1-carboxylic acid**

Evaluate Yourself

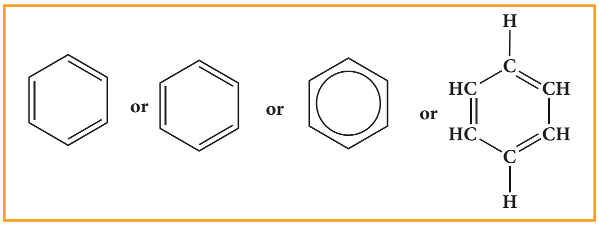
2) Write structural formula for the following compounds

(i) Cyclohexa-1, 4-diene (ii) Ethynyl cyclohexane

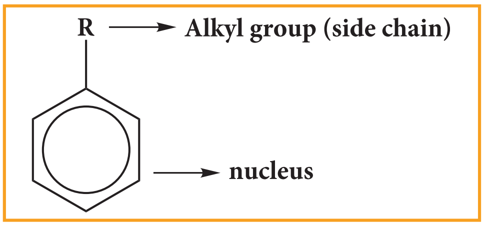
NOMENCLATURE OF AROMATIC COMPOUNDS:

An aromatic compound consists of two parts nucleus and side chain

(A) Nucleus: The benzene ring present in aromatic compound is called nucleus. It is represented as follows

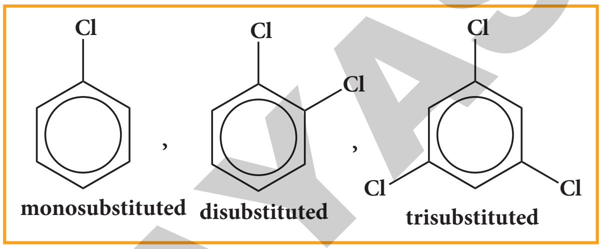


(B) Side chain: Alkyl or any other aliphatic group attached to the benzene nucleus by replacing one or more hydrogen atom is called the side chain

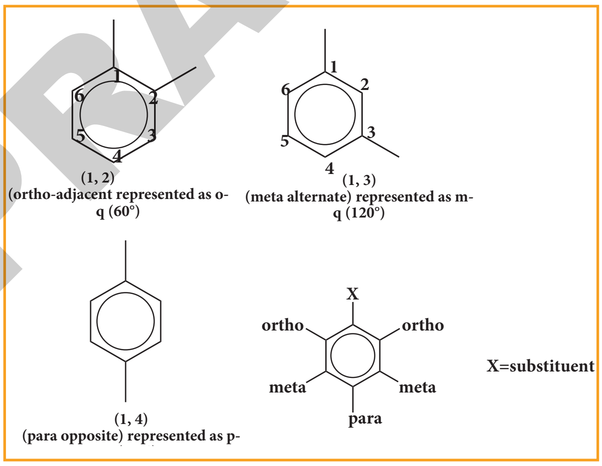


If one hydrogen atom, (or) two hydrogen atoms or three hydrogen atoms are replaced in the benzene ring by some other groups, they are termed as mono substituted, di substituted or tri substituted derivative respectively.

Example



monosubstituted , **disubstituted** , **trisubstituted**



(1, 2)
(ortho-adjacent represented as o-
q (60°)

(1, 3)
(meta alternate) represented as m-
q (120°)

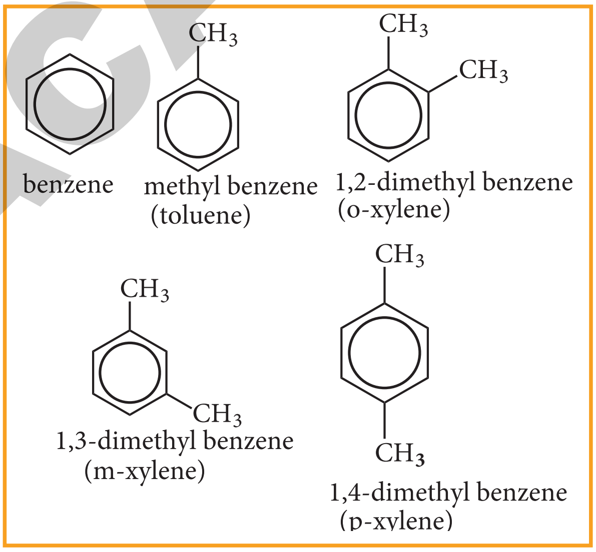
(1, 4)
(para opposite) represented as p-

If more than one hydrogen atom of benzene ring is replaced by some other atom or group, then their position is mentioned by Arabic numerals 1,2,3 ….. In case of disubstitution, respective position of two groups can also be mentioned as follows.

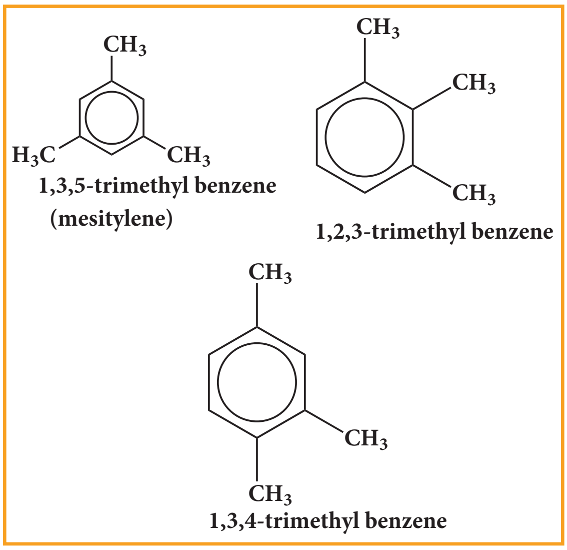
ortho - adjacent; represented as - o
meta - alternate; represented as - m
Para - opposite; represented as - p

Aromatic compounds are basically of two types:

1. Nuclear substituted aromatic compounds: These are the compounds in which the functional group is directly attached to the benzene ring. They are named as derivatives of benzene.



benzene
methyl benzene (toluene)
1,2-dimethyl benzene (o-xylene)
1,3-dimethyl benzene (m-xylene)
1,4-dimethyl benzene (p-xylene)

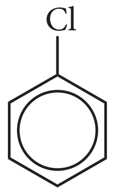


1,3,5-trimethyl benzene (mesitylene)

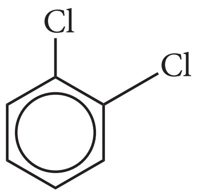
1,2,3-trimethyl benzene

1,3,4-trimethyl benzene

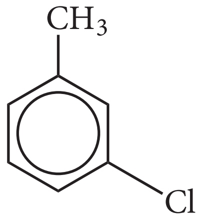
Nuclear substituaed aramatic Halogen derivatives compounds.



chlorobenzene



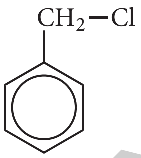
1,2-dichlorobenzene
o-dichlorobenzene



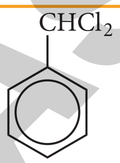
1-chloro-3-methylbenzene
m-chlorotoluene

2. Side chain substituted aromatic compounds: These are the compounds in which the functional group is present in the side chain of the benzene ring. These are named as phenyl derivatives of the corresponding aliphatic compounds.

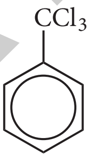
Side chain substituted



phenyl (chloromethane)
(benzyl chloride)

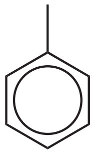


phenyldichloromethane
(benzaldichloride)



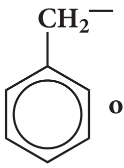
phenyltrichloromethane
(benzotrichloride)

Aryl groups



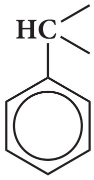
or C_6H_5—

phenyl



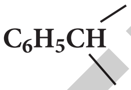
or C_6H_5-CH_2

benzyl

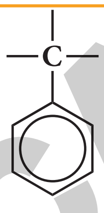


benzal

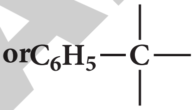
or



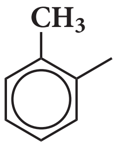
C_6H_5CH



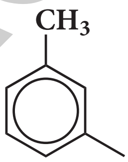
benzo



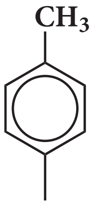
orC_6H_5—C—



o-tolyl or 2-tolyl



m-tolyl or 3-tolyl



p-tolyl or 4-tolyl

H_3C—C_6H_4- **=o/m/p tolyl**

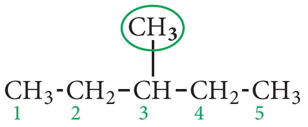
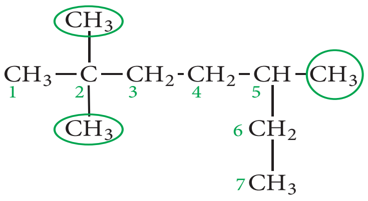
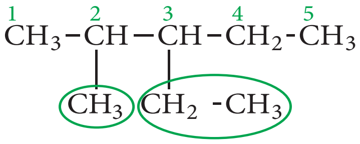
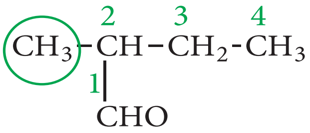
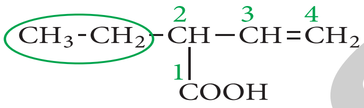
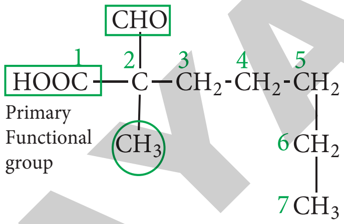
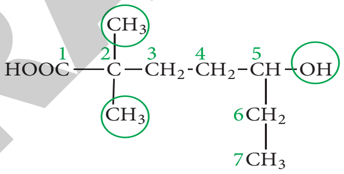
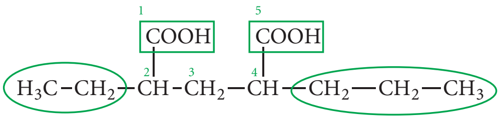
Selection of parent hydrocarbon out of side chain and benzene ring is based on (more or less) some rule as for the alicyclic compounds.

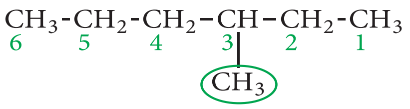
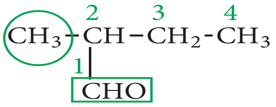
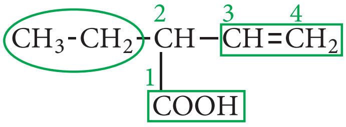
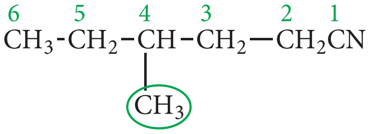
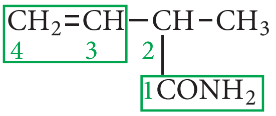
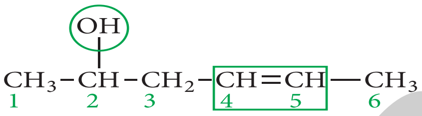
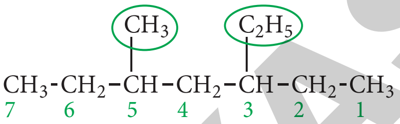
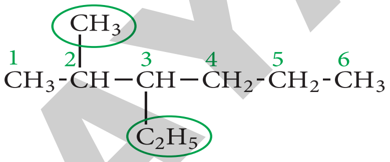
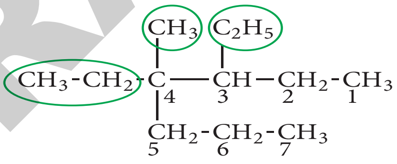
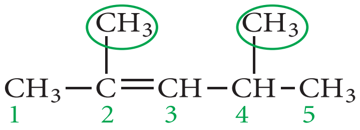
Evaluate Yourself

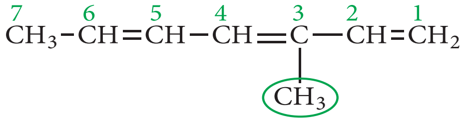
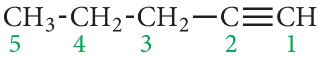
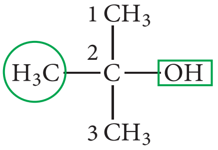
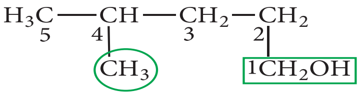
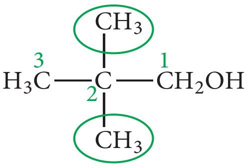
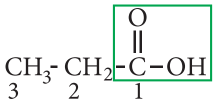
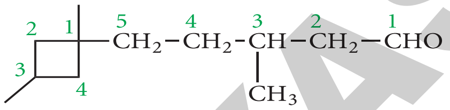
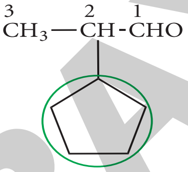
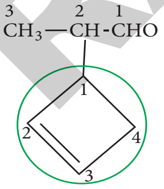
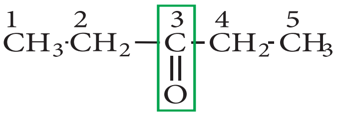
3) Write structural formula for the following compounds

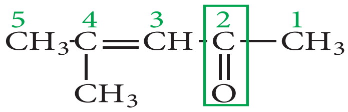
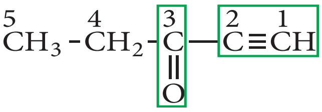
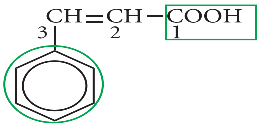
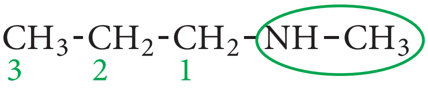
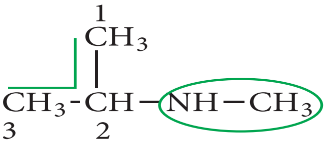
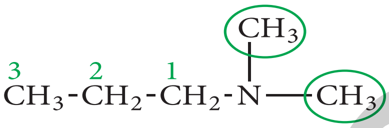
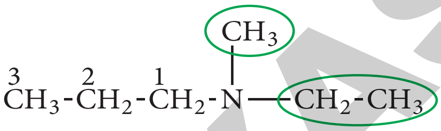
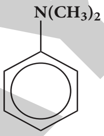
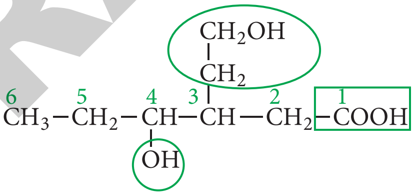
(i) m - dinitrobenzene (ii) p-dichloro benzene (iii)1, 3, 5- Trimethyl benzene

Table 11.3.1. 2

Compound Structure and IUPAC Name	Prefix with position number	Root word	Primary suffix	Secondary suffix
 3-methylpentane	3-methyl	pent	ane	–
 2,2,5-trimethylheptane	2,2,5- trimethyl	Hept	ane	–
 3-ethyl-2-methylpentane	3-ethyl- -2-methyl	pent	ane	–
 2-methylbutanal	2-methyl	but	an~~e~~	al
 2-ethylbut-3-enoic acid	2-ethyl	but	en~~e~~	oic acid
 2-formyl-2-methylheptanoic acid	2-formyl-2-methyl	hept	an~~e~~	oic acid
 5-hydroxy-2,2-dimethylheptanoic acid	5-hydroxy-2,2- dimethyl	hept	an~~e~~	oic acid
 2-ethyl-4-propylpentanedioic acid	2-ethyl- 4-propyl	pent	an~~e~~	oic acid

Compound Structure and IUPAC Name	Prefix with position number	Root word	Primary suffix	Secondary suffix
 $CH_3-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-CH_3$ 3-methylhexane	3-methyl	hex	ane	–
 $CH_3-\underset{\displaystyle CHO}{\underset{\vert}{CH}}-CH_2-CH_3$ 2-methylbutanal	2-Methyl	but	an~~e~~	al
 $CH_3-CH_2-\underset{\displaystyle COOH}{\underset{\vert}{CH}}-CH=CH_2$ 2-ethylbut-3-enoic acid	2-ethyl	but	3- en~~e~~	oic acid
 $CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-CH_2CN$ 4-methylhexanenitrile	4-methyl	hex	en~~e~~	nitrile
 $CH_2=CH-\underset{\displaystyle CONH_2}{\underset{\vert}{CH}}-CH_3$ 2-methylbut-3-enamide	2-methyl	but	3 - en~~e~~	amide
 $CH_3-\overset{\displaystyle OH}{\overset{\vert}{CH}}-CH_2-CH=CH-CH_3$ hex-4-en-2-ol		hex	4 - en~~e~~	2- ol
 $CH_3-CH_2-\overset{\displaystyle CH_3}{\overset{\vert}{CH}}-CH_2-\overset{\displaystyle C_2H_5}{\overset{\vert}{CH}}-CH_2-CH_3$ 3-ethyl-5-methylheptane	3-ethyl 5- methyl	hept	ane	–
 $CH_3-\overset{\displaystyle CH_3}{\overset{\vert}{CH}}-\underset{\displaystyle C_2H_5}{\underset{\vert}{CH}}-CH_2-CH_2-CH_3$ 3-ethyl-2-methylhexane	3-ethyl-2-methyl	hex	ane	–
 $CH_3-CH_2-\overset{\displaystyle CH_3}{\overset{\vert}{\underset{\displaystyle CH_2-CH_2-CH_3}{\underset{\vert}{C}}}}-\overset{\displaystyle C_2H_5}{\overset{\vert}{CH}}-CH_2-CH_3$ 3,4-diethyl-4-methylheptane	3,4-diethyl- 4-methyl	hept	ane	–
 $CH_3-\overset{\displaystyle CH_3}{\overset{\vert}{C}}=CH-\overset{\displaystyle CH_3}{\overset{\vert}{CH}}-CH_3$ 2,4-dimethylpent-2-ene	2,4-dimethyl	pent	2 - ene	–

Compound Structure and IUPAC Name	Prefix with position number	Root word	Primary suffix	Secondary suffix
 $CH_3-CH=CH-CH=\underset{CH_3}{\underset{\mid}{C}}-CH=CH_2$ 3-methylhepta-1,3,5-triene	3-methyl	hept	1, 3, 5 - triene	–
 $CH_3-CH_2-CH_2-C\equiv CH$ 1-pentyne (or) pent -1- yne	–	pent	1- yne	–
 $H_3C-\overset{CH_3}{\underset{CH_3}{C}}-OH$ 2-methyl propan-2-ol	2-methyl	prop	an~~e~~	2-ol
 $H_3C-\underset{CH_3}{CH}-CH_2-\underset{CH_2OH}{CH_2}$ 4-methylpentan -1- ol	4-methyl	pent	an~~e~~	1-ol
 $H_3C-\overset{CH_3}{\underset{CH_3}{C}}-CH_2OH$ 2,2-dimethyl propan -1- ol	2,2-dimethyl	prop	an~~e~~	1-ol
 $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH$ propanoic acid		prop	an~~e~~	oic acid
 3-methyl-5-(1,3-dimethylcyclobutyl)pentanal	3-methyl-5-(1,3-dimethylcyclobutyl)	pent	an~~e~~	al
 2-cyclopentylpropanal	2-cyclopentyl	prop	an~~e~~	al
 2-(cyclobut-2-enyl)propanal	2-(cyclobut-2-enyl)	prop	an~~e~~	al
 $CH_3-CH_2-\underset{O}{\underset{\|}{C}}-CH_2-CH_3$ pentan-3-one	–	pent	an~~e~~	3 - one

Compound Structure and IUPAC Name	**Prefix with position number**	**Root word**	**Primary suffix**	**Secondary suffix**
 $\overset{5}{CH_3}-\overset{4}{\underset{CH_3}{C}}=\overset{3}{CH}-\overset{2}{\underset{\overset{\Vert}{O}}{C}}-\overset{1}{CH_3}$ 4-methylpent-3-en-2-one	4-methyl	pent	3- en~~e~~	2-one
 $\overset{5}{CH_3}-\overset{4}{CH_2}-\overset{3}{\underset{\overset{\Vert}{O}}{C}}-\overset{2}{C}\equiv\overset{1}{CH}$ pent-1-yne-3-one	–	pent	1- yn~~e~~	3- one
 3phenyl prop -2-enoicacid	3-phenyl	prop	2- en~~e~~	oic acid
 $\underset{3}{CH_3}-\underset{2}{CH_2}-\underset{1}{CH_2}-NH-CH_3$ N-methylpropan-1-amine	N-methyl	prop	an~~e~~	1-amine
 $\underset{3}{CH_3}-\underset{2}{\overset{\overset{1}{CH_3}}{CH}}-NH-CH_3$ N-methylpropan-2-amine	N-methyl	prop	an~~e~~	2-amine
 $\overset{3}{CH_3}-\overset{2}{CH_2}-\overset{1}{CH_2}-\overset{CH_3}{N}-CH_3$ N,N-dimethylpropan-1-amine	N,N-dimethyl	prop	an~~e~~	1-amine
 $\overset{3}{CH_3}-\overset{2}{CH_2}-\overset{1}{CH_2}-\overset{CH_3}{N}-CH_2-CH_3$ N-ethyl-N-methylpropan-1-amine	N-ethyl- N-methyl	prop	an~~e~~	1-amine
 N,N-dimethylbenzenamine	N,N-dimethyl	benzene		amine
 $\overset{6}{CH_3}-\overset{5}{CH_2}-\overset{4}{\underset{OH}{CH}}-\overset{\overset{CH_2OH}{CH_2}}{\overset{3}{CH}}-\overset{2}{CH_2}-\overset{1}{COOH}$ 4-hydroxy-3-(2-hydroxyethyl) hexanoic acid	4-hydroxy-3-(2-hydroxyethyl)	hexa	an~~e~~	oic acid

11.2 Structural representation of organic compounds

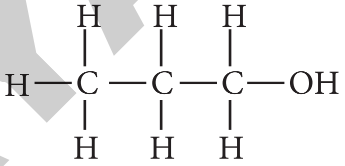
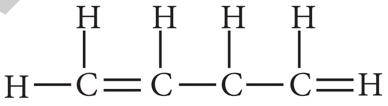
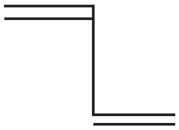
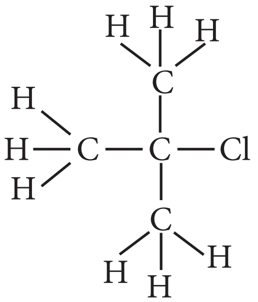
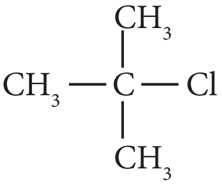
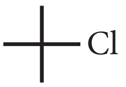
Molecular formula of a compound is the simplest, least informative representation, showing the ratio of atoms present. The structure of an organic compound can be represented using any one of the below mentioned methods.

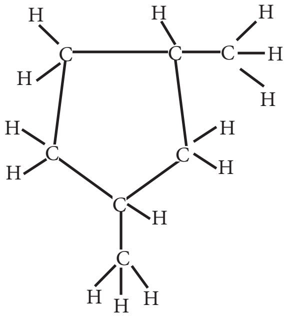
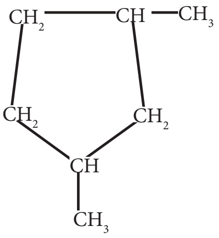
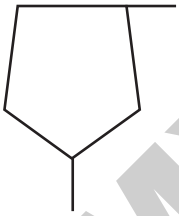
1. Lewis structure or dot structure,
2. Dash structure or line bond structure,
3. Condensed structure
4. Bond line structure

We know how to draw the Lewis structure for a molecule. The line bond structure is obtained by representing the two electron covalent bond by a dash or line (-) in a Lewis structure. A single line or dash represents single σ covalent bond, double line represents double bond (1σ bond, 1π bond) and a triple line represents triple bond (1σ bond, 2π bond). Lone pair of electrons on heteroatoms may or may not be shown. This represents the complete structural formula.

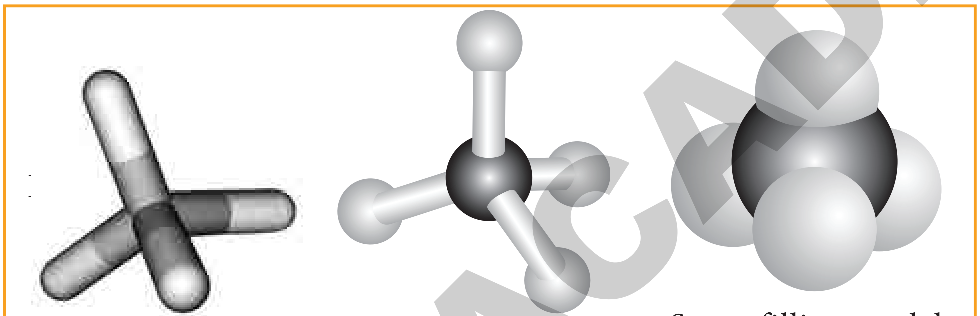
This structural formula can be further abbreviated by omitting some or all of the dashes representing covalent bonds and by indicating the number of identical groups attached to an atom by a subscript. The resulting expression of the compound is called a condensed structural formula.

For further simplification, organic chemists use another way of representing the structures in which only lines are used. In this type of representation of organic compounds, carbon and hydrogen atoms are not shown and the lines representing carbon-carbon bonds are shown in a zigzag fashion. The only atoms specifically written are oxygen, chlorine, nitrogen etc. These representations can be easily understood by the following illustration.

Molecular forumula	**Complete structural formula (dash line structure)**	**Condensed Structure**	**Bond line Structure**
n-propanol C_3H_8O		CH_3–CH_2–CH_2–OH	
1,3-butadiene C_4H_6		CH_2=CH–CH=CH_2	
t-butyl chloride C_4H_9Cl		 $CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-Cl$	

Molecular forumula	Complete structural formula (dash line structure)	Condensed Structure	Bond line Structure
1,3-dimethyl cyclopentane C_7H_{16}			

Molecular models



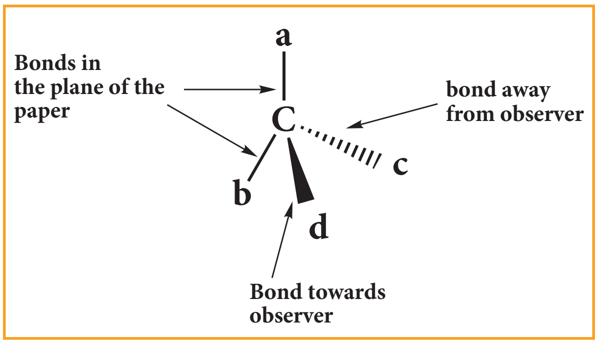
Frame work Model Ball and Stick Model Space filling model

Fig 11.3 Methane - Molecular Models

Molecular models are physical devices that are used for a better visualisation and perception of three dimensional shapes of organic molecules. These are made of wood, plastic or metal and are commercially available. (i) Frame work model (ii) Ball and stick model & (iii) space filling model. In the frame work model only the bonds connecting the atoms themselves are shown. This model emphasizes the pattern of bonds of a molecule while ignoring the size of the atom. In the ball and stick model, both the atoms and the bonds are shown. Ball represent atoms and the stick a bond. Compounds containing C=C can be best represented by using springs in place of sticks and this model is termed as ball and spring model. The space filling model emphasizes the relative size of each atom based on its vander-waals radius.

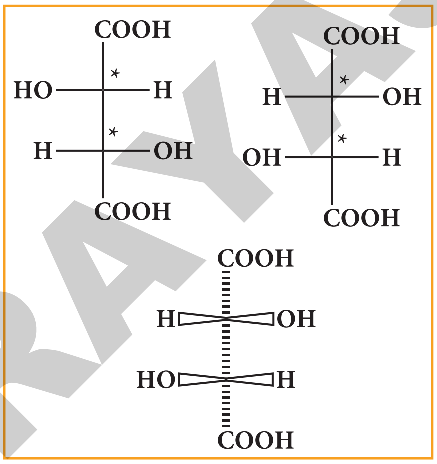
Three dimensional representation of organic molecules:

The simplest convention is solid and dashed wedge formula in which 3-D image of a molecule can be perceived from two dimensional picture. In this representation a tetrahedral molecule with four atoms or group a,b,c and d bonded to it can be represented by a wedge formula as follows. A solid wedge (▬) (or a heavy line) is used to indicate a bond projecting above the plane of the paper and the dashed wedge (··········) (or a dashed line) is used to depict the bond below the plane. The bonds lying in the plane of the paper are shown by normal lines.



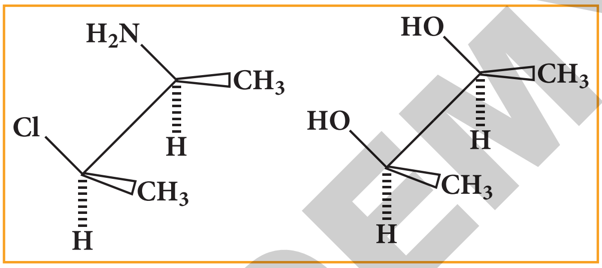
Fisher projection formula:

This is a method of representing three dimensional structures in two dimension. In this method, the chiral atom(s) lies in the plane of paper. The horizontal substituents are pointing towards the observer and the vertical substituents are away from the observer. Fisher projection formula for tartaric acid is given below.



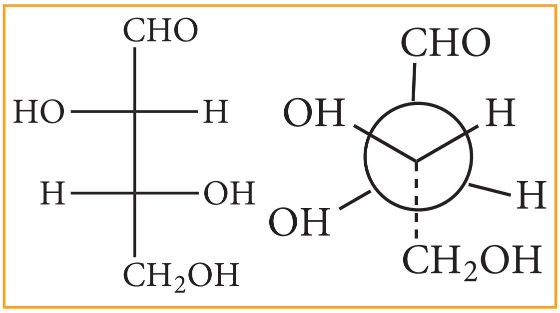
Sawhorse projection formula:

Here the bond between two carbon atoms is drawn diagonally and slightly elongated. The lower left hand carbon is considered lying towards the front and the upper right hand carbon towards the back. The Fischer projection inadequately portrays the spatial relationship between ligands attached to adjacent atoms. The sawhorse projection attempts to clarify the relative location of the groups.



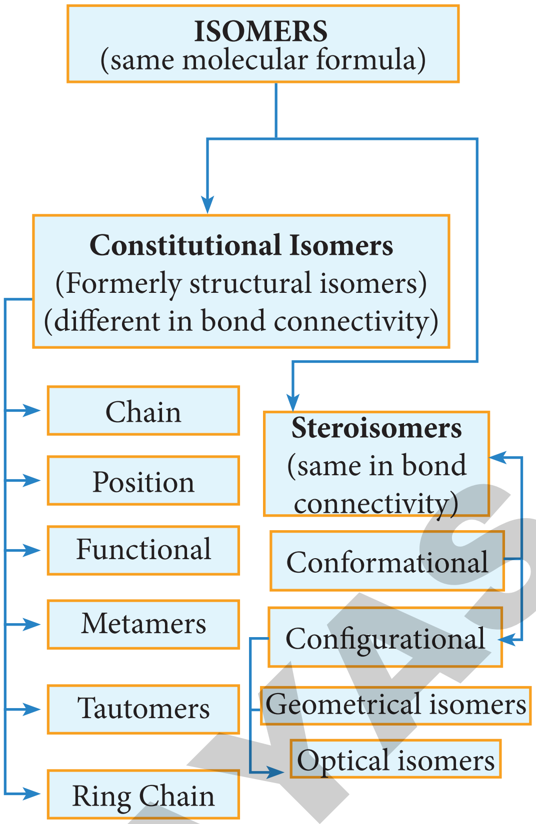
Newman projection formula:

In this method the molecules are viewed from the front along the carbon-carbon bond axis. The two carbon atom forming the σ bond is represented by two circles. One behind the other so that only the front carbon is seen. The front carbon atom is shown by a point where as the carbon lying further from the eye is represented by the origin of the circle. Therefore, the C-H bonds of the front carbon are depicted from the circle while C-H bonds of the back carbon are drawn from the circumference of the circle with an angle of 120^0 to each other.



11.5. Isomerism in organic compounds:

The term 'isomerism' was given by Berzelius, and its represents of existence of two or more compounds with the same molecular formula but different structure and properties (physical, chemical, or both). Compounds exhibiting this isomerism are called isomers. The difference in properties of two isomers is due to difference in (bond connectivity or spatial arrangement) the arrangement of atoms within their molecules. Isomerism is broadly divided into two types. i. Constitutional isomerism, ii. stereoisomerism.

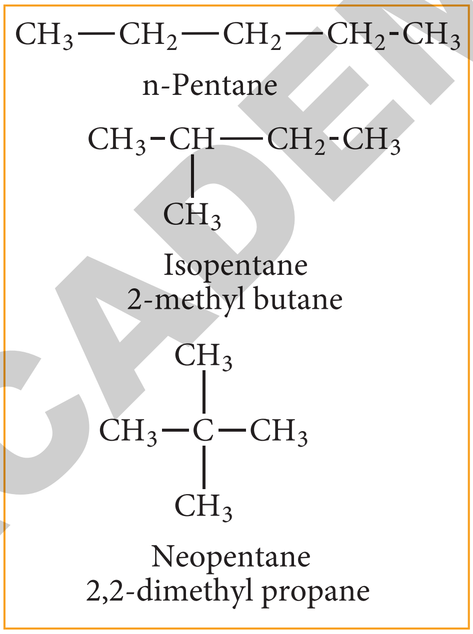


11.5.1 Constitutional isomers (Formerly structural isomers):

This type of isomers have same molecular formula but differ in their bonding sequence. Structural or constitutional isomerism is further classified into following types.

(a) Chain or nuclear or skeletal isomerism:

These isomers differ in the way in which the carbon atoms are bonded to each other in a carbon chain or in other words isomers have similar molecular formula but differ in the nature of the carbon skeleton (ie. Straight or branched)



$CH_3-CH_2-CH_2-CH_2-CH_3$

n-Pentane

$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_3$

Isopentane
2-methyl butane

$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3$

Neopentane
2,2-dimethyl propane

(b) Position isomerism:

If different compounds belonging to same homologous series with the same molecular formula and carbon skeleton, but differ in the position of substituent or functional group or an unsaturated linkage are said to exhibit position isomerism.

Example:

(i) Molecular formula C_5H_{10}

$CH_3-CH_2-CH_2-CH=CH_2$

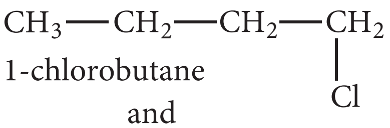
Pent-1-ene

and

$CH_3-CH_2-CH=CH-CH_3$

Pent-2-ene

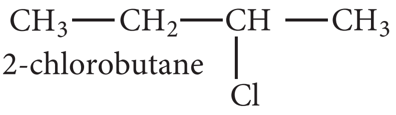
(ii) Mol. formula C_4H_9Cl



$CH_3-CH_2-CH_2-\underset{\underset{Cl}{|}}{CH_2}$

1-chlorobutane

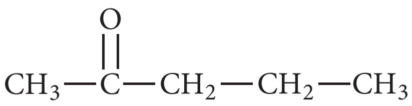
and



$CH_3-CH_2-\underset{\underset{Cl}{|}}{CH}-CH_3$

2-chlorobutane

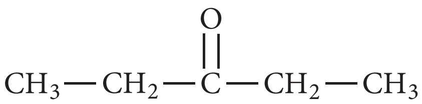
(iii) Mol. formula $C_5H_{10}O$



$CH_3-\overset{\overset{O}{||}}{C}-CH_2-CH_2-CH_3$

Pent-2-one

and



$CH_3-CH_2-\overset{\overset{O}{||}}{C}-CH_2-CH_3$

Pent-3-one

(c) Functional isomerism:

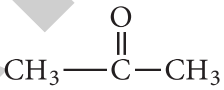
Different compounds having same molecular formula but different functional groups are said to exhibit functional isomerism.

Example:

(i) C_3H_6O $CH_3-CH_2 \cdot CHO$

Propanal

(aldehyde group)



$CH_3-\overset{\overset{O}{||}}{C}-CH_3$

Propanone

(keto group)

(ii) $C_3H_6O_2$ CH_3-CH_2-COOH

Propanoic acid

acid group

$CH_3-COOCH_3$

Methyl acetate

(ester group)

(d) Metamerism:

This type of isomerism is a special kind of structural isomerism arises due to the unequal distribution of carbon atoms on either side of the functional group or different alkyl groups attached to the either side of the same functional group and having same molecular formula. This isomerism is shown by compounds having functional group such as ethers, ketones, esters and secondary amines between two alkyl groups.

(i) $C_4H_{10}O$ $CH_3-O-C_3H_7$

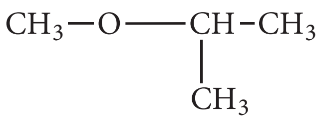
Methyl propyl ether

1-methoxypropane

$C_2H_5-O-C_2H_5$

diethyl ether

ethoxyethane

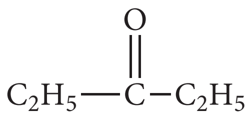


$CH_3-O-\underset{\underset{CH_3}{|}}{CH}-CH_3$

Methyl iso-propyl ether

2-methoxypropane

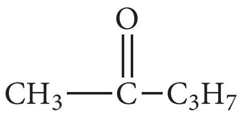
(ii) $C_5H_{10}O$



$C_2H_5-\overset{\overset{O}{||}}{C}-C_2H_5$

diethyl ketone

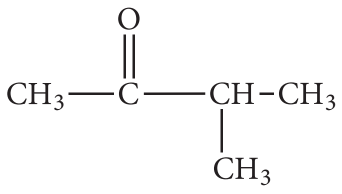
pentan-3-one



$CH_3-\overset{\overset{O}{||}}{C}-C_3H_7$

Methyl propyl ketone

pentan-2-one



$CH_3-\overset{\overset{O}{||}}{C}-\underset{\underset{CH_3}{|}}{CH}-CH_3$

Methyl isopropyl ketone

3-methylbutan-2-one

(e) Tautomerism: It is a special type of functional isomerism in which a single compound exists in two readily inter convertible structures that differ markedly in the relative position of atleast one atomic nucleus, generally hydrogen. The two different structures are known as tautomers. There are several types of tautomerism and the two important types are dyad and triad systems.

(i) Dyad system: In this system hydrogen atom oscillates between two directly linked polyvalent atoms. Eg:

$$H-C\equiv N \longleftrightarrow H-N\overset{\rightarrow}{\equiv}C$$

(hydrogencyanide) (hydrogen isocyanide)

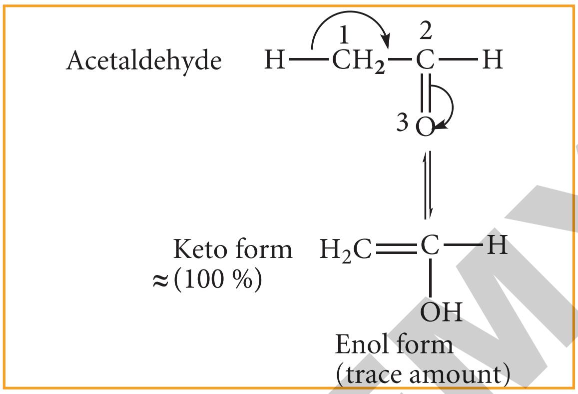
In this example hydrogen atom oscillates between carbon & nitrogen atom

Evaluate Yourself

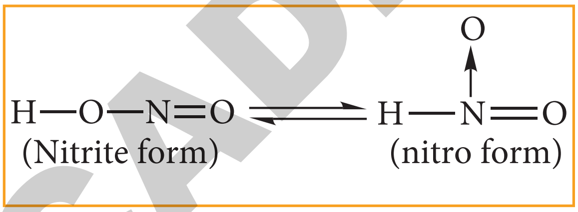
4) Write all the possible isomers of molecular formula $C_4H_{10}O$ and identify the isomerisms found in them.

(ii) Triad system: In this system hydrogen atom oscillates between three polyvalent atoms. It involves 1,3 migration of hydrogen atom from one polyvalent atom to other within the molecule. The most important type of triad system is keto–enol tautomerism and the two groups of tautomers are ketoform and enol-form. The polyvalent atoms involved are one oxygen and two carbon atoms. Enolisation is a process in which keto-form is converted to enol form. Both tautomeric forms are not equally stable. The less stable form is known as labile form

Example:



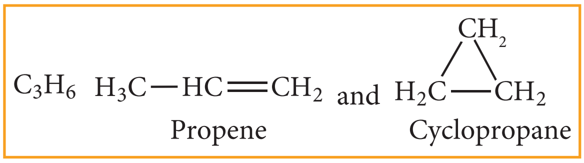
Nitro-aci tautomerism.

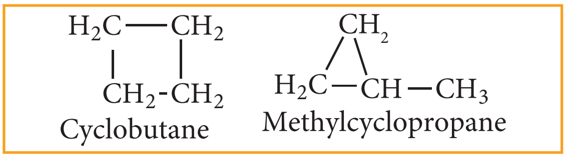


$$H-O-N=O \rightleftharpoons H-\overset{\overset{O}{\uparrow}}{N}=O$$

(Nitrite form) (nitro form)

(f) Ring chain isomerism: In this type of isomerism, compounds having same molecular formula but differ in terms of bonding of carbon atom to form open chain and cyclic structures for eg:





11.5.2 Stereoisomerism:

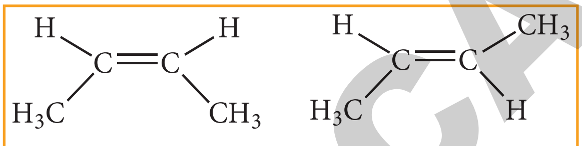
The isomers which have same bond connectivity but different arrangement of groups or atoms in space are known as stereoisomers. This branch of chemistry dealing with the study of three-dimensional nature (spactial arrangement) of molecules is known as stereo chemistry. The metabolic activities in living organisms, natural synthesis and drug synthesis involve various stereoisomers.

Steroisomerism:

11.5.3 Geometrical isomerism:

Geometrical isomers are the stereoisomers which have different arrangement of groups or atoms around a rigid frame work of double bonds. This type of isomerism occurs due to restricted rotation of double bonds, or about single bonds in cyclic compounds.

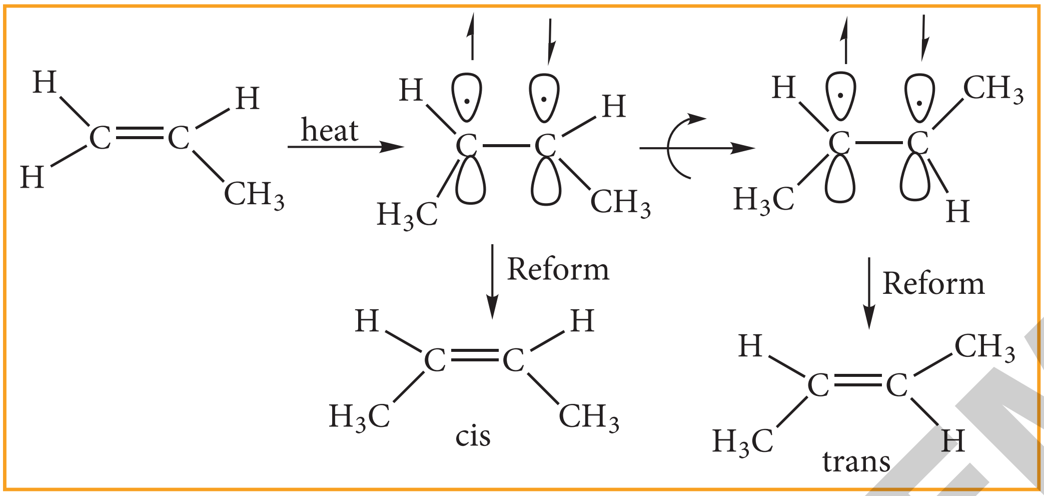
In alkenes, the carbon-carbon double bond is sp^2 hybridized. The carbon-carbon double bond consists of a σ bond and a π bond. The σ bond is formed by the head on overlap of sp^2 hybrid orbitals. The π bond is formed by the side wise overlap of 'p' orbitals. The presence of the π bond lock the molecule in one position. Hence, rotation around C=C bond is not possible. This restriction of rotation about C-C double bond is responsible for geometrical isomerism in alkenes.



cis - 2-butene *Trans* 2-butene

These two compounds are termed as geometrical isomers and are distinguished from each other by the terms cis and trans. The cis isomer is one in which two similar groups are on the same side of the double bond. The trans isomers is that in which the two similar groups are on the opposite side of the double bond, hence this type of isomerism is often called cis-trans isomerism.

The cis-isomer can be converted to trans isomer or vice versa is only if either isomer is heated to a high temperature or absorbs light. The heat supplies the energy (about 62kcal/ mole) to break the π bond so that rotation about σ bond becomes possible. Upon cooling, the reformation of the π bond can take place in two ways giving a mixture both cis and trans forms of trans-2-butene and cis-2-butane.

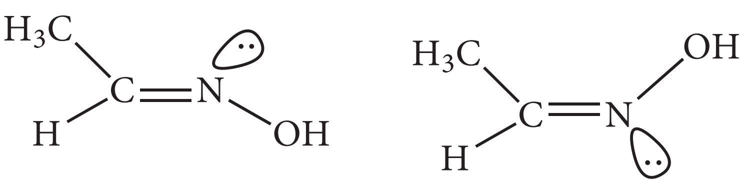


Generally the trans isomer is more stable than the corresponding *cis* isomers. This is because in the cis isomer, the bulky groups are on the same side of the double bond. The steric repulsion of the groups makes the cis isomers less stable than the trans isomers in which bulky groups are on the opposite side. These cis and trans isomers have different chemical property is. They can be separated by fractional distillation, gas chromatography etc., All alkenes with identical substrate do not show geometrical isomerism. Geometrical isomerism is possible only when each double bonded C atom is attached to two different atoms or groups eg. In propene no geometrical isomers are possible because one of the double bonded carbon has two identical H atoms.

Cis-trans isomerism is also seen around single bond. For eg: 1,3-butadiene has two double bonds in conjugation. CH_2=CH-CH=$CH_{2.}$ It can exist in infinite number of conformations, but the following two extreme conformations are important.

ii) Oximes and azo compounds:

Restricted rotation around C=N (oximes) gives rise to geometrical isomerism in oximes. Here 'syn' and 'anti' are used instead of cis and trans respectively. In the syn isomer the H atom of a doubly bonded carbon and –OH group of doubly bonded nitrogen lie on the same side of the double bond, while in the anti isomer, they lie on the opposite side of the double bond. For eg:



syn (cis) acetaldoxime anti (trans) acetadoxime

11.5.4 Optical Isomerism

Compounds having same physical and chemical property but differ only in the rotation of plane of the polarized light are known as optical isomers and the phenomenon is known as optical isomerism.

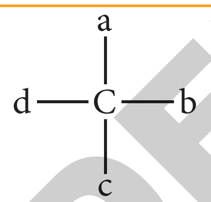
Some organic compounds such as glucose have the ability to rotate the plane of the plane polarized light and they are said to be optically active compounds and this property of a compound is called optical activity. The optical isomer, which rotates the plane of the plane polarised light to the right or in clockwise direction is said to be dextrorotary (dexter means right) denoted by the sign (+), whereas the compound which rotates to the left or anticlockwise is said to be leavo rotatory (leavues means left) denoted by sign(-). Dextrorotatory compounds are represented as 'd' or by sign (+) and lavorotatory compounds are represented as 'l' or by sign (-).

Enantiomerism and optical activity

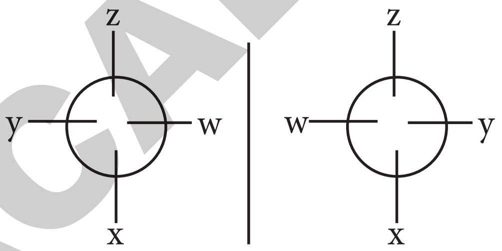
An optically active substance may exist in two or more isomeric forms which have same physical and chemical properties but differ in terms of direction of rotation of plane polarized light, such optical isomers which rotate the plane of polarized light with equal angle but in opposite direction are known as enantiomers and the phenomenon is known as enantiomerism. Isomers which are non-super impossible mirror images of each other are called enantiomers.

Conditions for enantiomerism or optical isomerism

A carbon atom whose tetra valency is satisfied by four different substituents (atoms or groups) is called asymmetric carbon or chiral carbon. It is indicated by an asterisk as C*. A molecule possessing chiral carbon atom and non-super impossible to its own mirror image is said to be a chiral molecule or asymmetric, and the property is called chirality or dissymmetry.



Assymetric Carbon atom



non superimpossible mirror images

11.6 Detection of elements in organic compounds

Introduction

The first step in the analysis of an organic compound is the detection of elements present in it. The principal elements are carbon, hydrogen and oxygen In addition to these they may contain nitrogen, sulphur and halogens. Phosphorous. Metals like Li, Mg, Zn are present in certain organometalic compounds.

Detection of carbon and hydrogen

If the compound under investigation is organic, there is no need to test for carbon. This test is performed only to establish whether a given compound is organic or not. With the exception of few compounds like CCl_4, CS_2 all organic compounds also contain hydrogen. The presence of both these elements is confirmed by the following common test.

Copper oxide test: The organic substance is mixed with about three times its weight of dry copper oxide by grinding. The mixture is then placed in a hard glass test tube fitted with a bent delivery tube. The other end of which is dipping into lime water in an another test tube. The mixture is heated strongly and the following reaction take place.

$$\boxed{\begin{array}{l} C + 2CuO \longrightarrow CO_2 + 2Cu \\ 2H + CuO \longrightarrow H_2O + Cu \end{array}}$$

Thus if carbon is present, it is oxidized to CO_2 which turns lime water milky. If hydrogen is also present, it will be oxidized to water which condenses in small droplets on the cooler wall of the test tube and inside the bulb. Water is collected on anhydrous $CuSO_4$ which turns anhydrous $CuSO_4$ blue. This confirms the presence of C and H in the compound.

Detection of nitrogen by lassaigne sodium fusion test: This is a good test for the detection of nitrogen in all classes of nitrogenous compound and it involves the preparation of sodium fusion extract

This method involves the conversion of covalently bonded N, S or halogen present in the organic compounds to corresponding water soluble ions in the form of sodium salts For this purpose a small piece of Na dried by pressing between the folds of a filter paper is taken in a fusion tube and it is gently heated. When it melts to a shining globule, put a pinch of the organic compound on it. Heat the tube till reaction ceases and becomes red hot. Plunge it in about 50 mL of distilled water taken in a china dish and break the bottom of the tube by striking against the dish. Boil the contents of the dish for about 10 mts and filter. This filtrate is known as lassaignes extract or sodium fusion extract and it used for detection of nitrogen, sulfur and halogens present in organic compounds.

ii) Test for Nitrogen: If nitrogen is present it gets converted to sodium cyanide which reacts with freshly prepared ferrous sulphate and ferric ion followed by conc. HCl and gives a Prussian blue color or green color or precipitate. It confirms the presence of nitrogen. HCl is added to dissolve the greenish precipitate of ferrous hydroxide produced by the excess of NaOH on $FeSO_4$ which would otherwise mark the Prussian blue precipitate. The following reaction takes part in the formation of Prussian blue.

$$\boxed{\begin{array}{l} Na + \underbrace{C \quad + \quad N}_{\text{from organic compounds}} \longrightarrow NaCN \\ FeSO_4 + 2NaOH \longrightarrow Fe(OH)_2 + Na_2SO_4 \\ \qquad \text{(from excess of sodium)} \end{array}}$$

$$\boxed{\begin{array}{l} 6NaCN + Fe(OH)_2 \longrightarrow \underset{\text{sod.ferrocyanide}}{Na_4\,[Fe(CN)_6]} \\ \qquad\qquad\qquad\qquad + 2NaOH \\ 3Na_4\,[Fe(CN)_6] + FeCl_3 \longrightarrow \underset{\substack{\text{ferric ferrocyanide} \\ \text{Prussian blue or green ppt}}}{Fe_4[Fe(CN)_6]_3} \\ \qquad\qquad\qquad\qquad + 12\,NaCl \end{array}}$$

Incase if both N & S are present, a blood red color is obtained due to the following reactions.

$$\mathrm{Na + C + N + S \xrightarrow{Heat} \underset{\text{sodium sulphocyanide}}{NaCNS}}$$

$$\mathrm{NaCNS + FeCl_3 \longrightarrow Fe(CNS)_3 + 3NaCl}$$

ferric sulphocyanide
(Blood red colour)

iii) Test for sulphur:

a) To a portion of the lassaigne's extract, add freshly prepared sodium nitro prusside solution. A deep violet or purple colouration is obtained. This test is also used to detect S^{2-} in inorganic salt analysis

$$\mathrm{Na_2S+Na_2\,[Fe\,(CN_5)\,NO]\rightarrow Na4\,[Fe\,(CN_5)\,NOS]}$$

sodium nitro prusside

b) Acidify another portion of lassaigne's extract with acetic acid and add lead acetate solution. A black precipitate is obtained.

$$\mathrm{(CH_3COO)_2Pb + Na_2S \longrightarrow \underset{\text{(black ppt)}}{PbS}\downarrow + 2CH_3COONa}$$

c) **Oxidation test:** The organic substances are fused with a mixture of KNO_3 and Na_2CO_3. The sulphur, if present is oxidized to sulphate.

$$\mathrm{Na_2CO_3 + S + 3O \longrightarrow Na_2SO_4 + CO_2}$$

The fused mass is extracted with water, acidified with HCl and then $BaCl_2$ solution is added to it. A white precipitate indicates the presence of sulphur.

$$\mathrm{BaCl_2 + Na_2SO_4 \longrightarrow BaSO_4 + 2NaCl}$$

iv) Test for halogens: To another portion of the lassaigne's filtrate add dil HNO_3 warm gently and add $AgNO_3$ solution.

a) Appearance of curdy white precipitate soluble in ammonia solution indicates the presence of chlorine.

b) Appearance of pale yellow precipitate sparingly soluble in ammonia solution indicates the presence of bromine.

c) Appearance of a yellow precipitate insoluble in ammonia solution indicates the presence of iodine.

$$\mathrm{Na + \underset{\text{from organic compound}}{X} \xrightarrow{heat} NaX}$$

(Where x= Cl, Br, I)

$$\mathrm{Nax + AgNO_3 \longrightarrow AgX + NaNO_3}$$

If N or S is present in the compound along with the halogen, we might obtain NaCN and Na_2S in the solution, which interfere with the detection of the halogen in the $AgNO_3$ test Therefore we boil the lassaignes extract with HNO_3 which decomposes NaCN and Na_2S as

$$\mathrm{NaCN + HNO_3 \xrightarrow{\Delta} NaNO_3 + HCN\uparrow}$$

$$\mathrm{Na_2S + 2HNO_3 \xrightarrow{\Delta} 2NaNO_3 + H_2S\uparrow}$$

further

$$\mathrm{NaCN + AgNO_3 \longrightarrow AgCN + NaNO_3}$$

white ppt confusing with AgCl

$$\mathrm{Na_2S + AgNO_3 \longrightarrow \underset{\text{black ppt}}{Ag_2S}\downarrow + NaNO_3}$$

V) Test for phosphorous: A solid compound is strongly heated with a mixture of Na_2CO_3 & KNO_3. phosphorous present in the compound is oxidized to sodium phosphate. The residue is extracted with water and boiled with Conc. HNO_3. A solution of ammonium molybdate is added to the above solution. A canary yellow coloration or precipitate shows the presence of phosphorous.

11.7 Estimation of elements

After detecting the various elements present in a given organic compound by qualitative analysis it is necessary to determine their composition by weight. The estimation of carbon, hydrogen, nitrogen, sulphur halogens are discussed here. No dependable method is however available for determination oxygen and hence its amount is always determined by difference.

Estimation of carbon and hydrogen:

Both carbon and hydrogen are estimated by the same method. A known weight of the organic substance is burnt in excess of oxygen and the carbon and hydrogen present in it are oxidized to carbon dioxide and water, respectively.

$$\boxed{C_x H_y + \underset{\text{(in excess)}}{O_2} \longrightarrow xCO_2 + \frac{y}{2}\ H_2O}$$

The weight of carbon dioxide and water thus formed are determined and the amount of carbon and hydrogen in the organic substance is calculated.

The apparatus employed for the purpose consists of three units (i) oxygen supply (2) combustion tube (3) absorption apparatus. (Refer Page 153 Fig. 11.2)

(1) Oxygen supply: To remove the moisture from oxygen it is allowed to bubble through sulphuric acid and then passed through a U-tube containing sodalime to remove CO_2. The oxygen gas free from moisture and carbondioxide enters the combustion tube.

(2) Combustion tube: A hard glass tube open at both ends is used for the combustion of the organic substance. It contains (i) an oxidized copper gauze to prevent the backward diffusion of the products of combustion (ii) a porcelain boat containing a known weight of the organic substance (iii) coarse copper oxide on either side and (iv) an oxidized copper gauze placed towards the end of the combustion tube. The combustion tube is heated by a gas burner.

(3) Absorption Apparatus The combustion products containing moisture and carbon-dioxide are then passed through the absorption apparatus which consists of (1) a weighed U-tube packed with pumice soaked in Conc. H_2SO_4 to absorb water (ii) a set of bulbs containing a strong solution of KOH to absorb CO_2 and finally (iii) a guard tube filled with anhydrous $CaCl_2$ to prevent the entry of moisture from atmosphere.

Procedure: The combustion tube is heated strongly to dry its content. It is then cooled slightly and connected to the absorption apparatus. The other end of the combustion tube is open for a while and the boat containing weighed organic substance is introduced. The tube is again heated strongly till the substance in the boat is burnt away. This takes about 2 hours. Finally, a strong current of oxygen is passed through the combustion tube to sweep away any traces of carbon dioxide or moisture which may be left in it. The U-tube and the potash bulbs are then detached and the increase in weight of each of them is determined.

Calculation:

Weight of the organic substance taken = w g

Increase in weight of H_2O = x g

Increase in weight of CO_2 = y g

18 g of H_2O contain 2g of hydrogen

$\therefore x$ g of H_2O contain $\left(\frac{2}{18} \times \frac{x}{w}\right)$ g of hydrogen

Percentage of hydrogen $= \left(\frac{2}{18} \times \frac{x}{w} \times 100\right)\%$

44g of CO_2 contains 12g of carbon

$\therefore y$ g of CO_2 contain $\left(\frac{12}{44} \times \frac{y}{w}\right)$ g of carbon

Percentage of Carbon $= \left(\frac{12}{44} \times \frac{y}{w} \times 100\right)\%$

Note:

1. If the organic substance under investigation also contain N, it will produce oxides of nitrogen on combustion. A spiral of copper is introduced at the combustion tube, to reduce the oxides of nitrogen to nitrogen which escapes unabsorbed.
2. If the compound contains halogen as well, a spiral of silver is also introduced in the combustion tube. It converts halogen into silver halide.
3. In case if the substance also contains sulphur, the copper oxide in the combustion tube is replaced by lead chromate. The SO_2 formed during combustion is thus converted to lead sulphate and prevented from passing into the absorption unit.

Worked out example: 1

0.26g of an organic compound gave 0.039 g of water and 0.245 g of carbon dioxide on combustion. Calculate the percentage of C & H

Weight of organic compound = 0.26g

Weight of water = 0.039g

Weight of CO_2 = 0.245g

Percentage of hydrogen

18 g of water contain 2 g of hydrogen

0.039 g of water contain $\frac{2}{18} \times \frac{0.039}{0.26}$

% of hydrogen $= \frac{0.039}{0.26} \times \frac{2}{18} \times 100 = 1.66\%$

Percentage of carbon

44 g of CO_2 contain 12 g of C

0.245 g of CO_2 contains $\frac{12}{44} \times \frac{0.245}{0.26}$ g of C

% of Carbon $= \frac{12}{44} \times \frac{0.245}{0.26} \times 100 = 25.69\ \%$

Evaluate Yourself

5) 0.2346g of an organic compound containing C, H & O, on combustion gives 0.2754g of H_2O and 0.4488g CO_2. Calculate the % composition of C, H & O in the organic compound [C=52.17, H = 13.04, O = 34.79]

Estimation of sulphur:

Carius method: A known mass of the organic substance is heated strongly with fuming HNO_3. C & H get oxidized to CO_2 & H_2O while sulphur is oxidized to sulphuric acid as per the following reaction.

$$\mathrm{C} \xrightarrow{\text{fum. }HNO_3} CO_2$$

$$2\mathrm{H} \xrightarrow{\text{fum. }HNO_3} H_2O$$

$$\mathrm{S} \longrightarrow SO_2 \xrightarrow{O + H_2O} H_2SO_4$$

The resulting solution is treated with excess of $BaCl_2$ solution H_2SO_4 present in the solution in quantitatively converted into $BaSO_4$, from the mass of $BaSO_4$, the mass of sulphur and hence the percentage of sulphur in the compound can be calculated.

Procedure:

A known mass of the organic compound is taken in clean carius tube and added a few mL of fuming HNO_3. The tube is the sealed. It is then placed in an iron tube and heated for about 5 hours. The tube is allowed to cool to temperature and a small hole is made to allow gases produced inside to escape. The carius tube is broken and the content collected in a beaker. Excess of $BaCl_2$ is added to the beaker H_2SO_4 acid formed as a result of the reaction is converted to $BaSO_4$. The precipitate of $BaSO_4$ is filtered, washed, dried and weighed. From the mass of $BaSO_4$, percentage of S is found.

Mass of the organic compound = w g

Mass of the $BaSO_4$ formed = x g

233g of $BaSO_4$ contains 32 g of Sulphur

$\therefore$ x g of $BaSO_4$ contain $\left(\frac{32}{233} \times \frac{x}{w}\right)$ g of S

Percentage of Sulphur = $\left(\frac{32}{233} \times \frac{x}{w} \times 100\right)\%$

Example -2

In an estimation of sulphur by carius method, 0.2175 g of the substance gave 0.5825 g of $BaSO_4$ calculate the percentage composition of S in the compound.

Weight of organic compound 0.2175 g

Weight of $BaSO_4$ 0.5825 g

233 g of $BaSO_4$ contains 32 g of S

0.5825 g of $BaSO_4$ contains $\frac{32}{233} \times \frac{0.5825}{0.2175}$

Percentage of S= $\frac{32}{233} \times \frac{0.5825}{0.2175} \times 100$

= 36.78 %

Evaluate Yourself

6) 0.16 g of an organic compound was heated in a carius tube and H_2SO_4 acid formed was precipitated with $BaCl_2$. The mass of $BaSO_4$ was 0.35g. Find the percentage of sulphur [30.04]

Estimation of halogens: carius method:

A known mass of the organic compound is heated with fuming HNO_3 and $AgNO_3$. C,H &S get oxidized to CO_2, H_2O & SO_2 and halogen combines with $AgNO_3$ to form a precipitate of silver halide.

$$\mathrm{X} \xrightarrow[AgNO_3]{\text{fum.}HNO_3} AgX\downarrow.$$

The ppt of AgX is filtered,

washed, dried and weighed. From the mass of AgX and the mass of the organic compound taken, percentage of halogens are calculated.

A known mass of the substance is taken along with fuming HNO_3 and $AgNO_3$ is taken in a clean carius tube. The open end of the Carius tube is sealed and placed in a iron tube for 5 hours in the range at 530-540 k Then the tube is allowed to cool and a small hole is made in the tube to allow gases produced to escape. The tube is broken and the ppt is filtered, washed, dried and weighed. From the mass of AgX obtained, percentage of halogen in the organic compound is calculated.

Weight of the organic compound: w g

Weight of AgCl precipitate = a g

143.5 g of AgCl contains 35.5 g of Cl

$\therefore$ a g of AgCl contains $\frac{35.5}{143.5} \times a$

W g Organic compound gives a g AgCl

Percentage of Cl in w g organic compound $= \left(\frac{35.5}{143.5} \times \frac{a}{w} \times 100\right)\%$

Let Weight of silver Bromide be 'b'g

188g of AgBr contains 80 g of Br

$\therefore$ b g of AgBr contains $\frac{80}{188} \times \frac{b}{w}$ of Br

W g Organic compound gives b g AgBr

Percentage of Br in w g organic compound $= \left(\frac{80}{188} \times \frac{b}{w} \times 100\right)\%$

Let Weight of silver Iodide be 'c'g

235g of AgI contains 127 g of I

$\therefore$ C g of AgI contains $\frac{127}{235} \times \frac{c}{w}$ of I

W g Organic compound gives c g AgI

Percentage of I in w g organic compound $= \left(\frac{127}{235} \times \frac{c}{w} \times 100\right)\%$

EXAMPLE : 0.284 g of an organic substance gave 0.287 g AgCl in a carius method for the estimation of halogen. Find the Percentage of Cl in the compound.

Weight of the organic substance = 0.284 g

Weight of AgCl is = 0.287 g

143.5 g of AgCl contains 35.5 g of chlorine

0.287 g of AgCl contains $\frac{35.5}{143.5} \times \frac{0.287}{0.284}$

% of chlorine is $\frac{35.5}{143.5} \times \frac{0.287}{0.284} \times 100 = 24.98$

Evaluate Yourself

7) 0.185 g of an organic compound when treated with Conc. HNO_3 and silver nitrate gave 0.320 g of silver bromide. Calculate the % of bromine in the compound. (Ag =108, Br = 80) Ans: 73.6

8) 0.40 g of an iodo-substituted organic compound gave 0.235 g of AgI by carius method. Calculate the percentage of iodine in the compound. (Ag = 108 I = 127) (Ans = 31.75)

Estimation of phosphorus:

Carius method: A known mass of the organic compound (w) containing phosphorous is heated with fuming HNO_3 in a sealed tube where C is converted into CO_2 and H to H_2O. phosphorous present in organic compound is oxidized to phosphoric acid which is precipitated, as ammonium phosphomolybdate by heating with Conc. HNO_3 and then adding ammonium molybdate.

$$H_3PO_4 + 12\,(NH_4)_2MoO_4 + 21\,HNO_3 \xrightarrow{heat} (NH_4)_3PO_4.12MoO_3 + 21NH_4NO_3 + 12\,HNO_3$$

The precipitate of ammonium phosphomolybdate thus formed is filtered washed, dried and weighed.

In an alternative method, the phosphoric acid is precipitated as magnesium-ammonium phosphate by adding magnesia mixture (a mixture containing $MgCl_2$, NH_4Cl and ammonia) This ppt is washed, dried and ignited to get magnesium pyrophosphate which is washed, dried a weighed. The following are the reaction that takes place.

By knowing the mass of the organic compound and the mass of ammonium phosphomolybdate or magnesium pyrophosphate formed, the percentage of P is calculated.

Mass of organic compound is wg

Weight of ammonium

phosphomolybdate = x g

Weight of magnesium pyrophosphate = y g

Mole mass of $(NH_4)_3PO_4.12MoO_3$is =1877g

[3 x(14 + 4) + 31 +4(16)] + 12 (96+3x16)

Molar mass of $Mg_3P_2O_7$ is 222 g

(2x24) + (31x2) + (7x16)

1877g of $(NH_4)_3PO_4.12MoO_3$contains 31g of P

Xg of$(NH_4)_3PO_4.12\ MoO_3$ in w g of organic compound contains $\frac{31}{1877}\times\frac{x}{w}$ of phosphorous

Percentage of Phosphorous=$\frac{31}{1877}\times\frac{x}{w}\times 100$

(or)

227 of $Mg_2P_2O_7$ contains 62 g of P

Y g of of $Mg_2P_2O_7$ in w g of Organic compound contains $\frac{62}{222}\times\frac{y}{w}$ of P.

Percentage Phosphorous = $\frac{62}{222}\times\frac{y}{w}\times 100$

Example 4: 0.24 g of organic compound containing phosphorous gave 0.66 g of $Mg_2P_2O_7$ by the usual analysis. Calculate the percentage of phosphorous in the compound

Weight of an organic compound = 0.24 g

Weight of $Mg_2P_2O_7$ = 0.66 g

222 g of $Mg_2P_2O_7$ contains 62 g of P

0.66 g contains $\frac{62}{222}\times\frac{0.66}{0.24}$

Percentage of P $\frac{62}{222}\times\frac{0.66}{0.24}\times 100$ =76.80 %

Evaluate Yourself

9) 0.33 g of an organic compound containing phosphorous gave 0.397 g of $Mg_2P_2O_7$ by the analysis. Calculate the percentage of P in the compound (Ans: 23.21) (MFW of $Mg_2P_2O_7$ is 222 P = 31)

Estimation of nitrogen: There are two methods for the estimation of nitrogen in an organic compound. They are 1. Dumas method 2. Kjeldahls method

1. Dumas method:

This method is based upon the fact that nitrogenous compound when heated with cupric oxide in an atmosphere of CO_2 yields free nitrogen. Thus

$$C_X H_Y N_Z + (2x + Y/2) CuO \longrightarrow x CO_2 + Y/2 H_2O + Z/2 N_2 + (2x + Y/2) Cu$$

Traces of oxide of nitrogen, which may be formed in some cases, are reduced to elemental nitrogen by passing over heated copper spiral.

The apparatus used in Dumas method consists of CO_2 generator, combustion tube, Schiffs nitrometer. (Refer Page 153 Fig. 11.4)

CO_2 generator:

CO_2 needed in this process is prepared by heating magnetite or sodium bicarbonate contained in a hard glass tube or by the action of dil. HCl on marble in a kipps apparatus. The gas is passed through the combustion tube after being dried by bubbling through Conc. H_2SO_4.

Combustion Tube: The combustion tube is heated in a furnace is charged with a) A roll of oxidized copper gauze to prevent the back diffusion of the products of combustion and to heat the organic substance mixed with CuO by radiation b) a weighed amount of the organic substance mixed with excess of CuO, C) a layer of course CuO packed in about 2/3 of the entire length of the tube and kept in position by loose asbestos plug on either side; this oxidizes the organic vapors passing through it, and d) a reduced copper spiral which reduces any oxides of nitrogen formed during combustion to nitrogen.

Schiff's nitro meter: The nitrogen gas obtained by the decomposition of the substance in the combustion tube is mixed with considerable excess of CO_2 It is estimated by passing nitrometer when CO_2 is absorbed by KOH and the nitrogen gets collected in the upper part of graduated tube.

Procedure: To start with the tap of nitro meter is left open. CO_2 is passed through the combustion tube to expel the air in it. When the gas bubbles rising through, the potash solution fails to reach the top of it and is completely absorbed it shows that only CO_2 is coming and that all air has been expelled from the combustion tube. The nitrometer is then filled with KOH solution by lowering the reservoir and the tap is closed. The combustion tube is now heated in the furnace and the temperature rises gradually. The nitrogen set free form the compound collects in the nitro meter. When the combustion is complete a strong current of CO_2 is sent through, the apparatus in order to sweep the last trace of nitrogen from it. The volume of the gas gets collected is noted after adjusting the reservoir so that the solution in it and the graduated tube is the same. The atmospheric pressure and the temperature are also recorded.

Calculations:

Weight of the substance taken = wg

Volume of nitrogen = V_1 L

Room Temperature = T_1 K

Atmospheric Pressure = P mm of Hg

Agueen tension at

room temperature = P^1 mm of Hg

Pressure of dry nitrogen = $(P-P^1) = P_1$ mm of Hg.

Let p_0 V_0 and T_0 be the pressure, Volume and temperature respectively of dry nutrogen at STP,

Then, $\frac{P_0V_0}{T_0} = \frac{P_1V_1}{T_1}$

$$\therefore V_0 = \frac{P_1V_1}{T_1} \times \frac{T_0}{P_0}$$

$$V_0 = \left(\frac{P_1V_1}{T_1} \times \frac{273K}{760}\right) \text{mmHg}$$

Calculation of percentage of nitrogen. 22.4 L of N_2 at STP weigh 28gof N_2

$\therefore$ V_0 L of N_2 at S.T.P weigh $\frac{28}{22.4} \times V_0$

Wg of Organic compound contain $\left(\frac{28}{22.4} \times \frac{V_0}{W}\right)$g of nitrogen

$\therefore$Percentage of nitrogen =

$$\left(\frac{28}{22.4} \times \frac{V_0}{W}\right) \times 100$$

Problem: 0.1688 g when analyzed by the Dumas method yield 31.7 mL of moist nitrogen measured at 14^0 C and 758 mm mercury pressure. Determine the % of N in the substance (Aqueous tension at 14^0 C =12 mm)

Weight of Organic compound = 0.168g
Volume of moist nitrogen (V_1) = 31.7mL
= 31.7×10^{-3} L
Temperature (T_1) = 14^0C
= 14 +273
= 287K
Pressure of Moist nitrogen (P) = 758 mm Hg
Aqueous tension at 14^0C = 14^0C
= 12 mm of Hg
$\therefore$Pressure of dry nitrogen = ($P-P^1$)
= 758- 12
= 746 mm of

Hg

$$\frac{P_1V_1}{T_1} = \frac{P_0V_0}{T_0}$$

$$\therefore V_0 = \frac{746 \times 31.7 \times 10^{-3}}{287} \times \frac{273}{760}$$

$$V_0 = 29.58 \times 10^{-3} \text{L}$$

Percentage of nitrogen= $\left(\frac{28}{22.4} \times \frac{V_0}{W}\right) \times 100$

$$= \frac{28}{22.4} \times \frac{29.58 \times 10^{-3}}{0.1688} \times 100$$

= 21.90%

DO YOU KNOW?

Dumas method is a high precision method and is generally preferred over Kjeldahl's method.

Kjeldahls method:

This method is carried much more easily than the Dumas method. It is used largely in the analysis of foods and fertilizers. Kjeldahls method is based on the fact that when an organic compound containing nitrogen is heated with Conc. H_2SO_4, the nitrogen in it is quantitatively converted to ammonium sulphate. The resultant liquid is then treated with excess of alkali and then liberated ammonia gas absorbed in excess of standard acid. The amount of ammonia (and hence nitrogen) is determined by finding the amount of acid neutralized by back titration with same standard alkali.

Procedure:

A weighed quantity of the substance (0.3 to 0.5 g) is placed in a special long – necked Kjeldahl flask made of pyrex glass. About 25 mL of Conc. H_2SO_4 together with a little K_2SO_4 and $CuSO_4$ (catalyst) are added to it the flask is loosely stoppered by a glass bulb and heated gently in an inclined position. The heating is continued till the brown color of the liquid first produced, disappears leaving the contents clear as before. At this point all the nitrogen in the substance is converted to $(NH_4)_2SO_4$. The Kjeldahl flask is then cooled and its contents are diluted with same distilled water and then carefully transferred into a 1 lit round bottom flask. An excess NaOH solution is poured down the side of the flask and it is fitted with a Kjeldahl trap and a water condenser. The lower end of the condenser dips in a measured volume of excess the $\frac{N}{20}$ H_2SO_4 solution. The liquid in the round bottom flask is then heated and the liberated ammonia is distilled into sulphuric acid. The Kjeldahl trap serves to retain any alkali splashed up on vigorous boiling. (Refer Page 153 Fig. 11.3)

When no more ammonia passes over (test the distillate with red litmus) the receiver is removed. The excess of acid is then determined by titration with alkali, using phenolphthalein as the indicator.

Calculation:

Weight of the substance = Wg.

Volume of H_2SO_4 required for the complete neutralisation of evolved NH_3 = V mL.
Strength of H_2SO_4 used to neutralise NH_3 = N

Let the Volume and the strength of NH_3 formed are V_1 and N_1 respectively

we know that $V_1N_1 = VN$

The amount of nitrogen present in the w g of

Organic Compound = $\frac{14 \times NV}{1 \times 1000 \times w}$

Percentage of Nitrogen = $\left(\frac{14 \times NV}{1000 \times w}\right) \times 100\%$

Example : 0.6 g of an organic compound was Kjeldalised and NH_3 evolved was absorbed into 50 mL of semi-normal solution of H_2SO_4. The residual acid solution was diluted with distilled water and the volume made up to 150 mL. 20 mL of this diluted solution required 35 mL of $\frac{N}{20}$ NaOH solution for complete neutralization. Calculate the % of N in the compound.

Weight of Organic compound = 0.6g
Volume of sulphuric acid taken= 50mL
Strength of sulphuric acid taken= 0.5 N
20 ml of diluted solution of unreacted sulphuric acid was neutralised by 35 mL of 0.05 N Sodium hydroxide

Strength of the diluted sulphuric acid = $\frac{35 \times 0.05}{20}$

= 0.0875 N

Volume of the sulphuric acid remaining after reaction with Organic compound = V_1 mL
Strength of H_2SO_4 = 0.5N
Volume of the diluted H_2SO_4 = 150 mL
Strength of the diluted sulphuric acid = 0.0875 N

$V_1 = \frac{150 \times 0.087}{0.5}$ = 26.25 mL

Volume of H_2SO_4 consumed by ammonia = 50 - 26.25

= 23.75 mL

23.75 mL of 0.5 N $H_2SO_4 \equiv$ 23.75mL of 0.5N NH_3

The amount of Nitrogen present in the 0.6 = $\frac{14g}{1000\ mL \times 1\ N} \times 23.75 \times 0.5N$

= 0.166g

$$\text{Percentage of Nitrogen} = \frac{0.166}{0.6} \times 100$$

$$= 27.66\ \%$$

Evaluate Yourself

10) 0.3 g of an organic compound on kjeldahl's analysis gave enough ammonia to just neutralize 30 mL of 0.1N H_2SO_4. Calculate the percentage of nitrogen in the compound.

11.8 Purification of organic compounds

Need for purification:

In order to study the structure, physical properties, chemical properties and biological properties of organic compounds they must be in the pure state. There are several methods by which organic compounds can be purified. The methods employed for purification depend upon the nature of impurity and the nature of organic compound. The most widely used technique for the separation and purification of organic compounds are: (a) Crystallisation, (b) Sublimation (c) Distillation (d) Fractional distillation (e) Steam distillation (f) Azeotropic distillation (g) Differential extraction and (h) Chromatography.

Solids are purified by
- Sublimation
- Crystallisation
- Fractional Crystallisation

Liquids are purified by
- distillation
- Fractional distillation
- Steam distillation
- Distillation under reduced pressure
- Azeotropic distillation
- Differential extraction
- Chromatography

11.8.1 Sublimation:

Few substances like benzoic acid, naphthalene and camphor when heated pass directly from solid to vapor without melting (ie liquid). On cooling the vapours will give back solids. Such phenomenon is called sublimation. It is a useful technique to separate volatile and non-volatile solid. It has limited application because only a few substance will sublime.

Substances to be purified is taken in a beaker. It is covered with a watch glass. The beaker is heated for a while and the resulting vapours condense on the bottom of the watch glass. Then the watch glass is removed and the crystals are collected. This method is applicable for organic substance which has high vapour pressure at temperature below their melting point. Substances like naphthalene, benzoic acid can be sublimed quickly. Substance which has very small vapour pressure will decompose upon heating are purified by sublimation under reduced pressure. This apparatus consists of large heating and large cooling surface with small distance in between because the amount of the substance in the vapour phase is much too small in case of a substance with low vapour pressure.

11.8.2 Crystallization:

It is the most widely used method for the purification of solid organic compound. This process is carried out in by the following step

(i) Selection of solvent: Most of the organic substances being covalent do not dissolve in polar solvents like water, hence selection of solvent (suitable) becomes necessary. Hence the powdered organic substance is taken in a test tube and the solvent is added little by little with constant stirring and heating, till the amount added is just sufficient to dissolve the solute(ie) organic compound. If the solid dissolves upon heating and throws out maximum crystals on cooling, then the solvent is suitable. This process is repeated with other solvents like benzene, ether, acetone and alcohol till the most suitably one is sorted out.

(ii) Preparation of solution: The organic substance is dissolved in a minimum quantity of suitable solvent. Small amount of animal charcoal can be added to decolorize any colored substance. The heating may be done over a wire gauze or water bath depending upon the nature of liquid (ie) whether the solvent is low boiling or high boiling.

(iii) Filtration of hot solution: The hot solution so obtained is filtered through a fluted filter paper placed in a funnel.

(iv) Crystallization: The hot filtrate is then allowed to cool. Most of the impurities are removed on the filter paper, the pure solid substance separate as crystal. When copious amount of crystal has been obtained, then the crystallization is complete. If the rate of crystallization is slow, it is induced either by scratching the walls of the beaker with a glass rod or by adding a few crystals of the pure compounds to the solution.

(iv) Isolation and drying of crystals: The crystals are separated from the mother liquor by filtration. Filtration is done under reduced pressure using a Bucher funnel. When the whole of the mother liquor has been drained into the filtration flask, the crystals are washed with small quantities of the pure cold solvent and then dried.

11.8.3 Distillation:

This method is to purify liquids from non-volatile impurities, and used for separating the constituents of a liquid mixture which differ in their boiling points. There are various methods of distillation depending upon the difference in the boiling points of the constituents. The methods are (i) simple distillation (ii) fractional distillation and (iii) steam distillation. The process of distillation involves the impure liquid when boiled gives out vapour and the vapour so formed is collected and condensed to give back the pure liquid in the receiver. This method is called simple distillation. Liquids with large difference in boiling point (about 40k) and do not decompose under ordinary pressure can be purified by simply distillation eg. The mixture of $C_6H_5NO_2$ (b.p 484k) & C_6H_6(354k) and mixture of diethyl ether (b.p 308k) and ethyl alcohol (b.p 351k)

Fractional distillation: This is one method to purify and separate liquids present in the mixture having their boiling point close to each other. In the fractional distillation, a fractionating column is fitted with distillation flask and a condenser. A thermometer is fitted in the fractionating column near the mouth of the condenser. This will enable to record the temperature of vapour passing over the condenser. The process of separation of the components in a liquid mixture at their respective boiling points in the form of vapours and the subsequent condensation of those vapours is called fractional distillation. The process of fractional distillation is repeated, if necessary. This method finds a remarkable application in distillation of petroleum, coal-tar and crude oil.

11.8.4 Steam distillation:

This method is applicable for solids and liquids. If the compound to be steam distilled the it should not decompose at the steam temperature, should have a fairly high vapour pressure at 373k, it should be insoluble in water and the impurities present should be non-volatile.

The impure liquid along with little water is taken in a round-bottom flask which is connected to a boiler on one side and water condenser on the other side, the flask is kept in a slanting position so that no droplets of the mixture will enter into the condenser on the brisk boiling and bubbling of steam. The mixture in the flask is heated and then a current of steam passed in to it. The vapours of the compound mix up with steam and escape into the condenser. The condensate obtained is a mixture of water and organic compound which can be separated. This method is used to recover essential oils from plants and flowers, also in the manufacture of aniline and turpentine oil. (Refer Page 153 Fig. 11.5)

11.8.5 Azeotropic Distillation

These are the mixture of liquids that cannot be separated by fractional distillation. The mixtures that can be purified only by azeotropic distillation are called as azeotropes. These azeotropes are constant boiling mixtures, which distil as a single component at a fixed temperature. For example ethanol and water in the ratio of 95.87:4.13.

In this method the presence of a third component like C_6H_6, CCl_4, ether, glycerol, glycol which act as a dehydrating agent depress the partial pressure of one component of azeotropic mixture and raises the boiling point of that component and thus other component will distil over.

Subtances like C_6H_6, CCl_4 have low boiling points and reduce the partial vapour pressure of alcohol more than that of water while subtances like glycerol & glycol etc. have high boiling point and reduce the partial vapour pressure of water more than that of alcohol.

11.8.6 Differential extraction:

The process of removing a substance from its aqueous solution by shaking with a suitable organic solvent is termed extraction. When an organic substance present as solution in water can be recovered from the solution by means of a separating funnel. The aqueous solution is taken in a separating funnel with little quantity of ether or chloroform ($CHCl_3$). The organic solvent immiscible with water will form a separate layer and the contents are shaken gently. The solute being more soluble in the organic solvent is transfered to it. The solvent layer is then separated by opening the tap of the separating funnel, and the substance is recovered.

11.8.7 Chromatography:

The most valuable method for the separation and purification of small quantity of mixtures. As name implies chroma-colour and graphed writing it was first applied to separation of different colored constituents of chlorophyll in 1906 by M.S Tswett, a Russian botanist. He achieved it by passing a petroleum ether solution of chlorophyll present in leaves through a column of $CaCO_3$ firmly packed into a narrow glass tube. Different components of the pigments got separated into land or zones of different colors and now this technique is equally well applied to separation of colorless substances.

The principle behind chromatography is selective distribution of the mixture of organic substances between two phases – a stationary phase and a moving phase. The stationary phase can be a solid or liquid, while the moving phase is a liquid or a gas. When the stationary phase is a solid, the moving phase is a liquid or a gas. If the stationary phase is solid, the basis is adsorption, and when it is a liquid, the basis is partition. So the Chromatography is defined as a technique for the separation of a mixture brought about by differential movement of the individual compound through porous medium under the influence of moving solvent. The various methods of chromatography are

1. Column chromatography (CC)
2. Thin layer chromatography (TLC)
3. Paper chromatography (PC)
4. Gas-liquid chromatography (GLC)
5. Ion–exchange chromatography

Adsorption chromatography: The principle involved is different compounds are adsorbed on an adsorbent to different degree. Silica gel and alumina are the commonly used adsorbent. The components of the mixture move by varying distances over the stationary phase. Column chromatography and thin layer chromatography are the techniques based on the principle of differential adsorption.

Column chromatography: This is the simplest chromatographic method carried out in long glass column having a stop cock near the lower end. This method involves separation of a mixture over a column of adsorbent (Stationery phase) packed in a column. In the column a plug of cotton or glass wool is placed at the lower end of the column to support the adsorbent powder. The tube is uniformLy packed with suitable absorbent constitute the stationary phase. (Activated aluminum oxides (alumina), Magnesium oxide, starch are also used as absorbents).

Fig 11.1
Column Chromatography

The mixture to be separated is placed on the top of the adsorbent column. Eluent which is a liquid or a mixture of liquids is allowed to flow down the column slowly. Different components depending upon the degree to which the components are adsorbed and complete separation takes place. The most readily adsorbed substances are retained near the top and others come down to various distances in the column.

Thin layer chromatography: This method is an another type of adsorption chromatography with this method it is possible to separate even minute quantities of mixtures. A sheet of a glass is coated with a thin layer of adsorbent (cellulose, silica gel or alumina). This sheet of glass is called chromoplate or thin layer chromatography plate. After drying the plate, a drop of the mixture is placed just above one edge and the plate is then placed in a closed jar containing eluent (solvent). The eluent is drawn up the adsorbent layer by capillary action. The components of the mixture move up along with the eluent to different distances depending upon their degree of adsorption of each component of the mixture. It is expressed in terms of its retention factor (ie) R_f value

$$R_f = \frac{\text{Distance moved by the substance from base line (x)}}{\text{Distance moved by the solvent from base line (y)}}$$

The spots of colored compounds are visible on TLC plate due to their original color. The colorless compounds are viewed under uv light or in another method using iodine crystals or by using appropriate reagent.

Partition chromatography: Paper chromatography (PC) is an example of partition chromatography. The same procedure is followed as in thin layer chromatography except that a strip of paper acts as an adsorbent. This method involves continues differential portioning of components of a mixture between stationary and mobile phase. In paper chromatography, a special quality paper known as chromatography paper is used. This paper act as a stationary phase.

A strip of chromatographic paper spotted at the base with the solution of the mixture is suspended in a suitable solvent which act as the mobile phase. The solvent rises up and flows over the spot. The paper selectively retains different components according to their different partition in the two phases where a chromatogram is developed. The spots of the separated colored compounds are visible at different heights from the position of initial spots on the chromatogram. The spots of the separated colorless compounds may be observed either under ultraviolent light or by the use of an appropriate spray reagent.

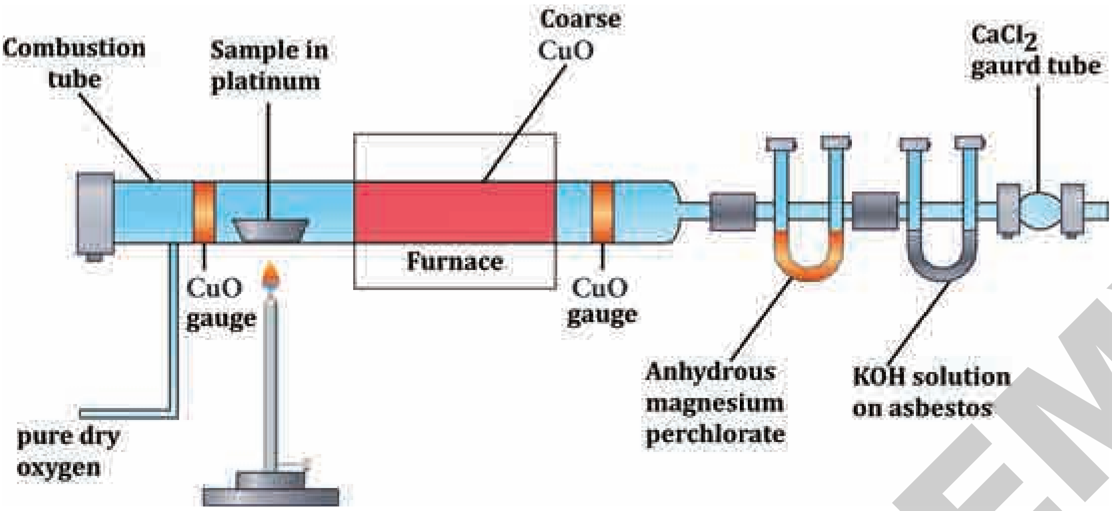


Fig 11.2 Estimation of Carbon and Hydrogen

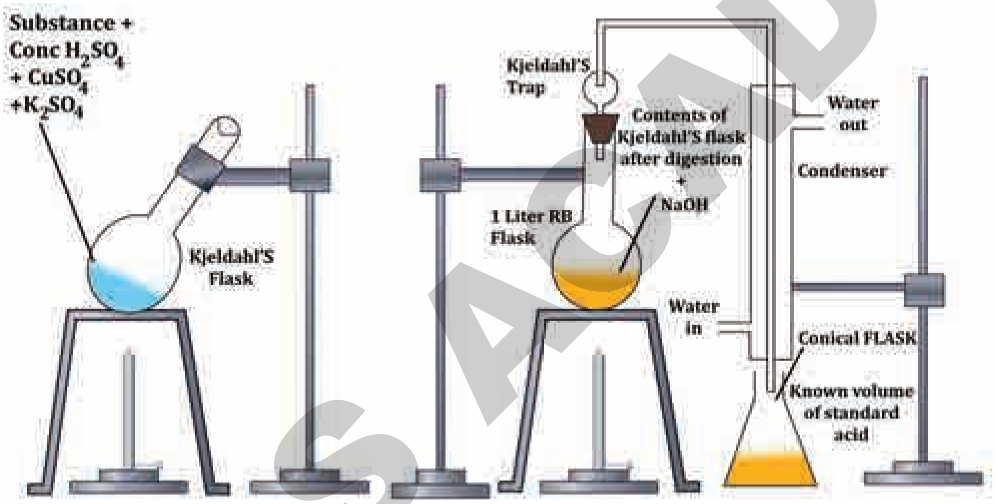


Fig 11.3 Kjeldahls method

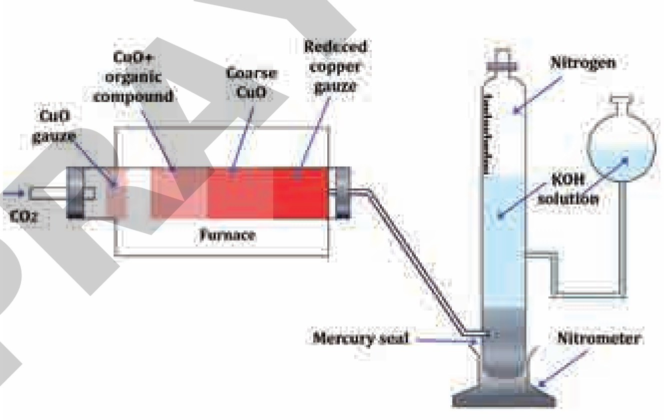


Fig 11.4 Dumas Method

Fig 11.5
Steam distillation

Evaluation

1. Select the molecule which has only one π bond.

   a) $CH_3-CH=CH-CH_3$

   b) $CH_3-CH=CH-CHO$

   c) $CH_3-CH=CH-COOH$

   d) All of these

2. In the hydrocarbon $\overset{7}{C}H_3-\overset{6}{C}H_2-\overset{5}{C}H=\overset{4}{C}H-\overset{3}{C}H_2-\overset{2}{C}\equiv\overset{1}{C}H$ the state of hybridisation of carbon 1,2,3,4 and 7 are in the following sequence.

   a) sp, sp, sp^3, sp^2, sp^3

   b) $sp^2, sp, sp^3, sp^2, sp^3$

   c) sp, sp, sp^2, sp, sp^3

   d) none of these

3. The general formula for alkadiene is

   a) C_nH_{2n}

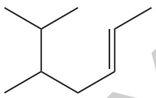
   b) C_nH_{2n-1}

   c) C_nH_{2n-2}

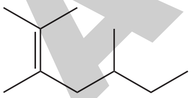
   d) C_nH_{n-2}

4. Structure of the compound whose IUPAC name is 5,6 - dimethylhept - 2 - ene is

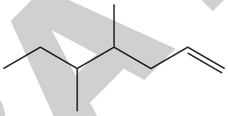
a)



b)

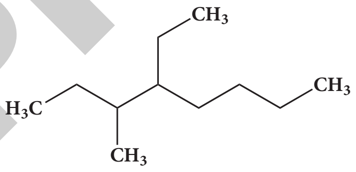


c)



d) None of these

5. The IUPAC name of the Compound is



   a) 2,3 - Diemethylheptane

   b) 3- Methyl -4- ethyloctane

   c) 5-ethyl -6-methyloctane

   d) 4-Ethyl -3 - methyloctane.

6. Which one of the following names does not fit a real name?

   a) 3 – Methyl –3–hexanone

   b) 4–Methyl –3– hexanone

   c) 3– Methyl –3– hexanol

   d) 2– Methyl cyclo hexanone.

7. The IUPAC name of the compound $CH_3-CH=CH-C\equiv CH$ is

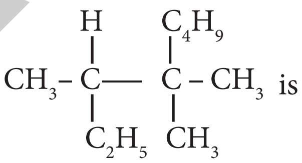
   a) Pent - 4 - yn-2-ene

   b) Pent -3-en-l-yne

   c) pent – 2– en – 4 – yne

   d) Pent – 1 – yn –3 –ene

8. IUPAC name of



$CH_3-\underset{C_2H_5}{\overset{H}{C}}-\underset{CH_3}{\overset{C_4H_9}{C}}-CH_3$ is

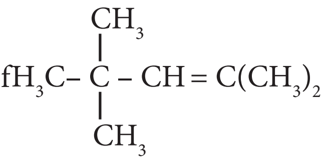
   a) 3,4,4 – Trimethylheptane

   b) 2 – Ethyl –3, 3– dimethyl heptane

   c) 3, 4,4 – Trimethyloctane

   d) 2 – Butyl -2 –methyl – 3 – ethyl-butane.

9. The IUPAC name of



$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-CH=C(CH_3)_2$ is

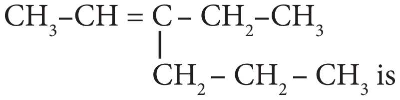
   a) 2,4,4 – Trimethylpent -2-ene

   b) 2,4,4 – Trimethylpent -3-ene

   c) 2,2,4 – Trimethylpent -3-ene

   d) 2,2,4 – Trimethylpent -2-ene

10. The IUPAC name of the compound



$CH_3-CH=\underset{CH_2-CH_2-CH_3}{C}-CH_2-CH_3$ is

   a) 3 – Ethyl -2– hexene

   b) 3 – Propyl -3– hexene

   c) 4 – Ethyl – 4 – hexene

   d) 3 – Propyl -2-hexene

11. The IUPAC name of the compound

$CH_3-\underset{\underset{OH}{|}}{CH}-COOH$ is

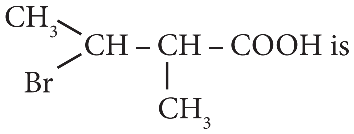
a) 2 – Hydroxypropionic acid

b) 2 – Hydroxy Propanoic acid

c) Propan – 2– ol –1 – oic acid

d) 1 – Carboxyethanol.

12. The IUPAC name of



$\overset{CH_3}{\underset{Br}{>}}CH-\underset{\underset{CH_3}{|}}{CH}-COOH$ is

a) 2 – Bromo -3 – methyl butanoic acid

b) 2 - methyl - 3- bromobutanoic acid

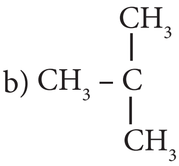
c) 3 - Bromo - 2 - methylbutanoic acid

d) 3 - Bromo - 2, 3 - dimethyl propanoic acid.

13. The structure of isobutyl group in an organic compound is

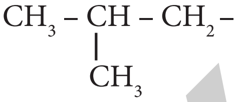
a) $CH_3-CH_2-CH_2-CH_2-$

b)



$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}$

c)



$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-$

d)

$CH_3-\underset{|}{CH}-CH_2-CH_3$

14. The number of stereoisomers of 1, 2 – dihydroxy cyclopentane

a) 1 b)2 c) 3 d) 4

15. Which of the following is optically active?

a) 3 – Chloropentane

b) 2 Chloro propane

c) Meso – tartaric acid

d) Glucose

16. The isomer of ethanol is

a) acetaldehyde b) dimethylether

c) acetone d) methyl carbinol

17. How many cyclic and acyclic isomers are possible for the molecular formula C_3H_6O?

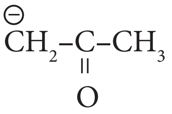
a) 4 b) 5 c) 9 d) 10

18. Which one of the following shows functional isomerism?

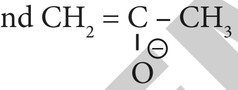
a) ethylene b) Propane

c) ethanol d) CH_2Cl_2

19.



$\overset{\ominus}{C}H_2-\underset{\underset{O}{\|}}{C}-CH_3$ and



$CH_2=\underset{\underset{O^{\ominus}}{|}}{C}-CH_3$ are

a) resonating structure b) tautomers

c) Optical isomers d) Conformers.

20. Nitrogen detection in an organic compound is carried out by Lassaigne's test. The blue colour formed is due to the formation of.

a) $Fe_3[Fe(CN)_6]_2$

b) $Fe_4[Fe(CN)_6]_3$

c) $Fe_4[Fe(CN)_6]_2$

d) $Fe_3\,[Fe(CN)_6]_3$

21. Lassaigne's test for the detection of nitrogen fails in

a) $H_2N-CO-NH.NH_2.HCl$

b) $NH_2-NH_2.\ HCl$

c) $C_6H_5-NH-NH_2.\ HCl$

d) $C_6H_5\ CONH_2$

22. Connect pair of compounds which give blue colouration / precipitate and white precipitate respectively, when their Lassaigne's test is separately done.

a) $NH_2\ NH_2\ HCl$ and $ClCH_2-CHO$

b) $NH_2\ CS\ NH_2$ and CH_3-CH_2Cl

c) $NH_2\ CH_2\ COOH$ and $NH_2\ CONH_2$

d) $C_6H_5NH_2$ and $ClCH_2-CHO$.

23. Sodium nitroprusside reacts with sulphide ion to give a purple colour due to the formation of

a) $[Fe(CN)_5\ NO]^{3-}$

b) $[Fe(NO)_5\ CN]^+$

c) $[Fe(CN)_5NOS]^{4-}$

d) $[Fe\ (CN)_5\ NOS]^{3-}$

24. An organic Compound weighing 0.15g gave on carius estimation, 0.12g of silver bromide. The percentage of bromine in the Compound will be close to

a) 46%	b) 34%
c) 3.4%	d) 4.6%

25. A sample of 0.5g of an organic compound was treated according to Kjeldahl's method. The ammonia evolved was absorbed in 50mL of 0.5M H_2SO_4. The remaining acid after neutralisation by ammonia consumed 80mL of 0.5 MNaOH, The percentage of nitrogen in the organic compound is.

a) 14%	b) 28%
c) 42%	d) 56%

26. In an organic compound, phosphorus is estimated as

a) $Mg_2P_2O_7$	b) $Mg_3(PO_4)_2$
c) H_3PO_4	d) P_2O_5

27. Ortho and para-nitro phenol can be separated by

a) azeotropic distillation

b) destructive distillation

c) steam distillation

d) cannot be separated

28. The purity of an organic compound is determined by

a) Chromatography

b) Crystallisation

c) melting or boiling point

d) both (a) and (c)

29. A liquid which decomposes at its boiling point can be purified by

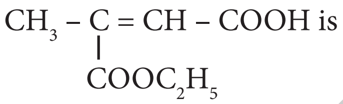
a) distillation at atmospheric pressure

b) distillation under reduced pressure

c) fractional distillation

d) steam distillation.

30. Assertion:



$CH_3 - \underset{\underset{COOC_2H_5}{|}}{C} = CH - COOH$ is

3– carbethoxy -2- butenoicacid.

Reason: The principal functional group gets lowest number followed by double bond (or) triple bond.

(a) both the assertion and reason are true and the reason is the correct explanation of assertion.

(b) both assertion and reason are true and the reason is not the correct explanation of assertion.

(c) assertion is true but reason is false

(d) both the assertion and reason are false.

31. Give the general characteristics of organic compounds?

32. Describe the classification of organic compounds based on their structure.

33. Write a note on homologous series.

34. What is meant by a functional group? Identify the functional group in the following compounds.

(a) acetaldehyde	(b) oxalic acid
(c) di methyl ether	(d) methylamine

35. Give the general formula for the following classes of organic compounds

(a) Aliphatic monohydric alcohol

(b) Aliphatic ketones.

(c) Aliphatic amines.

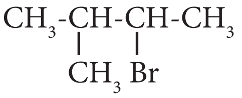
36. Write the molecular formula of the first six members of homologous series of nitro alkanes.

37. Write the molecular and possible structural formula of the first four members of homologous series of carboxylic acids.

38. Give the IUPAC names of the following compounds.

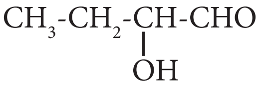
(i) $(CH_3)_2CH–CH_2–CH(CH_3)–CH(CH_3)_2$

(ii)


$CH_3\text{-}\underset{\underset{CH_3}{|}}{CH}\text{-}\underset{\underset{Br}{|}}{CH}\text{-}CH_3$

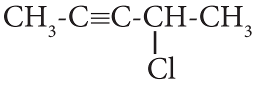
(iii) $CH_3\text{-}O\text{-}CH_3$

(iv)

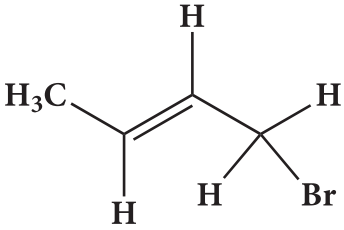

$CH_3\text{-}CH_2\text{-}\underset{\underset{OH}{|}}{CH}\text{-}CHO$

(v) $CH_2 = CH\text{-}CH{=}CH_2$

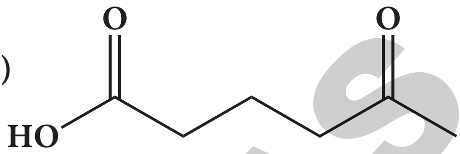
(vi)


$CH_3\text{-}C{\equiv}C\text{-}\underset{\underset{Cl}{|}}{CH}\text{-}CH_3$

(vii)



(viii)



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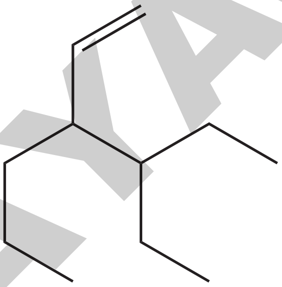
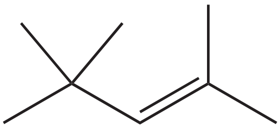


(x)



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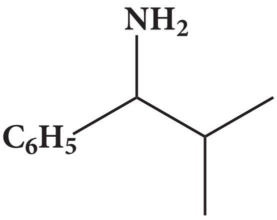

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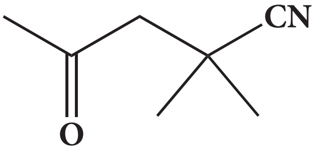

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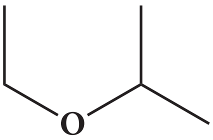

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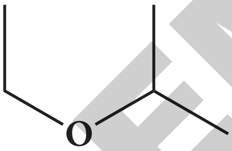

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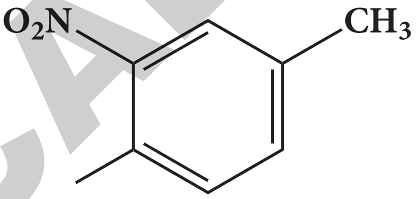

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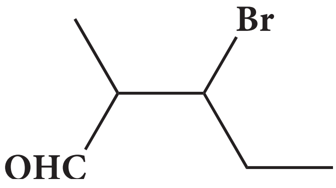

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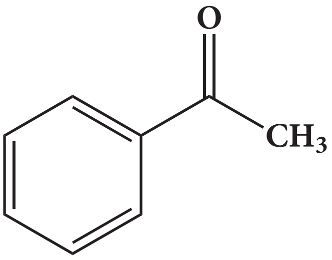

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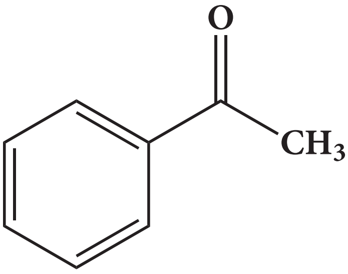


39) Give the structure for the following compound.

(i) 3- ethyl - 2 methyl -1-pentene

(ii) 1,3,5- Trimethyl cyclohex - 1 -ene

(iii) tertiary butyl iodide

(iv) 3 - Chlorobutanal

(v) 3 - Chlorobutanol

(vi) 2 - Chloro - 2- methyl propane

(vii) 2,2-dimethyl-1-chloropropane

(viii) 3 - methylbut -1- ene

(ix) Butan - 2, 2 - diol

(x) Octane - 1,3- diene

(xi) 1,5- Dimethylcyclohexane

(xii) 2-Chlorobut - 3 - ene

(xiii) 2 - methylbutan - 3 - ol

(xiv) acetaldehyde

40) Describe the reactions involved in the detection of nitrogen in an organic compound by Lassaigne method.

41) Give the principle involved in the estimation of halogen in an organic compound by carius method.

42) Give a brief description of the principles of

i) Fractional distillation

ii) Column Chromatography

43) Explain paper chromatography

44) Explain varions types of constitutional isomerism (structural isomerism) in organic compounds

45) Describe optical isomerism with suitable example.

46) Briefly explain geometrical isomerism in alkene by considering 2- butene as an example.

47) 0.30 g of a substance gives 0.88 g of carbon dioxide and 0.54 g of water calculate the percentage of carbon and hydrogen in it.

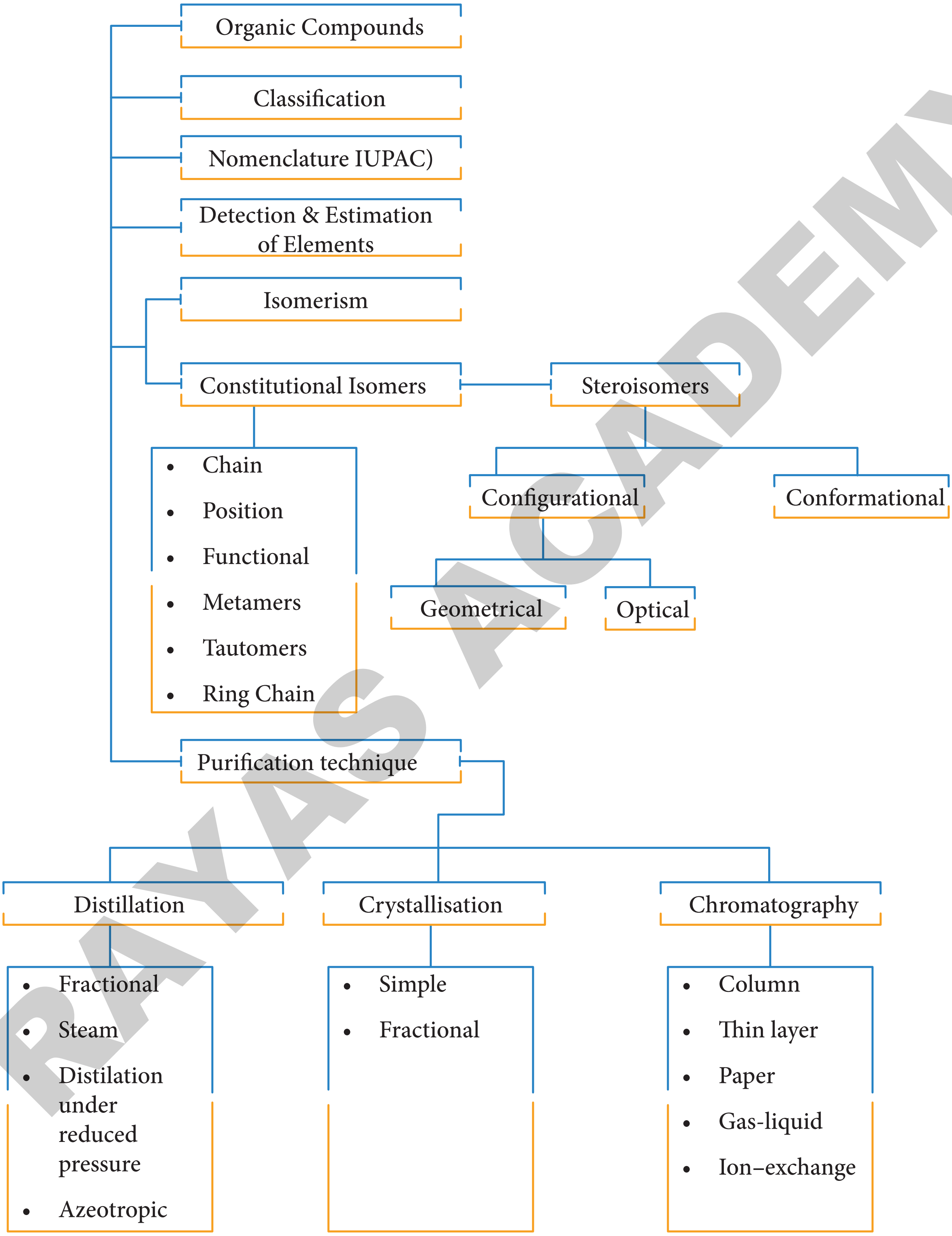
48) The ammonia evolved form 0.20 g of an organic compound by kjeldahl method neutralised 15ml of N/20 sulphare acid solution. Calculate the percentage of Nitrogen.

49) 0.32 g of an organic compound, after heating with fuming nitric acid and barium nitrate crystals is a sealed tube game 0.466 g of barium sulphate. Determine the percentage of sulphur in the compound.

50) 0.24g of an organic compound gave 0.287 g of silver chloride in the carius method. Calculate the percentage of chlorine in the compound.

51) In the estimation of nitrogen present in an organic compound by Dumas method 0.35 g yielded 20.7 mL of nitrogen at 150 C and 760 mm pressure. Calculate the percentage of nitrogen in the compound

CONCEPT MAP


Organic Compounds
Classification
Nomenclature IUPAC)
Detection & Estimation of Elements
Isomerism
Constitutional Isomers
• Chain
• Position
• Functional
• Metamers
• Tautomers
• Ring Chain
Steroisomers
Configurational
Conformational
Geometrical
Optical
Purification technique
Distillation
• Fractional
• Steam
• Distilation under reduced pressure
• Azeotropic
Crystallisation
• Simple
• Fractional
Chromatography
• Column
• Thin layer
• Paper
• Gas-liquid
• Ion–exchange

Unit 12

Basic concepts of organic reactions

Otto diels and Kurt Alder describe an important reaction mechanism for the reaction between a conjucated diene and a substituted alkene. For this work they were awarded nobel prize in chemistry in 1950 Diels - Alder reaction is a powerful tool in synthetic organic chemistry.

Learning Objectives

After learning this unit, students will be able to

- understand the concept of organic reaction mechanism
- describe homolytic and heterolytic fission of bonds
- identify free radicals, nucleophiles and electrophiles,
- classify organic reactions into substitution, elimination, addition, oxidation and reduction
- describe electron movement in organic reactions
- explain the electronic effects in co-valent bonds

12.1 Introduction

A chemical reaction can be treated as a process by which some existing bonds in the reacting molecules are broken and new bonds are formed. i.e., in a chemical reaction, a reactant is converted into a product. This conversion involves one or more steps. A In general an organic reaction can be represented as

$$\textit{Substrate} + \textit{Reagent} \longrightarrow [\textit{Intermediate state (and/or) Transition State}] \longrightarrow \textit{Product}$$

Here the substrate is an organic molecule which undergoes chemical change. The reagent which may be an organic, inorganic or any agent like heat, photons etc., that brings about the chemical change

Many chemical reactions are depicted in one or more simple steps. Each step passes through an energy barrier, leading to the formation of short lived intermediates or transition states. The series of simple steps which collectively represent the chemical change, from substrate to product is called as the mechanism of the reaction. The slowest step in the mechanism determines the overall rate of the reaction.

12.1.1 Fundamental concepts in organic reaction mechanism

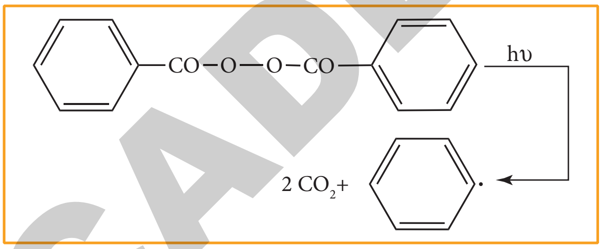
The mechanism is the theoretical pathway which describes the changes occurring in each step during the course of the chemical change. An organic reaction can be understood by following the direction of flow of electrons and the type of intermediate formed during the course of the reaction. The direction of flow of electron is represented by curved arrow. The movement of a pair of electron is represented by a double headed arrow which starts from the negative and ends with the atom to which the electrons needs to be transferred.

12.1.2 Fission of a covalent bond

All organic molecules contain covalent bonds which are formed by the mutual sharing of electrons between atoms. These covalent bonds break in two different ways, namely homolytic cleavage (symmetrical splitting) and heterolytic cleavage (unsymmetrical splitting). The cleavage of a bond in the substrate is influenced by the nature of the reagent (attacking agent).

Homolytic Cleavage

Homolytic cleavage is the process in which a covalent bond breaks symmetrically in such way that each of the bonded atoms retains one electron. It is denoted by a half headed arrow (fish hook arrow). This type of cleavage occurs under high temperature or in the presence of UV light in a compound containing non polar covalent bond formed between atoms of similar electronegativity. In such molecules, the cleavage of bonds results into free radicals. They are short lived and are highly reactive. The type of reagents that promote holmolytic cleavage in substrate are called as free radical initiators. For example Azobisisobutyronitile (AIBN) and peroxides such as benzoyl peroxide are used as free radical initiators in polymerisation reactions.



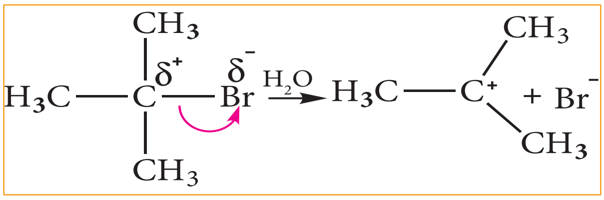
As a free radical with an unpaired electron is neutral and unstable, it has a tendency to gain an electron to attain stability. Organic reactions involve homolytic fission of C-C bonds to form alkyl free radicals. The stability of alkyl free radicals is in the following order

$$^{\bullet}C(CH_3)_3 > {}^{\bullet}CH(CH_3)_2 > {}^{\bullet}CH_2CH_3 > {}^{\bullet}CH_3$$

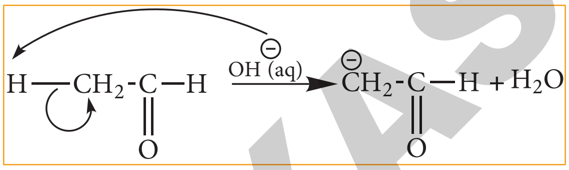
Heterolytic Cleavage

Heterolytic cleavage is the process in which a covalent bond breaks unsymmetrically such that one of the bonded atoms retains the bond pair of electrons. It results in the formation of a cation and an anion. Of the two bonded atoms, the most electronegative atom becomes the anion and the other atom becomes the cation. The cleavage is denoted by a curved arrow pointing towards the more electronegative atom.

For example, in tert-butyl bromide, the C-Br bond is polar as bromine is more electronegative than carbon. The bonding electrons of the C-Br bond are attracted more by bromine than carbon. Hence, the C-Br undergoes heterolytic cleavage to form a tert-butyl cation during hydrolysis.



Let us consider the cleavage in a carbon-hydrogen (C-H) bond of aldehydes or ketones We know that the carbon is more electronegative than hydrogen and hence the heterolytic cleavage of C-H bonds results in the formation of carbanion (carbon bears a negative charge). For example in aldol condensation the OH^- ion abstracts a α-hydrogen from the aldehyde, which leads to the formation of the below mentioned carbanion.



Hybridisation of carbon in carbocation:

In a carbocation, the carbon bearing positive charge is sp^2 hybridised and hence it has a planar structure. In the reaction involving such a carbocation, the attack of a negatively charged species (nucleophiles) take place on either side of the carbocation as shown below.

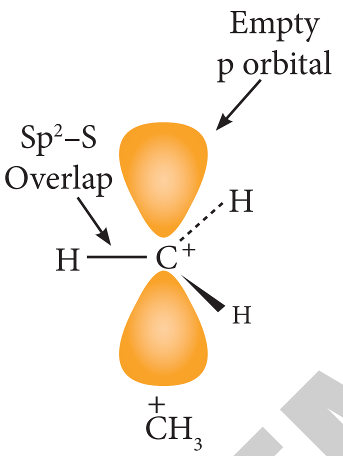
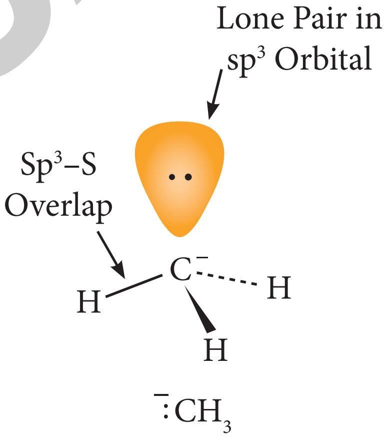
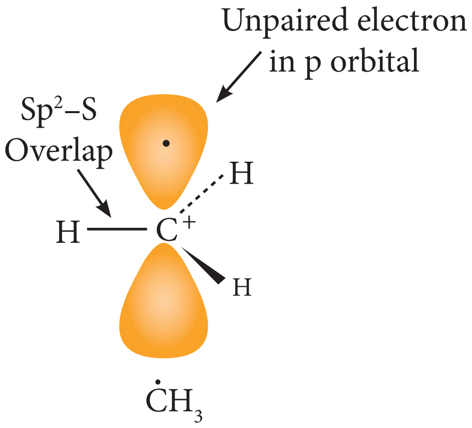


Fig 12.1 Shape of Carbocation, Carbanion and free radicals

The carbanions are generally pyramidal in shape and the lone pair occupies one of the sp^3 hybridised orbitals. An alkyl free radical may be either pyramidal or planar.





The relative stability of the alkyl carbocations and carbanions are given below.

Relative stability carbocations.

$^{+}C(CH_3)_3 > {}^{+}CH(CH_3)_2 > {}^{+}CH_2CH_3 > {}^{+}CH_3$

relative stability of carbanions

$^{-}C(CH_3)_3 < {}^{-}CH(CH_3)_2 < {}^{-}CH_2CH_3 < {}^{-}CH_3$

The energy required to bring about homolytic splitting is greater than that of heterolytic splitting.

12.1.3 Nucleophiles and elctrophiles

Nucleophiles are reagents that has high affinity for electro positive centers. They possess an atom has an unshared pair of electrons, and hence it is in search for an electro positive centre where it can have an opportunity to share its elections to form a covalent bond, and gets stabilised. They are usually negatively charged ions or electron rich neutral molecules (contains one or more lone pair of electrons). All Lewis bases act as nucleophiles.

Types	Examples	Electron rich site
Neutral molecules having unshared pair of electron	Ammonia (NH_3) and amines (RNH_2)	N:
	Water (H_2O), alcohols (ROH) and ethers (R-O-R)	:O:
	Hydrogen sulphide (H_2S) and thiols (RSH)	:S:
Negatively charged nucleophiles	Chlorides (Cl^-), bromides (Br^-) and iodides (I^-)	X^-
	Hydroxide (HO^-), alkoxide (RO^-) and Carboxlate ions ($RCOO^-$)	O^-
	Cyanide (CN^-)	N^-

Electrophiles are reagents that are attracted towards negative charge or electron rich center. They are either positively charged ions or electron deficient neutral molecules. All Lewis acids act as electrophiles. Neutral molecules like SnCl4 can also act as an electrophile, as it has vacant d-orbitals which can accommodate the electrons from others.

Types	Examples	Electron deficient entity
Neutral electrophiles	Carbon dioxide (CO_2), dichlorocarbene ($:CCl_2$)	C
	Aluminium chloride ($AlCl_3$), boron trifluoride (BF_3) and ferric chloride ($FeCl_3$)	Metal (M)
Positively charged electrophiles	Carbocations (R^+)	C^+
	Proton (H^+)	H^+
	Alkyl halides (RX)	X^+
	Oxonium ion (H_3O^+) and nitrosonium ion (NO^+)	O^+
	Nitronium ion ($^{+}NO_2$)	N^+

DO YOU KNOW?

Human body produces free radicals when it is exposed to x-rays, cigarette smoke, industrial chemicals and air pollutants. Free radicals can disrupt cell membranes, increase the risk of many forms of cancer, damage the interior lining of blood vessels and lead to a high risk of heart disease and stroke. Body uses vitamins and minerals to counter the effects of free radicals. Fruits contains antioxidants which decrease the effects of free radicals.

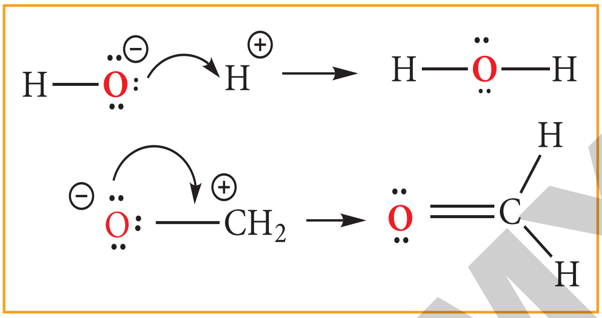
12.1.4 Electron movement in organic reactions

All organic reactions can be understood by following the electron movements, i.e. the electron redistribution during the reaction. The electron movement depends on the nature of the substrate, reagent and the prevailing conditions. The flow of electrons is represented by curved arrows which show how electrons move as shown in the figure. These electron movements result in breaking or formation of a bond (sigma or pi bond). The movement of single electron is indicated by a half-headed curved arrows.

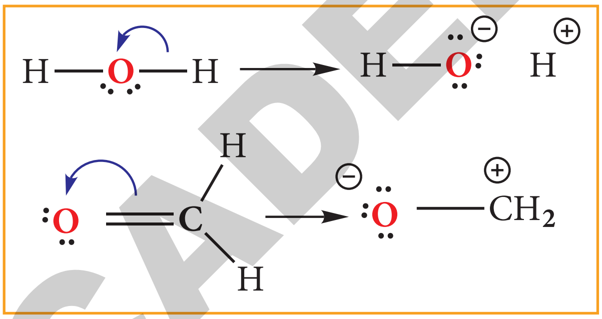
There are three types of electron movement viz.,

- lone pair becomes a bonding pair.
- bonding pair becomes a lone pair
- a bond breaks and becomes another bond.

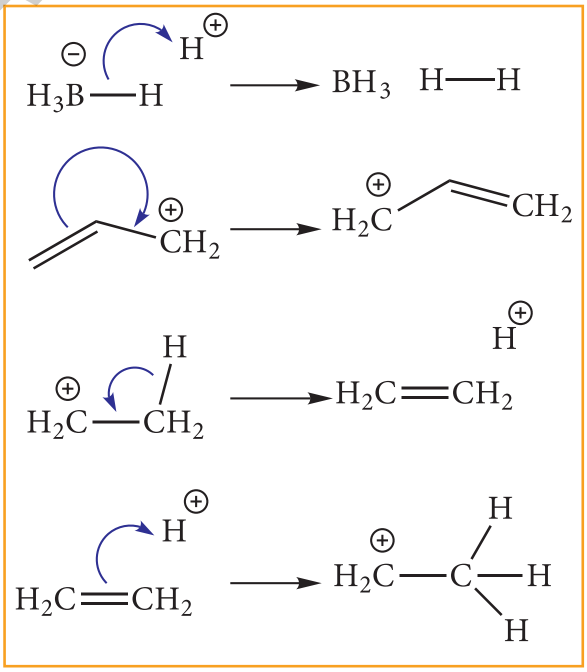
Type 1: A lone pair to a bonding pair



Type 2: A bonding pair to a lone pair



Type 3: A bonding pair to an another bonding pair



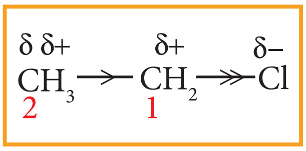
12.1.5 Electron displacement effects in co-valent bonds

Some of the properties of organic molecules such as stability, reactivity, basicity etc., are affected by the displacement of electrons that takes place in its covalent bonds. This movement can be influenced by either the atoms/groups present in close proximity to the bond or when a reagent approaches a molecule. The displacement effects can either be permanent or a temporary. In certain cases, the electron displacement due to an atom or a substituent group present in the molecule cause a permanent polarisation of the bond and it leads to fission of the bond under suitable conditions. The electron displacements are catagorised into inductive effect (I), resonance effect (R), electromeric effect (E) and hyper conjugation.

Inductive effect (I)

Inductive effect is defined as the change in the polarisation of a covalent bond due to the presence of adjacent bonds, atoms or groups in the molecule. This is a permanent phenomenon.

Let us explain the inductive effect by considering ethane and ethylchloride as examples. The C-C bond in ethane is non polar while the C-C bond in ethyl chloride is polar. We know that chlorine is more electronegative than carbon, and hence it attracts the shared pair of electron between C-Cl in ethyl chloride towards itself. This develops a slight negative charge on chlorine and a slight positive charge on carbon to which chlorine is attached. To compensate it, the C_1 draws the shared pair of electron between itself and C_2. This polarisation effect is called inductive effect. This effect is greatest for the adjacent bonds, but they also be felt farther away. However, the magnitude of the charge separation decreases rapidly, as we move away from C_1 and is observed maximum for 2 carbons and almost insignificant after 4 bonds from the active group.



$$\overset{\delta\,\delta+}{\underset{2}{CH_3}} \rightarrow \overset{\delta+}{\underset{1}{CH_2}} \twoheadrightarrow \overset{\delta-}{Cl}$$

It is important to note that the inductive effect does not transfer electrons from one atom to another but the displacement effect is permanent. The inductive effect represents the ability of a particular atom or a group to either withdraw or donate electron density to the attached carbon. Based on this ability the substituents are classified as +I groups and -I groups. Their ability to release or withdraw the electron through sigma covalent bond is called +I effect and -I effect respectively.

Highly electronegative atoms and atoms of groups which are carry a positive charge are electron withdrawing or -I group

Example: -F, -Cl, -COOH, -NO$_2$, NH$_2$

Higher the electronegativity of the substitutent, greater is the -I effect. The order of the –I effect of some groups are given below.

$NH_3^+ > NO_2 > CN > SO_3H > CHO > CO > COOH > COCl > CONH_2 > F > Cl > Br > I > OH > OR > NH_2 > C_6H_5 > H$

Highly electropositive atoms and atoms are groups which carry a negative charge are electron donating or +I groups.

Example. Alkali metals, alkyl groups such as methyl, ethyl, negatively charged groups such as CH_3O^-, $C_2H_5O^-$, COO^- etc

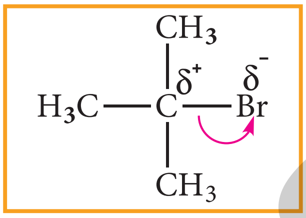
Lesser the electronegativity of the elements, greater is the +I effect. The relative order of +I effect of some alkyl groups is given below

$$\mathbf{-C(CH_3)_3 > -CH(CH_3)_2 > -CH_2CH_3 > -CH_3}$$

Let us understand the influence of inductive effect on some properties of organic compounds.

Reactivity:

When a highly electronegative atom such as halogen is attached to a carbon then it makes the C-X bond polar. In such cases the -I effect of halogen facilitates the attack of an incoming nucleophile at the polarised carbon, and hence increases the reactivity.

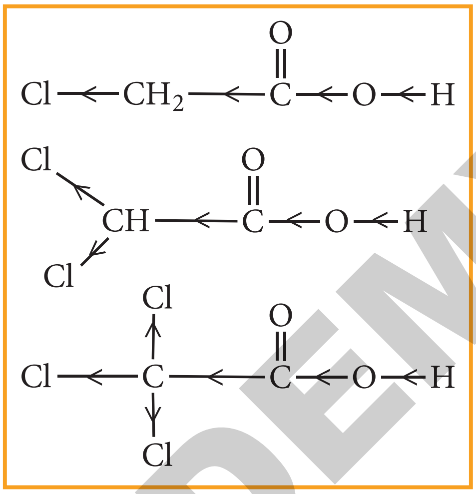


If a -I group is attached nearer to a carbonyl carbon, it decreases the availability of electron density on the carbonyl carbon, and hence increases the rate of the nucelophilic addition reaction.

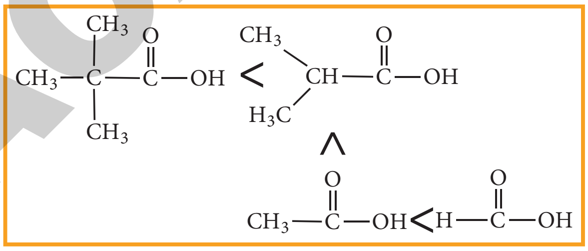
Acidity of carboxylic acids:

When a halogen atom is attached to the carbon which is nearer to the carboxylic acid group, its -I effect withdraws the bonded electrons towards itself and makes the ionisation of H^+ easy. The acidity of various chloro acetic acid is in the following order. The strength of the acid increases with increase in the -I effect of the group attached to the carboxyl group.

Trichloro acetic acid > Dichloro acetic acid > Chloro acetic acid > acetic acid



Similarly, the following order of acidity in the carboxylic acids is due to the +I effect of alkyl group.

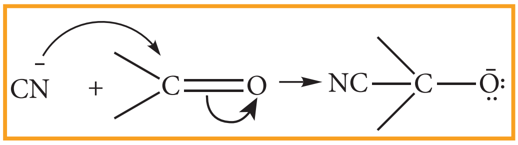


Electrometric effect (E)

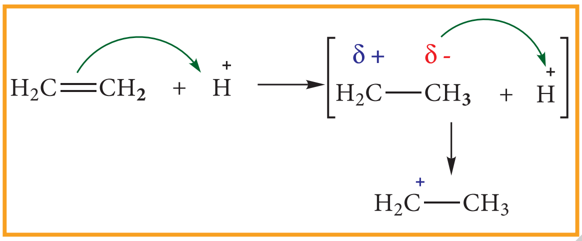
Electromeric is a temporary effect which operates in unsaturated compounds (containing >C=C<, >C=O, etc...) in the presence of an attacking reagent.

Let us consider two different compounds (i) compounds containing carbonyl group (>C=O) and (ii) unsaturated compounds such as alkenes (>C=C<).

When a nucleophile approaches the carbonyl compound, the π electrons between C and O is instantaneously shifted to the more electronegative oxygen. This makes the carbon electron deficient and thus facilitating the formation of a new bond between the incoming nucleophile and the carbonyl carbon atom.

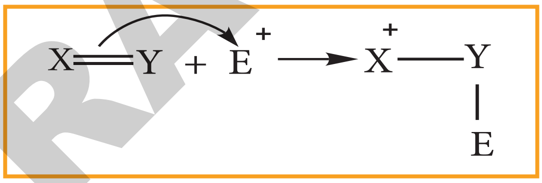


On the other hand when an electrophile such as H^+ approaches an alkene molecule, the π **electrons** are instantaneously shifted to the electrophile and a new bond is formed between carbon and hydrogen. This makes the other carbon electron deficient and hence it acquires a positive charge.



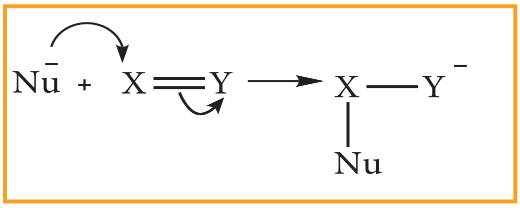
The electromeric effect, is denoted as E effect. Like the inductive effect, the electromeric effect is also classified as +E and -E based on the direction in which the pair of electron is transfered to form a new bond with the attacking agent.

When the π electron is transferred towards the attacking reagent, it is called + E (positive electromeric) effect.



The addition of H^+ to alkene as shown above is an example of +E effect.

When the π electron is transfered away from the attacking reagent, it is called, -E (negative electromeric) effect



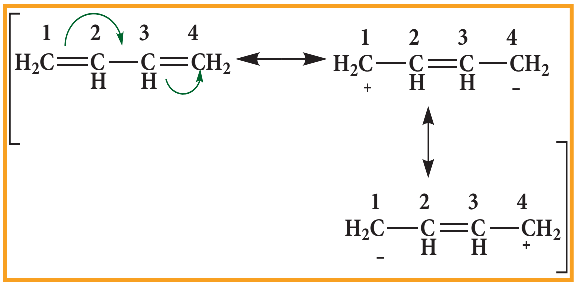
The attack of CN^- on a carbonyl carbon, as shown above, is an example of -E effect.

Resonance or Mesomeric effect

The resonance is a chemical phenomenon which is observed in certain organic compounds possessing double bonds at a suitable position. Certain organic compounds can be represented by more than one structure and they differ only in the position of bonding and lone pair of electrons. Such structures are called resonance structures (canonical structures) and this phenomenon is called resonance. This phenomenon is also called mesomerism or mesomeric effect.

For example, the structure of aromatic compounds such as benzene and conjugated systems like 1,3-butadiene cannot be represented by a single structure, and their observed properties can be explained on the basis of a resonance hybrid.

In 1,3 buta diene, it is expected that the bond between C^1-C^2 and C^3 –C^4 should be shorter than that of C^2-C^3, but the observed bond lengths are of same. This property cannot be explained by a simple structure in which two π bonds localised between C^1-C^2 and C^3 –C^4. Actually the π electrons are delocalised as shown below.



These resonating structures are called canonical forms and the actual structure lies between these three resonating structures, and is called a resonance hybrid. The resonance hybrid is represented as below.

$$H_2C\,\overset{\text{----}}{=}\,\underset{H}{C}\,\overset{\text{----}}{=}\,\underset{H}{C}\,\overset{\text{----}}{=}\,CH_2$$

Similar to the other electron displacement effect, mesomeric effect is also classified into positive mesomeric effect (+M or +R) and negative mesomeric effect (-M of -R) based on the nature of the functional group present adjacent to the multiple bond.

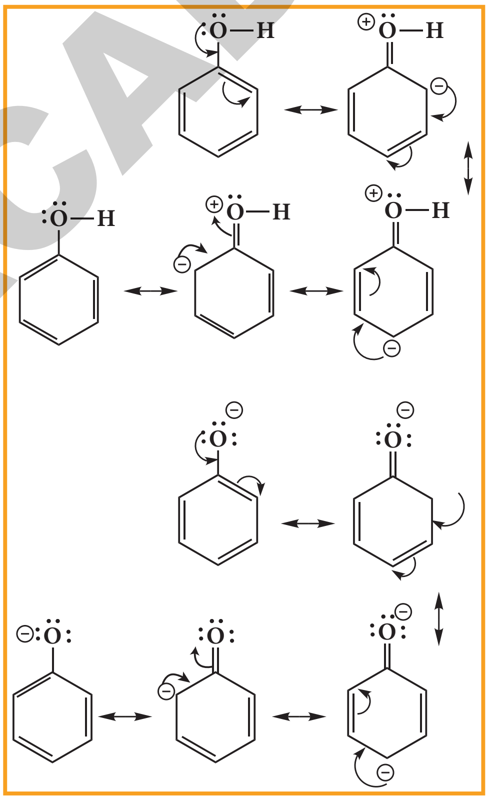
Positive Mesomeric Effect:

Positive resonance effect occurs, when the electrons move away from substituent attached to the conjugated system. It occurs, if the electron releasing substituents are attached to the conjugated system. In such cases, the attached group has a tendency to release electrons through resonance. These electron releasing groups are usually denoted as +R or +M groups. **Examples : -OH, -SH, -OR,-SR, -NH$_2$, -O- etc...**

Negative Mesomeric Effect

Negative resonance effect occurs, when the electrons move towards the substituent attached to the conjugated system. It occurs if the electron withdrawing substituents are attached to the conjugated system. In such cases, the attached group has a tendency to withdraw electrons through resonance. These electron withdrawing groups are usually denoted as -R or -M groups. **Examples : NO$_2$, >C=O, -COOH,-C≡N etc**

Resonance is useful in explaining certain properties such as acidity of phenol. The phenoxide ion is more stabilised than phenol by resonance effect(+M effect) and hence resonance favours ionisation of phenol to form H$^+$ and shows acidity.



The above structures shows that there is a charge separation in the resonance structure of phenol which needs energy, where as there is no such hybrid structures in the case of phenoxide ion. This increased stability accounts for the acidic character of phenol.

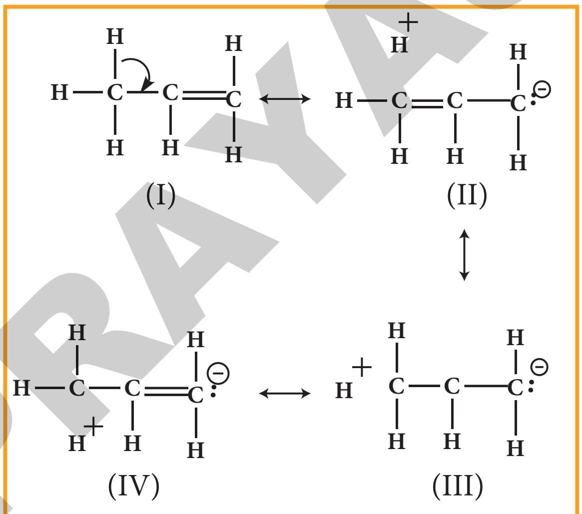
Hyper conjugation

The delocalisation of electrons of **σ** bond is called as hyper conjugation. It is a special stabilising effect that results due to the interaction of electrons of a **σ**-bond (usually **C-H** or **C-C**) with the adjacent, empty non-bonding p-orbital or an anti-bonding **σ*** or **π***-orbitals resulting in an extended molecular orbital. Unlike electromeric effect, hyper conjugation is a permanent effect.

It requires an α-CH group or a lone pair on atom like N, O adjacent to a **π** bond (sp^2 hybrid carbon). It occurs by the overlapping of the σ-bonding orbital or the orbital containing a lone pair with the adjacent π-orbital or p-orbital.

Example 1:

In propene, the *σ*-electrons of C-H bond of methyl group can be delocalised into the *π*-orbital of doubly bonded carbon as represented below.

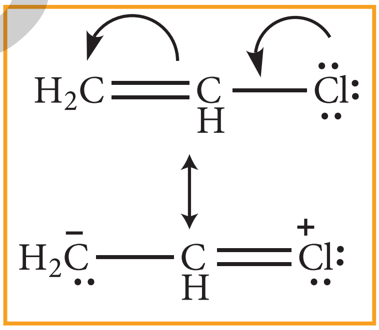


No bond resonance structures shown by propene are due to hyperconjugation

In the above structure the sigma bond is involved in resonance and breaks in order to supply electrons for delocalisation giving rise to 3 new canonical forms. In the contributing canonical structures: (II), (III) & (IV) of propene, there is no bond between an α-carbon and one of the hydrogen atoms. Hence the hyperconjugation is also known as "no bond resonance" or "Baker-Nathan effect". The structures (II), (III) & (IV) are polar in nature.

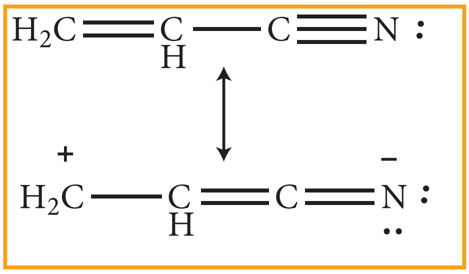
Example 2:

Hyper conjugation effect is also observed when atoms / groups having lone pair of electrons are attached by a single bond, and in conjugation with a **π bond**. The lone pair of electrons enters into resonance and displaces **π** electrons resulting in more than one structure



Example 3:

When electronegative atoms or group of atoms are in conjugation with a **π** -bond,they pull **π** - electrons from the multiple bond.



In case of carbocations, greater the number of alkyl groups attached to the carbon bearing positive charge, greater is number of the hyper conjugate structure. thus the stability of various carbocations decreases in the order

3^0 Carbocation > 2^0 Carbocation > 1^0 Carbocation

12.2 Different types of organic reactions

Organic compounds undergo many number of reactions, however in actual sense we can fit all those reactions into the below mentioned six categories.

- Substitution reactions
- Addition reactions
- Elimination reactions
- Oxidation and reduction reactions
- Rearrangement reactions
- Combination of the above

12.2.1 Substitution reaction (Displacement reaction)

In this reaction an atom or a group of atoms attached to a carbon atom is replaced by a new atom or a group of atoms. Based on the nature of the attacking reagent, this reactions can be classified as

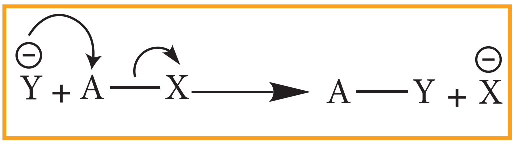
i) Nucleophilic substitution

ii) Electophilic substitution

iii) Free radical substitution

Nucelophilic substituion:

This reaction can be represented as



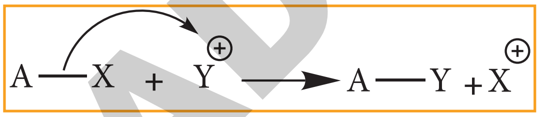
Here Y^- is the incoming nucleophile or and attacking species and x^- is the leaving group.

Example: Hydrolysis of alkyl halides

$$CH_3Br \xrightarrow{\text{aqueous } OH^{\ominus}} CH_3OH + Br^{\ominus}$$

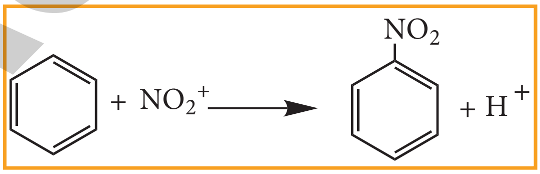
Aliphatic nucleophilic substitution reactions take places either by S_N1 or S_N2 mechanism. Detailed study of the mechanisms is given in unit 14.

Electrophilic Substitution



Here Y^+ is an electrophile

Example: Nitration of Benzene



Mechanism of aromatic electrophilic substitution reactions (EAS) is discussed in detail in unit 13.

Free radical substitution

$$A—X + \dot{Y} \longrightarrow A—Y + \dot{X}$$

$$CH_4 + \dot{Cl} \longrightarrow \dot{C}H_3 + HCl$$

Aliphatic electrophilic substitution

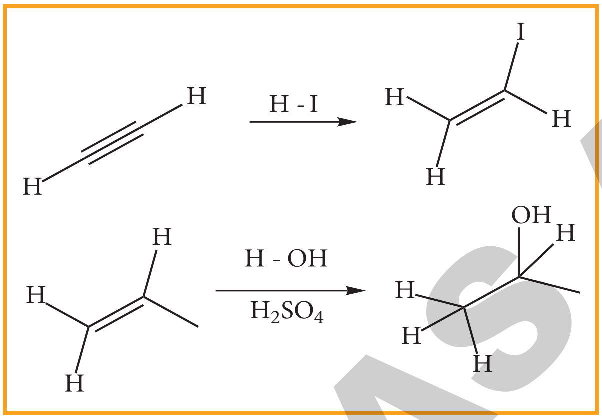
A general aliphatic electrophilic substitution is represented as

$$R\text{-}X + E^{\oplus} \longrightarrow R\text{-}E + X^{\oplus}$$

$$R_2NH + \overset{+}{NO} \rightarrow R_2N\text{–}NO + H^+$$

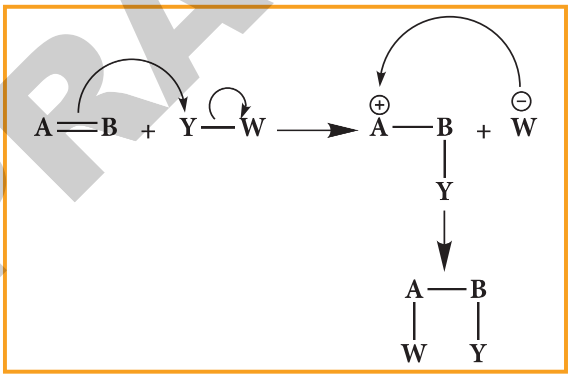
12.2.2 Addition reactions

It is a characteristic reaction of an unsaturated compound (compounds containing C-C localised double or triple bond). In this reaction two molecules combine to give a single product. Like substitution this reaction also can be classified as nucleophilic, electrophilic and freeradical addition reactions depending the type of reagent which initiates the reaction. During the addition reaction the hydridisation of the substrate changes (from $sp^2 \rightarrow sp^3$ in the addition reaction of alkenes or $sp \rightarrow sp^2$ in the addition reaction of alkynes) as only one bond breaks and two new bonds are formed.

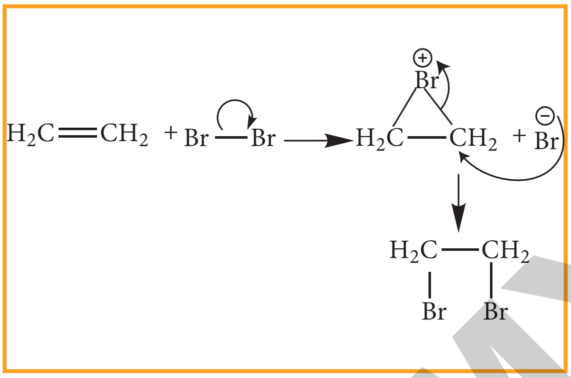


Electrophilic Addition reaction

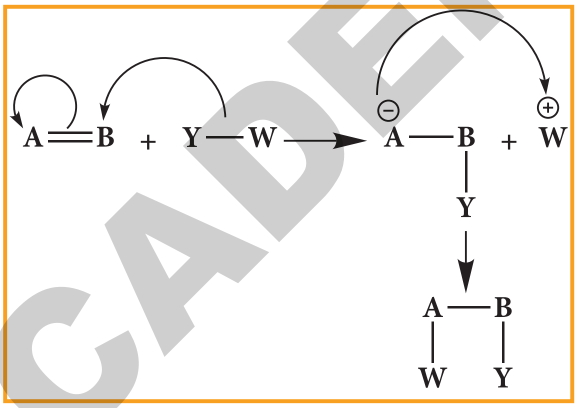
A general electrophilic addition reaction can be represented as below.



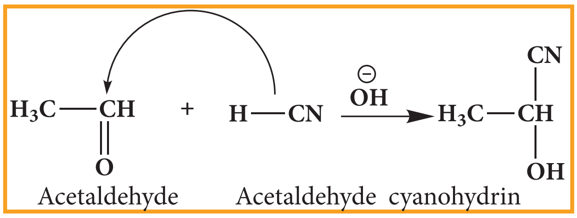
Brominatin of alkene to give bromo alkane is an example for this reaction.



Nucleophilic addition reaction

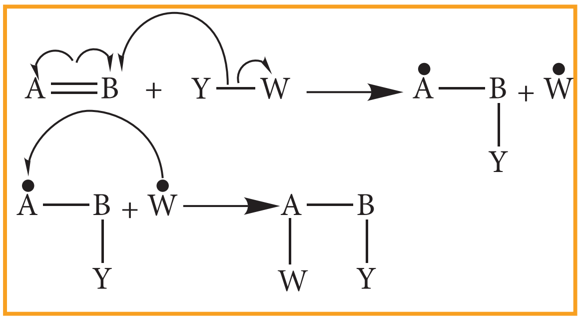


Example: addition of HCN to acetaldehyde



Free radical addition Reaction:

A General freeradical addition reaction can be represented as below.



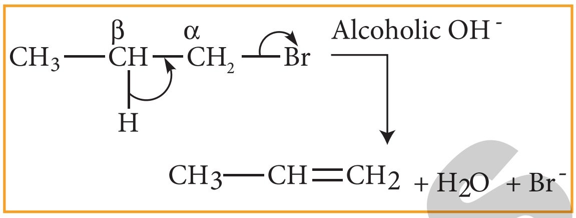
$$H_2C{=}CH_2 + H{-}Br \xrightarrow{\text{Benzoyl Peroxide}} CH_3{-}CH_2{-}Br$$

In the above reaction, Benzoyl peroxide acts as a radical initiator. The mechanism involves free radicals.

Elimination reactions:

In this reaction two substituents are eliminated from the molecule, and a new C-C double bond is formed between the carbon atoms to which the eliminated atoms/groups are previously attached. Elimination reaction is always accompanied with change in hybridisation.

Example: n-Propyl bromide on reaction with alcoholic KOH gives propene. In this reaction hydrogen and Br are eliminated.

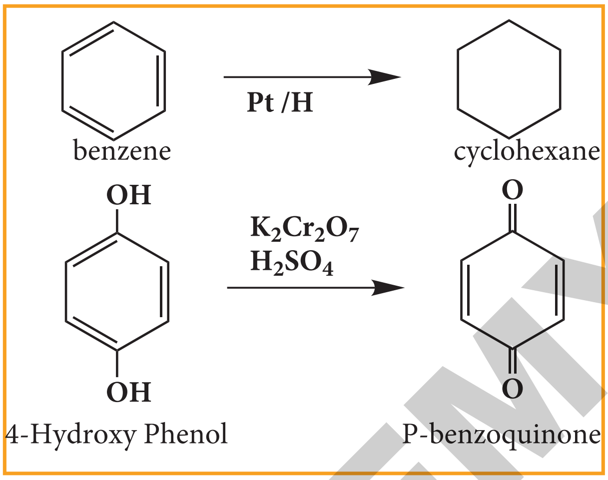


Oxidation and reduction reactions:

Many oxidation and reduction reactions of organic compounds fall into one of the four types of reaction that we already discussed but others do not. Most of the oxidation reaction of organic compounds involves gain of oxygen or loss of hydrogen Reduction involves gain of hydrogen and loss of oxygen.

Examples:

$$\underset{\text{Acetaldihyde}}{CH_3CHO} \xrightarrow[\text{Acidic dichromate}]{(o)} \underset{\text{Acetic acid}}{CH_3COOH}$$



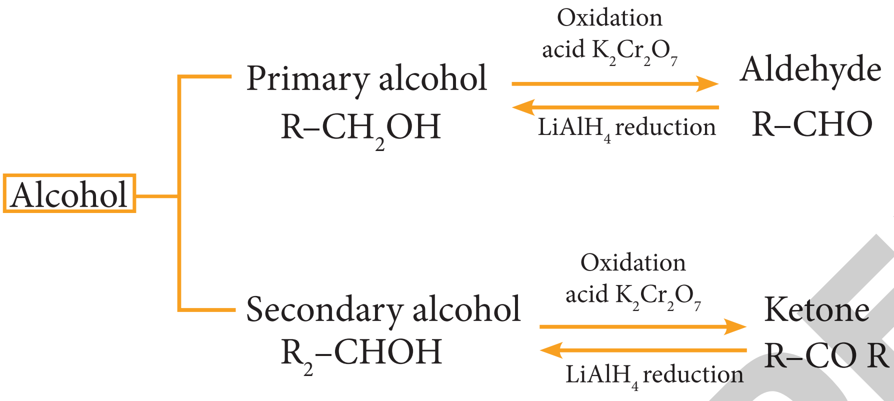
DO YOU KNOW?

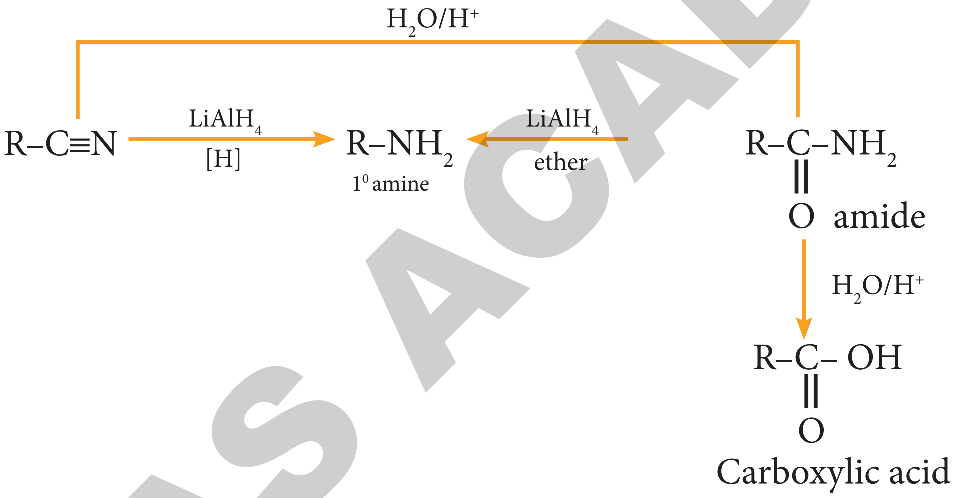
Apples contain an enzyme called polyphenol oxidase (PPO), also known as tyrosinase. Cutting an apple exposes its cells to the atmospheric oxygen and oxidizes the phenolic compounds present in apples. This is called the enzymatic browning that turns a cutapple brown. In addition to apples, enzymatic browning is also evident in bananas, pears, avocados and even potatoes

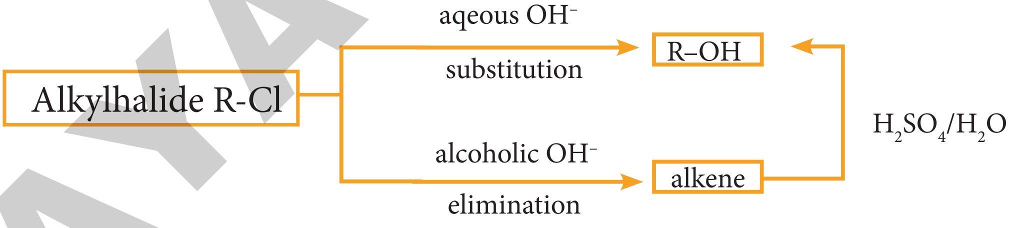
12.3 Functional Group inter conversion

Organic synthesis involves functional group inter conversions. A particular functional group can be converted into other functional group by reacting it with suitable reagents. For example: The carboxylic acid group (–COOH) presents in organic acids can be transformed to a variety of other functional group such as – CH_2–OH, – $CONH_2$, – COCl by treating the acid with $LiAlH_4$, NH_3 and $SOCl_2$ respectively.

Some of the important functional group interconversions of Organic compounds are summarised in the below mentioned Flow chart.





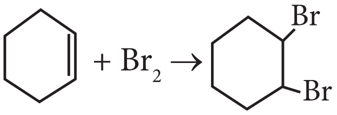


Evaluation

1. For the following reactions

(A) $CH_3CH_2CH_2Br + KOH \rightarrow$
$CH_2 = CH_2 + KBr + H_2O$

(B) $(CH_3)_3CBr + KOH \rightarrow (CH_3)_3\,COH + KBr$

(C) 

Which of the following statement is correct?

(a) (A) is elimination, (B) and (C) are substitution

(b) (A) is substitution, (B) and (C) are elimination

(c) (A) and (B) are elimination and (C) is addition reaction

(d) (A) is elimination, B is substitution and (C) is addition reaction.

2. What is the hybridisation state of benzyl carbonium ion?

(a) sp^2 (b) spd^2
(c) sp^3 (d) sp^2d

3. Decreasing order of nucleophilicity is

(a) $OH^- > NH_2^- > {}^-OCH_3 > RNH_2$
(b) $NH_2^- > OH^- > {}^-OCH_3 > RNH_2$
(c) $NH_2^- > CH_3O^- > OH^- > RNH_2$
(d) $CH_3O^- > NH_2^- > OH^- > RNH_2$

4. Which of the following species is not electrophilic in nature?

(a) Cl^+ (b) BH_3 (c) H_3O^+ (d) ${}^+NO_2$

5. Homolytic fission of covalent bond leads to the formation of

(a) electrophile (b) nucleophile
(c) Carbo cation (d) free radical

6. Hyper Conjugation is also known as

(a) no bond resonance
(b) Baker - nathan effect
(c) both (a)and (b)
(d) none of these

7. Which of the group has highest +I effect?

(a) CH_3- (b) CH_3-CH_2-
(c) $(CH_3)_2$-CH- (d) $(CH_3)_3$-C-

8. Which of the following species does not exert a resonance effect?

(a) C_6H_5OH (b) C_6H_5Cl
(c) $C_6H_5NH_2$ (d) $C_6H_5\overset{+}{N}H_3$

9. -I effect is shown by

(a) -Cl (b) -Br
(c) both (a) and (b) (d) $-CH_3$

10. Which of the following carbocation will be most stable?

(a) $Ph_3C\text{-}^+$ (b) $CH_3\text{-}\overset{+}{C}H_2\text{-}$
(c) $(CH_3)_2\text{-}\overset{+}{C}H$ (d) $CH_2{=}\,CH - \overset{+}{C}H_2$

11. Assertion: Tertiary Carbocations are generally formed more easily than primary Carbocations ions.

Reason: Hyper conjugation as well as inductive effect due to additional alkyl group stabilize tertiary carbonium ions.

(a) both assertion and reason are true and reason is the correct explanation of assertion.

(b) both assertion and reason are true but reason is not the correct explanation of assertion.

(c) Assertion is true but reason is false

(d) Both assertion and reason are false

12. Heterolytic fission of C-Br bond results in the formation of

(a) free radical (b) Carbanion

(c) Carbocation (d) Carbanion and Carbocation

13. Which of the following represent a set of nuclephiles?

(a) BF_3, H_2O, NH^{2-}

(b) $AlCl_3$, BF_3, NH_3

(c) CN^-, RCH_2^-, ROH

(d) H^+, RNH_3^+, $:CCl_2$

14. Which of the following species does not acts as a nucleophile?

(a) ROH (b) ROR

(c) PCl_3 (d) BF_3

15. The geometrical shape of carbocation is

(a) Linear (b) tetrahedral
(c) Planar (d) Pyramidal

16. Write short notes on

(a) Resonance
(b) Hyperconjucation

17. What are electrophiles and nucleophiles? Give suitable examples for each.

18. Show the heterolysis of covalent bond by using curved arrow notation and complete the following equations. Identify the nucleophile is each case.

(i) $CH_3 - Br + KOH \rightarrow$

(ii) $CH_3 - OCH_3 + HI \rightarrow$

19. Explain inductive effect with suitable example.

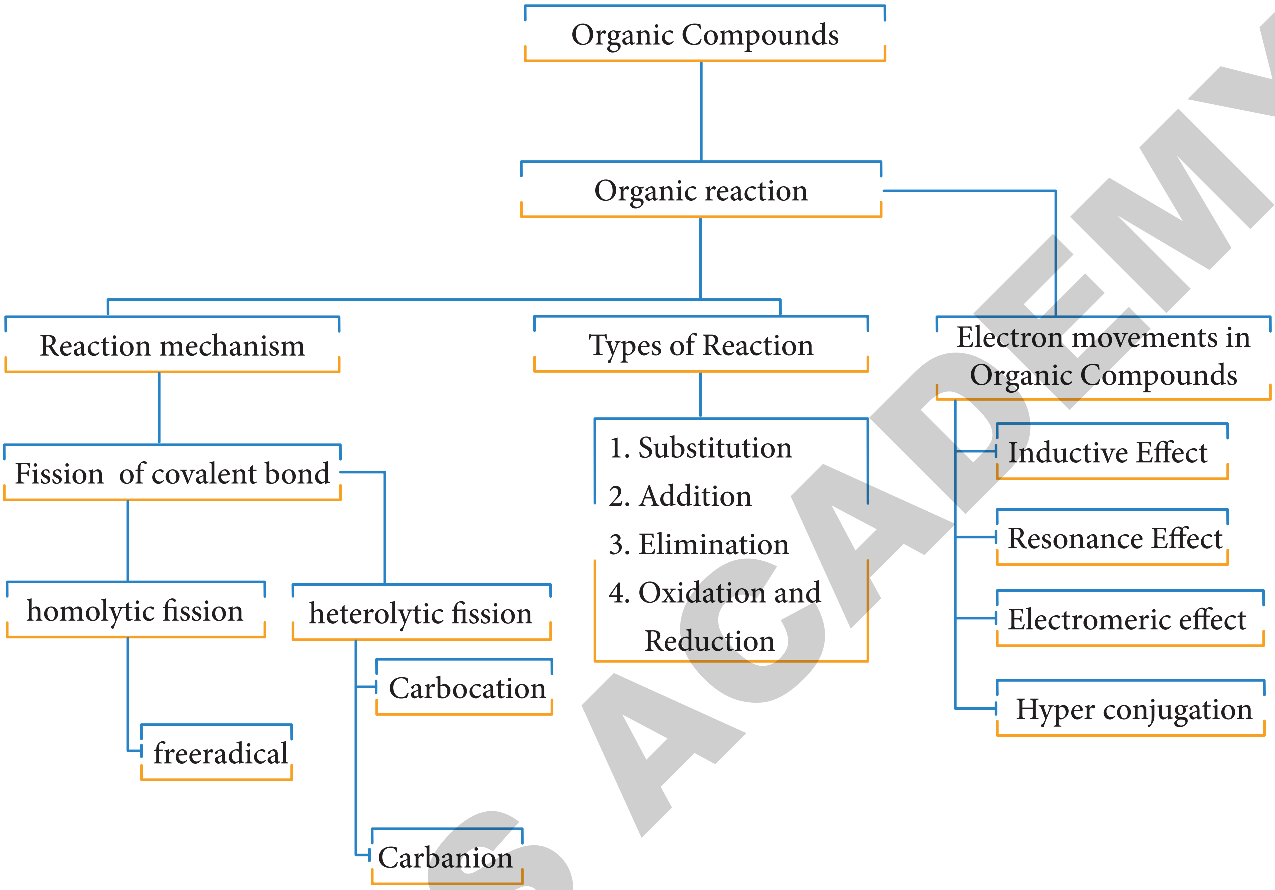
20. Explain electromeric effect.

21. Give examples for the following types of organic reactions

(i) β - elimination

(ii) electrophilic substitution.

CONCEPT MAP


Organic Compounds
Organic reaction
Reaction mechanism
Types of Reaction
Electron movements in Organic Compounds
Fission of covalent bond
homolytic fission
heterolytic fission
freeradical
Carbocation
Carbanion
1. Substitution
2. Addition
3. Elimination
4. Oxidation and Reduction
Inductive Effect
Resonance Effect
Electromeric effect
Hyper conjugation

Unit 13 Hydrocarbons

CHARLES ADOLPHE WURTZ

He is a French organic Chemist. He discovered phosphoryl chlorides. He showed that alkylhalides react with sodium to produce higher alkanes. This reaction was later named as Wurtz reaction. He is also known for his discoveries of ethylamine glycol and aldol condensation reactions.

Learning Objectives

After studying this unit, the students will be able to

- classify hydrocarbons according to nature of bond between the carbon atoms.
- name hydrocarbons according to IUPAC system of nomenclature.
- describe various methods of preparing hydrocarbon.
- interpret and use the following terminology in organic chemistry like free radicals, initiation, propagation and termination.
- describe chemistry of alkanes by the following reaction of halogenations, combustion, cracking.
- predict the formation of addition products of unsymmetrical alkenes which applies both Markovnikov's rule and peroxide effect.
- deduce acidic hydrogen in alkynes.
- comprehend the structure of benzene, explain aromaticity and understand mechanism of electrophilic substitutions reactions.
- predict the directive influence of substituents on mono substituted benzene.
- recognize the toxicity and carcinogenic nature of aromatic hydrocarbons.

Introduction

The hydrocarbons are compounds composed entirely of Carbon and Hydrogen. They occur widely in nature. The crude oil consists of complex mixtures of hydrocarbons, mangoes contain cyclohexane, a cyclic hydrocarbon, cockroaches secretes a hydrocarbon, undecane which attract opposite gender of its species. Hydrocarbons are primarily used as fuel. For example, Liquefied mixture of propane and butane is used as Liquefied petrolium gas (LPG). They also finds many applications in industries such as solvents etc. In this unit we will study the classification, preparation, properties and uses of aliphatic and aromatic hydrocarbons.

13.1 Introduction and classification of alkanes:

Depending upon the characteristic pattern of bonding between the carbon atoms, hydrocarbons are divided into two main classes: aliphatic and aromatic. The word aliphatic was derived from the Greek word 'aleiphar' meanings fat. Important sources of aliphatic hydrocarbons are oils and fats. The word 'aroma' means odour, which is obtained by chemical treatment of pleasant-smelling plant extracts.

Aliphatic hydrocarbons include three major groups: alkanes, alkenes and alkynes. Alkanes are saturated hydrocarbons in which all the bonds between the carbon atoms are single bond, alkenes consist of atleast one carbon-carbon double bond, and alkynes have atleast one carbon-carbon triple bond. Hydrocarbons having localised carbon - carbon multiple bonds are called unsaturated hydrocarbons.

Aromatic hydrocarbons are cyclic compounds which contain characteristic benzene ring or its derivatives. The classification of hydrocarbons is as shown below .

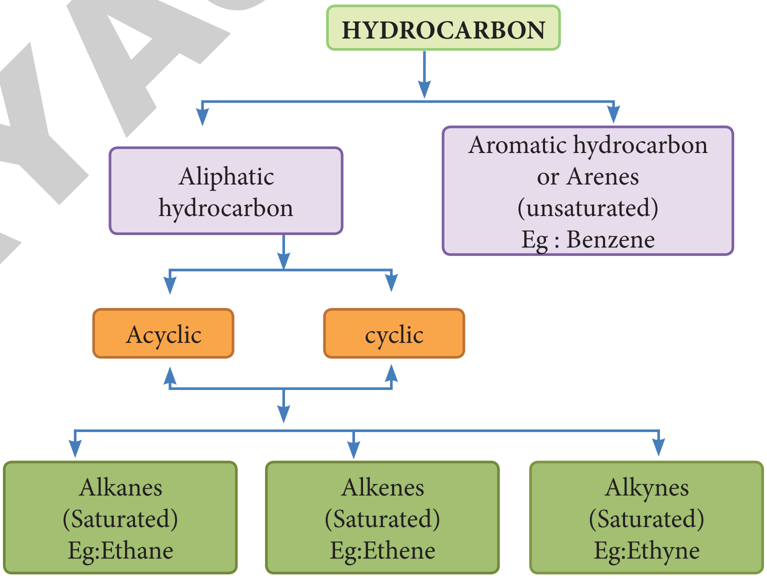


Fig.13.1. Classification of Hydrocarbons

13.2. Alkanes:

Alkanes are saturated hydrocarbons represented by the general formula C_nH_{2n+2} where 'n' is the number of carbon atoms in the molecule. Methane CH_4, is the first member of alkane family. The successive members are ethane C_2H_6, propane C_3H_8,butane C_4H_{10}, pentane C_5H_{12} and so on. It is evident that each member differs from its proceeding or succeeding member by a $-CH_2$ group.

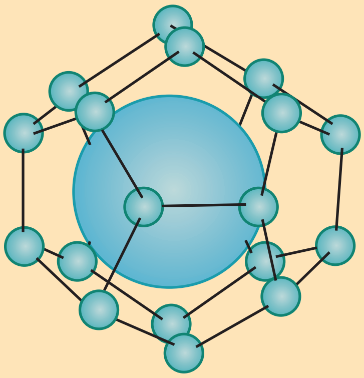
DO YOU KNOW?

Methane is the major component of the atmosphere of Jupiter, Saturn, Uranus and Neptune but only minor component of earth atmosphere. However, decomposition of plant and animal matter in an oxygen deficient environment like swamps, marshes, bogs and the sediments of lakes produces methane gas. So, it is otherwise known as marsh gas. It is also associated with coal and petroleum deposits.

DO YOU KNOW?

"FLAMMABLE ICE"

This catchy phrase describes a frozen mixture of water and methane gas chemically known as methane clathrates. The methane molecule which is produced by biological process under the deep-ocean, (at 4°C & 50 atm) doesn't simply reach the surface, instead each molecule is trapped inside clusters of 6 to18 water molecules forming methane clathrates. Many countries are working on how to tap out these vast resources of natural gas but mining and extracting are very difficult.

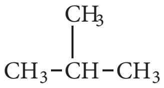
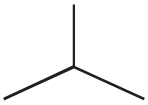


Nomenclature and isomerism:

We have already discussed the nomenclature of organic compound in Unit:11. Let us understand the nomenclature and isomerism in few examples. The first three members methane CH_4, ethane C_2H_6 and propane C_3H_8 have only one structure.

IUPAC Name	**Molecular Formula**	**Condensed Structural formula**
Methane	CH_4	CH_4
Ethane	C_2H_6	CH_3-CH_3
Propane	C_3H_8	CH_3-CH_2-CH_3

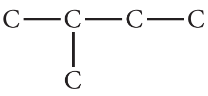
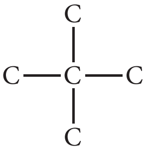
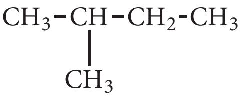
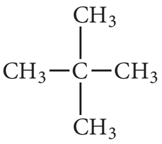
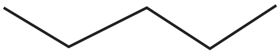
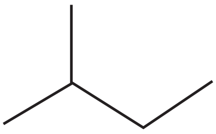
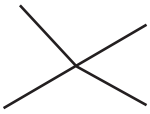
However, higher members can have more than one structure leading to constitutional isomers (differ in connectivity) or structural isomers. For example, an alkane with molecular formula C_4H_{10} can have two structures. They are n-butane and iso-butane. In n-butane, all the four carbon atoms are arranged in a continuous chain. The 'n' in n-butane stand for 'normal' and means that the carbon chain is unbranched. The second isomer iso-butane has a branched carbon chain. The word iso indicates it is an isomer of butane.

<table>
<tr><th>Molecular Formula</th><th>Structural Formula</th><th>Bond line Formula</th><th>IUPAC name</th><th>Common Name</th></tr>
<tr><td>C_4H_{10}</td><td>CH_3-CH_2-CH_2-CH_3</td><td></td><td>butane</td><td>n-butane</td></tr>
<tr><td></td><td>$\begin{array}{c} CH_3 \\ | \\ CH_3-CH-CH_3 \end{array}$</td><td></td><td>2-methylpropane</td><td>iso-butane</td></tr>
</table>

Though both the structures have same molecular formula but their carbon chains differ leading to chain isomerism

Let us understand the chain isomerism by writing the isomers of pentane C_5H_{12}

Solution:

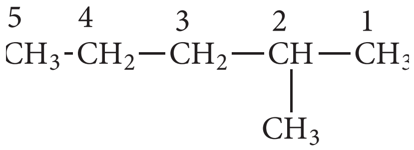
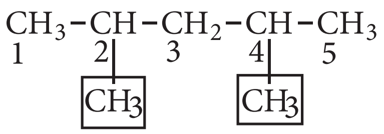
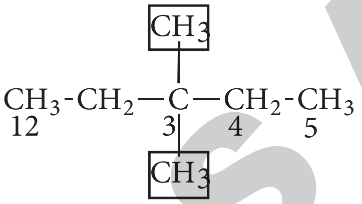
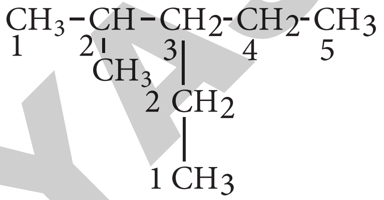
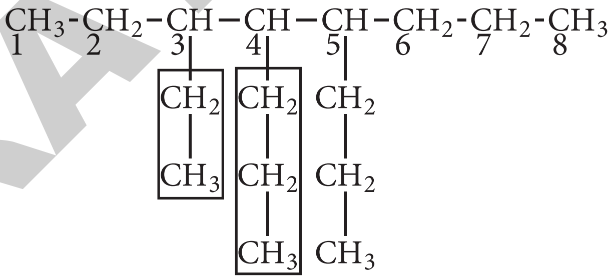
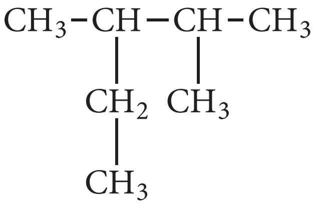
<table>
<tr><td>To begin, draw the carbon backbone of the straight chain-isomer</td><td>C—C—C—C—C</td></tr>
<tr><td>Determine the carbon backbone structure of the other isomers by arranging the carbon atoms in the other way</td><td>$\begin{array}{l} C-C-C-C \\ \ \ \ \ | \\ \ \ \ \ C \end{array}$
$\begin{array}{c} C \\ | \\ C-C-C \\ | \\ C \end{array}$</td></tr>
<tr><td colspan="2">Fill in all the hydrogen atoms so that each carbon forms four bonds
CH_3-CH_2-CH_2-CH_2-CH_3
$\begin{array}{l} CH_3-CH-CH_2-CH_3 \\ \qquad\ \ | \\ \qquad CH_3 \end{array}$
$\begin{array}{c} CH_3 \\ | \\ CH_3-C-CH_3 \\ | \\ CH_3 \end{array}$</td></tr>
<tr><td colspan="2">

</td></tr>
</table>

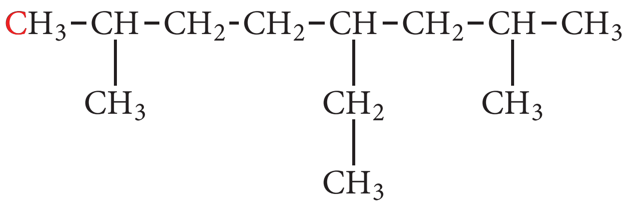
Evaluate Yourself

1) Write the structural formula and carbon skeleton formula for all possible chain isomers of C_6H_{14} (Hexane)

IUPAC name for some branched alkanes

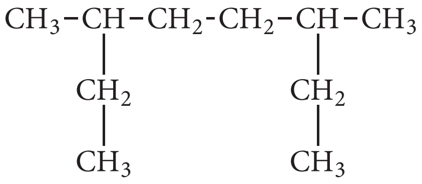
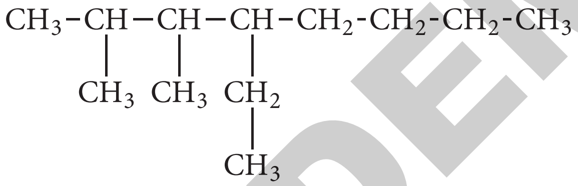
Let us write the IUPAC name for the below mentioned alkanes by applying the general rules of nomenclature that we already discussed in unit No.11

S.NO	COMPOUND	IUPAC NAME
1	 $\overset{5}{CH_3}-\overset{4}{CH_2}-\overset{3}{CH_2}-\underset{\displaystyle CH_3}{\underset{\vert}{\overset{2}{CH}}}-\overset{1}{CH_3}$	2- Methyl pentane
2	 $\underset{1}{CH_3}-\underset{\displaystyle \boxed{CH_3}}{\underset{2\vert}{CH}}-\underset{3}{CH_2}-\underset{\displaystyle \boxed{CH_3}}{\underset{4\vert}{CH}}-\underset{5}{CH_3}$	2,4- Dimethyl pentane
3	 $\underset{12}{CH_3}-CH_2-\overset{\displaystyle \boxed{CH_3}}{\underset{\displaystyle \boxed{CH_3}}{\underset{3\vert}{C}}}-\underset{4}{CH_2}-\underset{5}{CH_3}$	3,3- Dimethyl pentane
4	 $\underset{1}{CH_3}-\underset{CH_3}{\underset{2\vert}{CH}}-\underset{\displaystyle \underset{\displaystyle 1\,CH_3}{\underset{\vert}{2\,CH_2}}}{\underset{3\vert}{CH}}-\underset{4}{CH_2}-\underset{5}{CH_3}$	3-Ethyl-2-methylpentane
5	 $\underset{1}{CH_3}-\underset{2}{CH_2}-\underset{\displaystyle \boxed{\begin{matrix}CH_2\\ \vert\\ CH_3\end{matrix}}}{\underset{3\vert}{CH}}-\underset{\displaystyle \boxed{\begin{matrix}CH_2\\ \vert\\ CH_2\\ \vert\\ CH_3\end{matrix}}}{\underset{4\vert}{CH}}-\underset{\displaystyle \begin{matrix}CH_2\\ \vert\\ CH_2\\ \vert\\ CH_3\end{matrix}}{\underset{5\vert}{CH}}-\underset{6}{CH_2}-\underset{7}{CH_2}-\underset{8}{CH_3}$	3-Ethyl-4,5-dipropyl octane
6	 $CH_3-\underset{\displaystyle \begin{matrix}CH_2\\ \vert\\ CH_3\end{matrix}}{\underset{\vert}{CH}}-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_3$	2,3 - Dimethylpentane

7	 $CH_3-\underset{\underset{CH_3}{\vert}}{CH}-CH_2-CH_2-\underset{\underset{\underset{\underset{CH_3}{\vert}}{CH_2}}{\vert}}{CH}-CH_2-\underset{\underset{CH_3}{\vert}}{CH}-CH_3$	4 - Ethyl - 2,7 - Dimethyloctane

Evaluate Yourself

2) Give the IUPAC name for the following alkane.

a)	b)
 $CH_3-\underset{\underset{\underset{\underset{CH_3}{\vert}}{CH_2}}{\vert}}{CH}-CH_2-CH_2-\underset{\underset{\underset{\underset{CH_3}{\vert}}{CH_2}}{\vert}}{CH}-CH_3$	 $CH_3-\underset{\underset{CH_3}{\vert}}{CH}-\underset{\underset{CH_3}{\vert}}{CH}-\underset{\underset{\underset{\underset{CH_3}{\vert}}{CH_2}}{\vert}}{CH}-CH_2-CH_2-CH_2-CH_3$

How to draw structural formula for given IUPAC name :

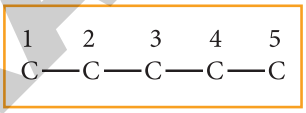
After you learn the rules for naming alkanes, it is relatively easy to reverse the procedure and translate the name of an alkane into a structural formula. The example below show how this is done.

Let us draw the structural formula for

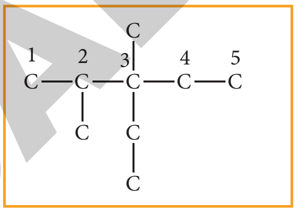
a) 3-ethyl-2,3-dimethyl pentane

Solution:

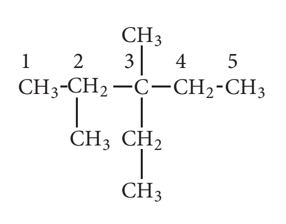
Step: 1 The parent hydrocarbon is pentane. Draw the chain of five carbon atoms and number it.



Step :2 Complete the carbon skeleton by attaching the alkyl group as they are specified in the name. An ethyl group is attached to carbon 3 and two methyl groups are attached to carbon 2 and 3.



Step: 3 Add hydrogen atoms to the carbon skeleton so that each carbon atoms has four bonds



$$\overset{1}{CH_3}-\underset{\underset{CH_3}{|}}{\overset{2}{CH_2}}-\underset{\underset{\underset{\underset{CH_3}{|}}{CH_2}}{|}}{\overset{\overset{CH_3}{|}}{\overset{3}{C}}}-\overset{4}{CH_2}-\overset{5}{CH_3}$$

Evaluate Yourself

3) Draw the structural formula for 4,5 -diethyl -3,4,5- trimethyl octane

13.2.1 Preparation of alkanes:

Alkanes are not laboratory curiosities but they are extremely important naturally occurring compounds. Natural gas and petroleum (crude oil) are the most important natural sources. However, it can be prepared by the following methods.

1. Preparation of alkanes from catalytic reduction of unsaturated hydrocarbons.

When a mixture hydrogen gas with alkene or alkyne gas is passed over a catalysts such as platinum or palladium at room temperature, an alkane is produced. This process of addition of H_2 to unsaturated compounds is known as hydrogenationThe above process can be catalysed by nickel at 298K. This reaction is known as Sabatier-Sendersens reaction

for example:

$$\underset{\text{propene}}{CH_3-CH=CH_2} + H_2 \xrightarrow{Pt} \underset{\text{propane}}{CH_3-CH_2-CH_3}$$

$$\underset{\text{ethene}}{CH_2=CH_2} + H_2 \xrightarrow[298K]{Ni} \underset{\text{ethane}}{CH_3-CH_3}$$

$$\underset{\text{prop-1-yne}}{CH_3-C\equiv CH} + 2H_2 \xrightarrow{Pt} \underset{\text{propane}}{CH_3-CH_2-CH_3}$$

2. Preparation of alkanes from carboxylic acids:

i) Decarboxylation of sodium salt of carboxylic acid

When a mixture of sodium salt of carboxylic acid and soda lime (sodium hydroxide + calcium oxide) is heated, alkane is formed. The alkane formed has one carbon atom less than carboxylic acid. This process of eliminating carboxylic group is known as decarboxylation.

for example:

$$\underset{\text{Sodium acetate}}{CH_3COONa} + NaOH \xrightarrow[\Delta]{CaO} \underset{\text{Methane}}{CH_4} + Na_2CO_3$$

ii) Kolbe's Electrolytic method

When sodium or potassium salt of carboxylic acid is electrolyzed, a higher alkane is formed. The decarboxylative dimerization of two carboxylic acid occurs. This method is suitable for preparing symmetrical alkanes(R-R).

$$\begin{array}{c} 2CH_3COONa + 2H_2O \\ \downarrow \text{Electrolysis} \\ \underbrace{H_3C-CH_3 + 2CO_2}_{\text{at Anode}} + \underbrace{H_2 + 2NaOH}_{\text{at Cathode}} \end{array}$$

3. Preparation of alkanes using alkyl halides (or) halo alkanes

i) By reduction with nascent hydrogen

Except alkyl fluorides, other alkyl halides can be converted to alkanes by reduction with nascent hydrogen. The hydrogen for reduction may be obtained by using any of the following reducing agents: Zn+HCl, Zn+CH_3COOH, Zn-Cu couple in ethanol, $LiAlH_4$ etc.,

for example:

$$\begin{array}{c} \underset{\text{chloro propane}}{CH_3-CH_2-CH_2-Cl} \\ [H] \downarrow Zn/HCl \\ \underset{\text{propane}}{CH_3-CH_2-CH_3} + HCl \end{array}$$

ii) Wurtz reaction

When a solution of halo alkanes in dry ether is treated with sodium metal, higher alkanes are produced. This reaction is used to prepare higher alkanes with even number of carbon atoms.

for example:

$$\underset{\text{methyl bromide}}{CH_3{-}Br} + 2Na + Br{-}CH_3 \xrightarrow[\text{ether}]{\text{dry}} \underset{\text{ethane}}{CH_3{-}CH_3} + NaBr$$

iii) Corey- House Mechanism

An alkyl halide and lithium di alkyl cuprate are reacted to give higher alkane.

for example:

$$\underset{\text{ethyl bromide}}{CH_3CH_2Br} + (CH_3)_2LiCu$$

$$\downarrow$$

$$CH_3CH_2CH_3 + CH_3Cu + LiBr$$

4) Preparation of Alkanes from Grignard reagents

Halo alkanes reacts with magnesium in the presence of dry ethers to give alkyl magnesium halide which is known as Grignard reagents. Here the alkyl group is directly attached to the magnesium metal make it to behave as carbanion. So, any compound with easily replaceable hydrogen reacts with Grignard reagent to give corresponding alkanes.

for example:

$$\underset{\text{chloromethane}}{CH_3{-}Cl} + Mg \xrightarrow{\text{Dry ether}} \underset{\text{methyl magnesium bromide}}{CH_3MgCl}$$

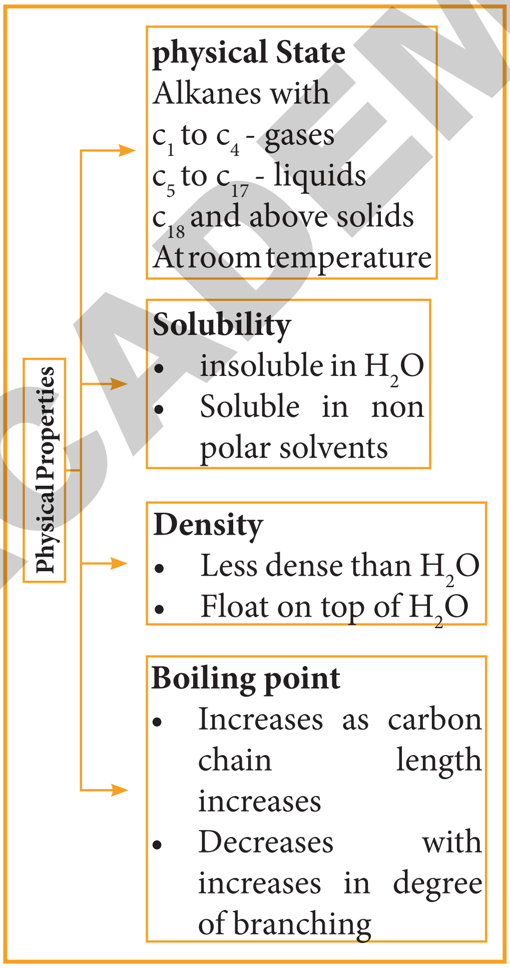
$$CH_3MgCl + H_2O \longrightarrow \underset{\text{methane}}{CH_4} + Mg(OH)Cl$$

Evaluate Yourself

4) Water destroys Grignard reagents why?

5) Is it possible to prepare methane by Kolbe's Electrolytic method

13.2.2 Physical Properties:



Physical Properties

physical State
Alkanes with
c_1 to c_4 - gases
c_5 to c_{17} - liquids
c_{18} and above solids
At room temperature

Solubility
- insoluble in H_2O
- Soluble in non polar solvents

Density
- Less dense than H_2O
- Float on top of H_2O

Boiling point
- Increases as carbon chain length increases
- Decreases with increases in degree of branching

1) Boiling Point and Physical state

The boiling point of continuous chain alkanes increases with increases in length of carbon chain roughly about 30°C for every added carbon atom to the chain. Being non polar, alkanes have weak Vanderwal's force which depends upon molecular surface area and hence increases with increase molecular size. We observe that with same number of carbon atoms, straight chain isomers have higher boiling point compared to branch chain isomers. The boiling point decreases with increase in branching as the molecule becomes compact and the area of the contact decreases.

2) Solubility and density

Water molecules are polar and alkanes are non-polar. The insolubility of alkanes in water makes them good water repellent for metals which protects the metal surface from corrosion. Because of their lower density than water, they form two layers and occupy top layer. The density difference between alkanes and water explains why oil spills in aqueous environment spread so quickly.

DO YOU KNOW?

Apples produce its own wax which contains long unbranched alkanes ($C_{27}H_{56}$ and $C_{29}H_{60}$). This natural wax helps the apple to resist moisture lost, enhances the fruit firmness and slowdowns its natural degradation. The consumption of apple with artificial wax coating is harmful to the digestive system

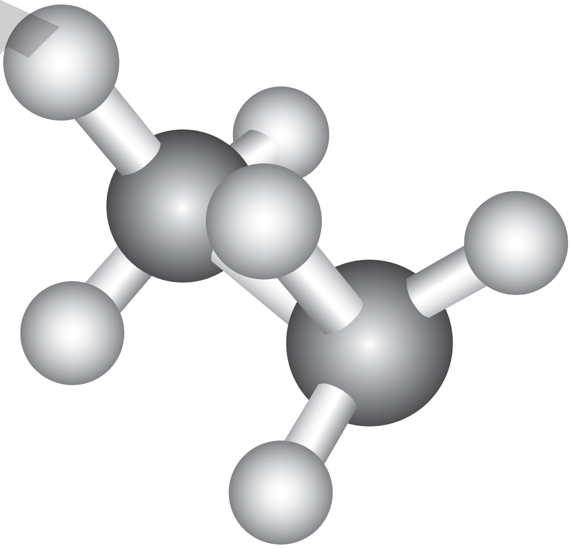
13.2.3 Conformations of alkane:

Each carbon in alkanes is sp^3 hybridized and the four groups or atoms around the carbon are tetrahedrally bonded. In alkanes having two or more carbons, there exists free rotation about C-C single bond. Such rotation leaves all the groups or atoms bonded to each carbon into an infinite number of readily interconvertible three dimensional arrangements. Such readily interconvertible three dimensional arrangement of a molecule is called conformations.

(i) Conformations of ethane:

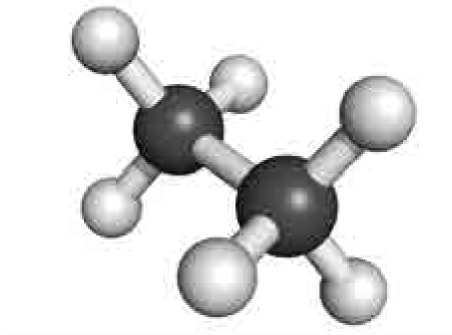
The two tetrahedral methyl groups can rotate about the carbon – carbon bond axis yielding several arrangements called conformers. The extreme conformations are staggered and eclipsed conformation. There can be number of other arrangements between staggered and eclipsed forms and their arrangements are known as skew forms.

Eclipsed conformation:



In this conformation, the hydrogen's of one carbon are directly behind those of the other. The repulsion between the atoms is maximum and it is the least stable conformer.

Staggered conformation:



In this conformation, the hydrogens of both the carbon atoms are far apart from each other. The repulsion between the atoms is minimum and it is the most stable conformer.

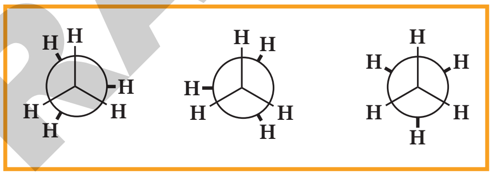
Skew Conformation :

The infinite numbers of possible intermediate conformations between the two extreme conformations are referred as skew conformations.

The stabilities of various conformations of ethane are

Staggered > Skew > Eclipsed

The potential energy difference between the staggered and eclipsed conformation of ethane is around 12.5 $KJmol^{-1}$. The various conformations can be represented by new man projection formula.



Eclipsed Skew Staggered

Newman projection formula for Ethane

Conformations of n-Butane:

n-Butane may be considered as a derivative of ethane, as one hydrogen on each carbon is replaced by a methyl group

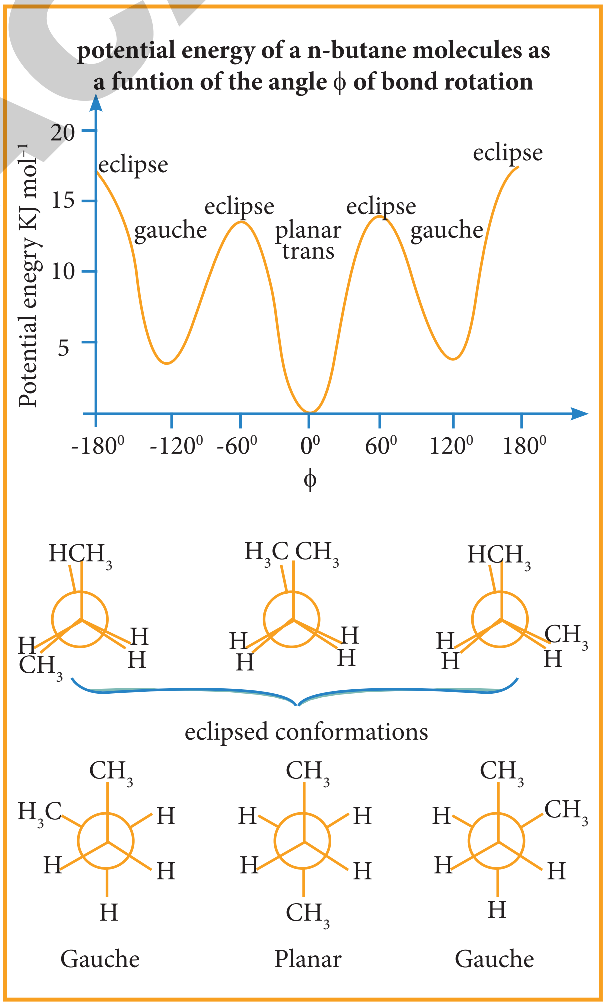
Eclipsed conformation:

In this conformation, the distance between the two methyl group is minimum. So there is maximum repulsion between them and it is the least stable conformer.

Anti or staggered form

In this conformation, the distance between the two methyl groups is maximum and so there is minimum repulsion between them. And it is the most stable conformer.

The following potentially energy diagram shows the relative stabilities of various conformers of n-butane.



potential energy of a n-butane molecules as a funtion of the angle ϕ of bond rotation

13.2.4 Chemical properties:

Alkanes are quite unreactive towards most reagents. However under favorable conditions, alkanes undergo the following type of reaction.

Paraffin is the older name for the alkane group family of compounds. This name comes from the Latin which means 'little activity'

1) Combustion:

A combustion reaction is a chemical reaction between a substances and oxygen with evolution of heat and light (usually as a flame). In the presence of sufficient oxygen, alkanes undergoes combustion when ignited and produces carbondioxide and water.

The combustion reaction is expressed as follows

for example:

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O \quad \Delta H^\circ = -890.4 kJ$$

When alkanes burn in insufficient supply of oxygen, they form carbonmonoxide and carbon black.

$$CH_4 + 3O_2 \xrightarrow[1273K]{Ni} 2CO + 4H_2O$$

$$CH_4 + O_2 \longrightarrow C + 2H_2O$$

Evaluate Yourself

6) Write down the combustion reaction of propane whose $\Delta H^\circ = -2220$ kJ

2) Halogenation:

Ahalogenation reaction is the chemical reaction between an alkane and halogen in which one or more hydrogen atoms are substituted by the halogens.

Chlorination and Bromination are two widely used halogenation reactions. Fluorination is too quick and iodination is too slow. Methane reacts with chlorine in the presence of light or when heated as follows.

$$CH_4 + Cl_2 \xrightarrow[Heat]{Light\ or} \underset{\text{methyl chloride}}{CH_3Cl} + HCl$$

$$CH_3Cl + Cl_2 \xrightarrow[Heat]{Light\ or} \underset{\text{methylene chloride}}{CH_3Cl_2} + HCl$$

$$CH_2Cl_2 + Cl_2 \xrightarrow[Heat]{Light\ or} \underset{\text{chloroform}}{CHCl_3} + HCl$$

$$CHCl_3 + Cl_2 \xrightarrow[Heat]{Light\ or} \underset{\text{carbontetrachloride}}{CCl_4} + HCl$$

Mechanism:

The reaction proceeds through the free radical chain mechanism. This mechanism is characterized by three steps initiation, propagation and termination.

i) CHAIN INITITATION: The chain is initiated by UV light leading to homolytic fission of chlorine molecules into free radicals (chlorine atoms).

$$Cl-Cl \longrightarrow 2Cl^{\cdot}$$

Here we choose Cl-Cl bond for fission because C-C & C-H bonds are stronger than Cl-Cl.

ii) **PROPAGATION:** It proceeds as follows,

(a) Chlorine free radial attacks the methane molecule and breaks the C-H bond resulting in the generation of methyl free radical

$$CH_3-H + \dot{C}l \xrightarrow{h\upsilon} \dot{C}H_3 + HCl$$

(b) The methyl free radical thus obtained attacks the second molecule of chlorine to give chloromethane (CH_3Cl) and a chlorine free radical as follows.

$$\dot{C}H_3 + Cl\text{-}Cl \longrightarrow CH_3Cl + \dot{C}l$$

(c) This chlorine free radical then cycles back to step (a) and both step (a) and (b) are repeated many times and thus chain of reaction is set up.

iii) Chain termination:

After sometimes, the reactions stops due to consumption of reactant and the chain is terminated by the combination of free radicals.

(a) $\dot{C}l + \dot{C}l \longrightarrow Cl-Cl$

(b) $\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3\text{-}CH_3$

(c) $\dot{C}H_3 + \dot{C}l \longrightarrow CH_3Cl$

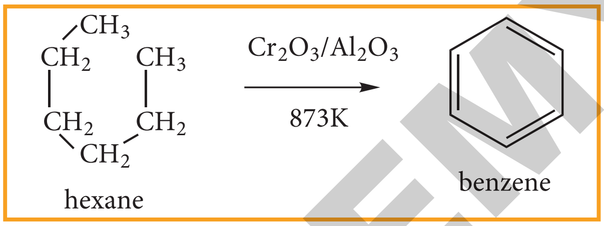
Evaluate Yourself

7) Why ethane is produced in chlorination of methane?

3) Aromatisation

Alkanes with six to ten carbon atoms are converted into homologous of benzene at high temperature and in the presence of catalyst. This process is known as aromatization. It occurs by simultaneous cyclisation followed by dehydrogenation of alkanes.

n-Hexane passed over Cr_2O_3 supported on alumina at 873 K gives benzene.



Evaluate Yourself

8) How toluene can be prepared by this method?

4) Reaction With Steam:

Methane reacts with steam at 1273K in the presence of Nickel and decomposes to form carbon monoxide and hydrogen gas.

$$CH_4(g) + H_2O(g) \xrightarrow[1273K]{Ni} CO(g) + 3H_2(g)$$

Production of H_2 gas from methane is known as steam reforming process and it is a well-established industrial process for the production of H_2 gas from hydrocarbons.

5) Pyrolysis

Pyrolysis is defined as the thermal decomposition of organic compound into smaller fragments in the absence of air through the application of heat. 'Pyro' means 'fire' and 'lysis' means 'separating'. Pyrolysis of alkanes also named as cracking.

In the absence of air, when alkane vapours are passed through red-hot metal it breaks down into simpler hydrocarbons.

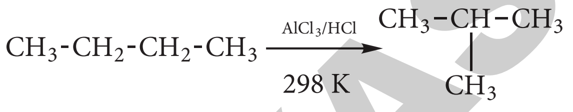
1) $$CH_3-CH_2-CH_3 \xrightarrow{773K} CH_3-CH=CH_2 + CH_2=CH_2 + H_2 + CH_4$$

2) $$2CH_3-CH_3 \xrightarrow{773K} CH_2=CH_2 + 2\,CH_4$$

The products depends upon the nature of alkane, temperature, pressure and presence or absence of catalyst. The ease of cracking in alkanes increases with increase in molecular weight and branching in alkanes. Cracking plays an important role in petroleum industry.

6) Isomerisation:

Isomerisation is a chemical process by which a compound is transformed into any its isomeric forms. Normal alkanes can be converted into branched alkanes in the presence of $AlCl_3$ and HCl at 298 k.



$$CH_3-CH_2-CH_2-CH_3 \xrightarrow[298\ K]{AlCl_3/HCl} CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$$

This process is of great industrial importance. The quality of gasoline is improved by isomerising its components.

Uses

The exothermic nature of alkane combustion reaction explains the extensive use of alkanes as fuels. Methane present in natural gas is used in home heating. Mixture of propane and butane are known as LPG gas which is used for domestic cooking purpose. GASOLINE is a complex mixture of many hydrocarbons used as a fuel for internal-combustion engines.

Carbon black is used in the manufacture of ink, printer ink and black pigments. It is also used as fillers.

No of Carbon Atoms	State at room temperature	Major uses
1-4	Gas	Heating fuel,Cooking fuel
5-7	Low boiling liquid	Solvents, Gasoline
6-12	Liquid	Gasoline
12-24	Liquid	Jet fuel-portable stove fuel
18-50	High boiling liquid	Diesel fuel, lubricant, heating oil
50+	Solid	Petroleum jelly and paraffin wax

13.3.Alkenes:

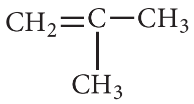
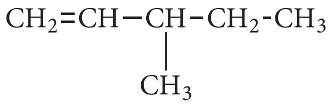
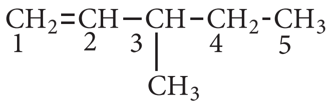
Alkenes are unsaturated hydrocarbons that contain carbon-carbon double bond. They are represented by the general formulae C_nH_{2n} where 'n' stands for number of carbon atoms in the molecule. Alkenes are also known as olefins (in Latin - oil maker) because the first member ethene combines with chlorine gas to form an oily liquid as a product.

(I) Nomenclature Of Alkenes:

Let us write the IUPAC name for the below mentioned alkanes by applying the general rules of nomenclature that we

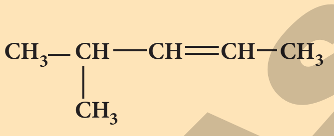
already discussed in unit No.11

TAB 13.4 IUPAC NAMES FOR ALKENES

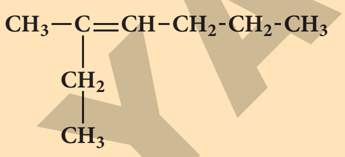
S No	Structure	IUPAC name
1	$CH_3-CH=CH_2$	propene
2	$CH_3-CH=CH-CH_3$	2-butene
3	 $CH_2=\underset{\underset{CH_3}{\vert}}{C}-CH_3$	2-methyl-1-propene
4	 $CH_2=CH-\underset{\underset{CH_3}{\vert}}{CH}-CH_2-CH_3$	3-methyl-1-propane
5	 $\underset{1}{CH_2}=\underset{2}{CH}-\underset{\underset{CH_3}{\vert}}{\underset{3}{CH}}-\underset{4}{CH_2}-\underset{5}{CH_3}$	3-methyl-1-pentene

Evaluate Yourself

1. Write the IUPAC names for the following alkenes.

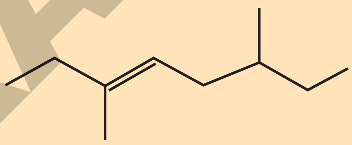
i) 

$CH_3-\underset{\underset{CH_3}{\vert}}{CH}-CH=CH-CH_3$

ii) 

$CH_3-\underset{\underset{CH_3}{\underset{\vert}{\underset{CH_2}{\vert}}}}{C}=CH-CH_2-CH_2-CH_3$

iii) 

iv) 

2. Draw the structures for the following alkenes.

i) 6 – Bromo – 2,3 – dimethyl – 2 – hexene

ii) 5 – Bromo – 4 – chloro – 1 – heptene

iii) 2,5 – Methyl – 4 – octene

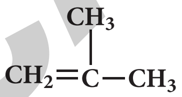
iv) 4 – Methyl – 2 pentene

(ii) Isomerism:

Presence of double bond in Alkene provides the possibility of both structural and geometrical isomerism.

Structural Isomerism:

The first two member's ethene C_2H_4 and propene C_3H_6 do not have isomers because the carbon atoms in the molecules can be arranged only one distinct way. However from the third member of alkene family butene C_4H_{10}, structural isomerism exists.

(i)	$CH_3-CH=CH-CH_3$	1-butene
(ii)	$CH_2=CH-CH_2-CH_3$	2-butene
(iii)	 $CH_2=\overset{\overset{CH_3}{\vert}}{C}-CH_3$	2-methyl-1-propene

structures (i) & (ii) are position isomers. structures (i) & (iii), (ii) & (iii) are chain isomers.

Evaluate Yourself

9) Draw the structure and write down the IUPAC name for the isomerism exhibited by the molecular formulae:

(i) C_5H_{12} – Pentene (3 isomers)

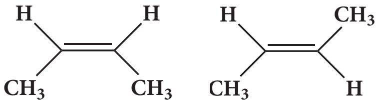
(ii) C_6H_{14} – Hexene (5 isomers)

Geometrical isomerism:

It is a type of stereoisomerism and it is also called cis-trans isomerism. Such type of isomerism results due to the restricted rotation of doubly bounded carbon atoms.

If the similar groups lie on the same side, then the geometrical isomers are called Cis-isomers. When the similar groups lie on the opposite side, it is called a Trans isomer.

for example: the geometrical isomers of 2-Butane is expressed as follows



Cis-2-butene | Trans-2-butene

Evaluate Yourself

10) Determine whether each of the following alkenes can exist in cis-trans isomers?

(a) 1 – Chloro propene

(b) 2 – Chloro propene

11) Draw cis-trans isomers for the following compounds

(a) 2- chloro – 2 – butene

(b) $CH_3 - CCl = CH- CH_2CH_3$

13.3.1: General methods of preparation of alkenes:

(1) Preparation of alkene by dehydration of alcohol:

When an alcohol is heated at 430-440 K with excess of concentrated sulphuric acid, a molecule of water from alcohol is removed and an alkene is formed. This reaction is called elimination reaction.

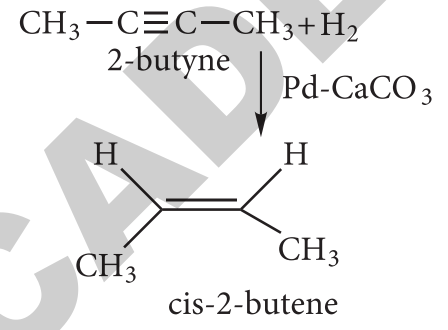
$$\underset{\text{ethanol}}{C_2H_5OH} \xrightarrow[\text{430 -440K}]{\text{Conc. } H_2SO_4} \underset{\text{ethene}}{CH_2{=}CH_2}$$

Ethene can also be prepared in laboratory by catalytic dehydration of alcohol.

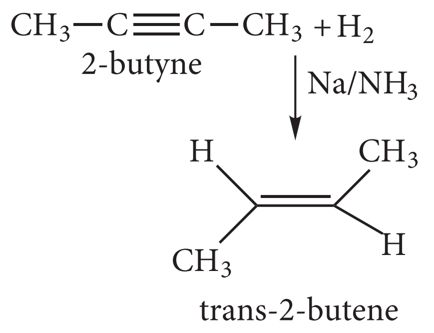
$$\underset{\text{ethanol}}{C_2H_5OH} \xrightarrow[\text{623K-723K}]{Al_2O_3} \underset{\text{ethene}}{CH_2{=}CH_2}$$

(2) Preparation of alkenes from alkynes:

Alkynes can be reduced to cis-alkenes using Lindlar's catalyst ($CaCO_3$ supported in palladuium partially deactivated with sulphur (or) gasoline). This reaction is stero specific giving only the cis- alkene.



Alkynes can also be reduced to trans-alkenes using sodium in liquid ammonia. This reaction is stereospecific giving only the trans-alkene.



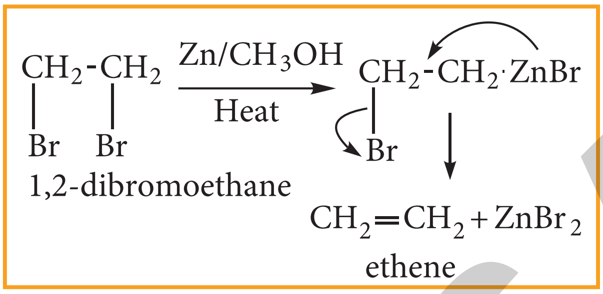
(3) Preparation of alkenes by dehydrohalogenaton of halo alkanes.

Halo alkanes react with alcoholic KOH and eliminate hydrohalide resulting in the formation of alkene.

$$\underset{\text{1-bromopropane}}{CH_3-CH_2-CH_2-Br} \xrightarrow{\text{alc. KOH}} \underset{\text{prop-1-ene}}{CH_3-CH=CH_2} + KBr + H_2O$$

(4) Preparation of alkenes from vicinal dihalogen derivative of alkanes or vicinal dihalides

The compound in which two halogen atoms are attached to adjacent carbon-atoms are called as vicinal dihalides. When vicinal dihalides are warmed with granulated zinc in methanol, they lose a molecule of ZnX_2 to form an alkene.



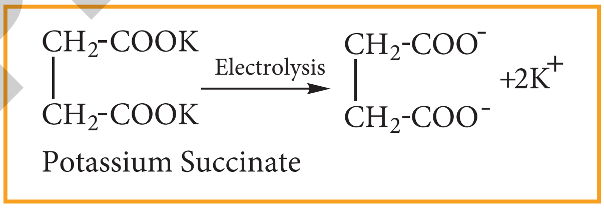
$$\underset{\text{1,2-dibromoethane}}{\begin{array}{ll}CH_2-&CH_2\\ |&|\\ Br&Br\end{array}} \xrightarrow[\text{Heat}]{Zn/CH_3OH} \begin{array}{ll}CH_2-&CH_2\cdot ZnBr\\ |&\\ Br&\end{array} \longrightarrow \underset{\text{ethene}}{CH_2=CH_2} + ZnBr_2$$

Evaluate Yourself

12) How propene is prepared form 1, 2-dichloro propane?

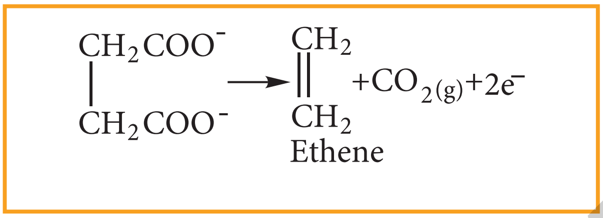
(5) Preparation of ethene by kolbe's electrolytic method:

When an aqueous solution of potassium succinate is electrolyzed between two platinum electrodes, ethene is produced at the anode.



$$\underset{\text{Potassium Succinate}}{\begin{array}{l}CH_2-COOK\\ |\\ CH_2-COOK\end{array}} \xrightarrow{\text{Electrolysis}} \begin{array}{l}CH_2-COO^-\\ |\\ CH_2-COO^-\end{array} + 2K^+$$

At anode



$$\begin{array}{l}CH_2COO^-\\ |\\ CH_2COO^-\end{array} \longrightarrow \underset{\text{Ethene}}{\begin{array}{c}CH_2\\ \|\\ CH_2\end{array}} + CO_{2(g)} + 2e^-$$

13.3.2. Physical properities of alkenes:

The first three members (Ethene, Propene and Butene) are gases, next fourteen members are liquids and the higher alkenes are waxy solids. They are all colourless and odourless except ethene which has a sweet smell.

1. The melting and boiling point of alkenes increases along the homologous series. Like alkanes, straight chain alkenes have high boiling point compared to its isomeric branched alkenes.
2. Alkenes are slightly soluble in water but readily in organic solvents.

13.3.3. Chemical properties of alkenes:

Alkenes are more reactive than alkanes due to the presence of a double bond. The σ- bond is strong but the π- bond is weak. The typical reactions of alkenes involve addition of an electrophile across the double bonds proceeding through ionic mechanism. However addition reactions proceed through free-radical mechanism. Ozonolysis and polymerization are some of the characteristic reactions of alkenes.

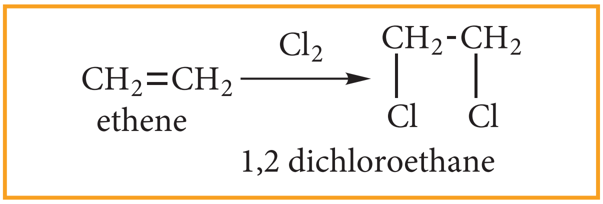
(i) Addition Reactions

(ii) Addition of hydrogen: (Hydrogenation of alkenes)

hydrogen adds on to alkenes in the presence of a metal catalyst (Ni, Pd (or) Pt) to yield corresponding alkanes. This is known as catalytic hydrogenation. This process is of great importance in the manufacture of vanaspathi from vegetable oil. This helps to prevent rancidity of vegetable oils.

(ii) Addition of halogens: (Halogenation of alkenes)

When alkene is treated with halogens like chlorine or bromine, addition takes place rapidly and forms 1, 2- dihalo alkane (or) vicinal dihalide.

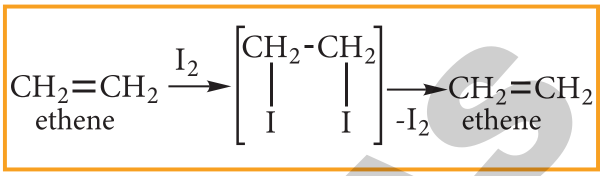


$$CH_2{=}CH_2 \xrightarrow{Cl_2} \underset{Cl}{\underset{|}{CH_2}}-\underset{Cl}{\underset{|}{CH_2}}$$

ethene

1,2 dichloroethane

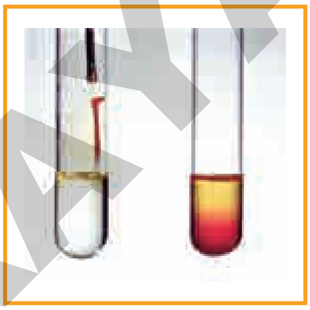
Iodine reacts very slowly to form 1, 2 – diiodo alkane which are unstable and regenerate the original alkene by elimination of iodine.



$$CH_2{=}CH_2 \xrightarrow{I_2} \left[\underset{I}{\underset{|}{CH_2}}-\underset{I}{\underset{|}{CH_2}}\right] \xrightarrow[-I_2]{} CH_2{=}CH_2$$

ethene ethene

TEST FOR ALKENE:



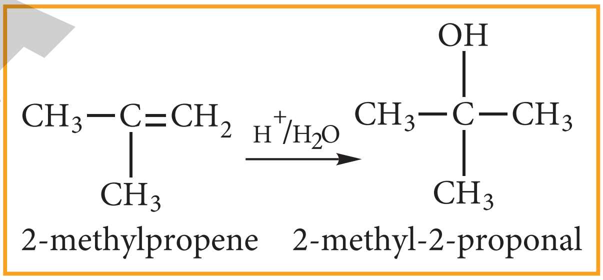
Bromine in water is reddish brown colour. When small about of bromine water is added to an alkene, the solution is decolourised as it forms dibromo compound. So, this is the characteristic test for unsaturated compounds.

Markovnikoff's rule:

"When an unsymmetrical alkene reacts with hydrogen halide, the hydrogen adds to the carbon that has more number of hydrogen and halogen add to the carbon having fewer hydrogen". This rule can also be stated as in the addition reaction of alkene / alkyne, the most electro negative part of the reagent adds on to the least hydrogen attached doubly bonded carbon.

(iii) Addition of water:- (Hydration of alkenes)

Normally, water does not react with alkenes. In the presence of concentrated sulphuric acid, alkenes react with water to form alcohols. This reaction follows carbocation mechanism and Markovnikoff's rule.



$$CH_3-\underset{CH_3}{\underset{|}{C}}{=}CH_2 \xrightarrow{H^+/H_2O} CH_3-\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_3$$

2-methylpropene 2-methyl-2-proponal

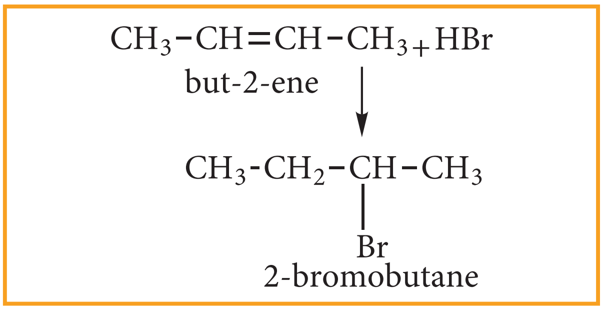
(iv) Addition of hydrohalides: (Hydrohalogenation of Alkenes)

Hydrogen halides (HCl, HBr and HI) add to alkene to yield alkyl halides. The order of reactivity of different hydrogen halides is HI>HBr>HCl. It is an example for electrophilic addition.

(a) Addition of HBr to symmetrical alkene:

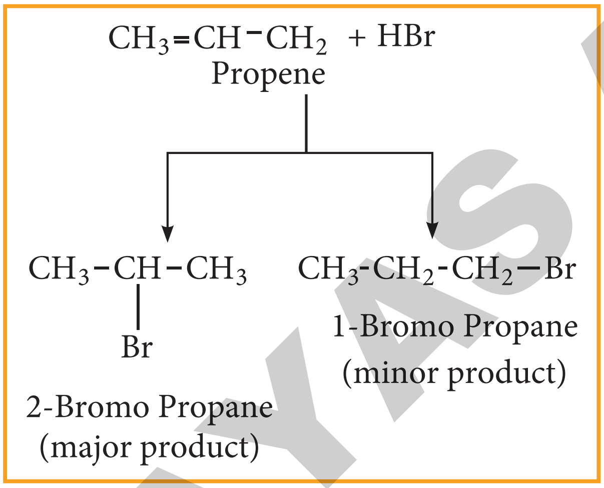
Addition of HBr to symmetrical alkene (similar groups are attached to double bond) yields alkyl halides (haloalkanes)

$$\underset{\text{ethene}}{CH_2=CH_2} + HBr \longrightarrow \underset{\text{bromoethane}}{CH_3-CH_2-Br}$$



(b) Addition HBr to unsymmetrical alkene:

In the addition of hydrogen halide to an unsymmetrical alkene, two products are obtained.

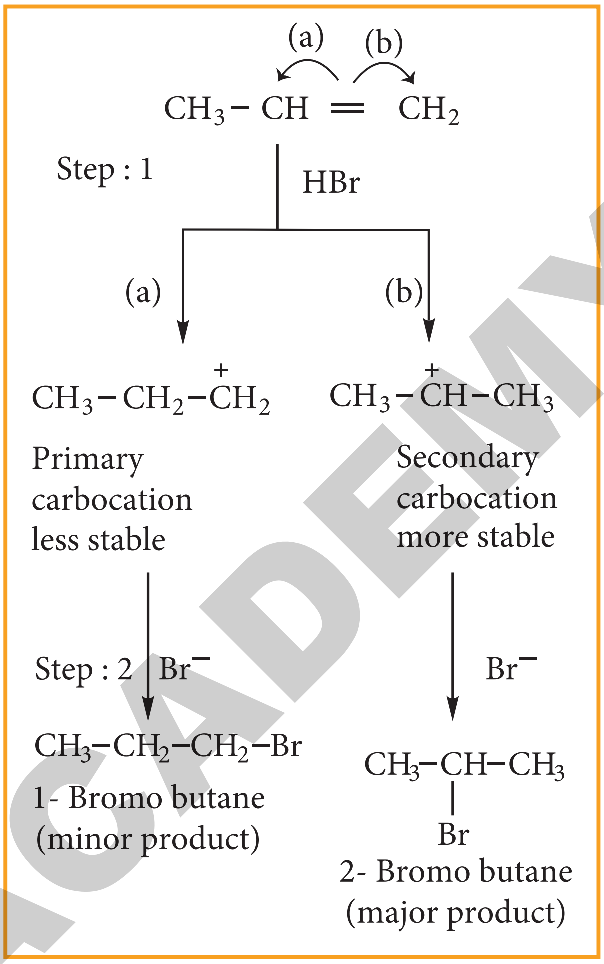


Mechanism:

Consider addition of HBr to propene

Step: 1 Formation of electrophile:

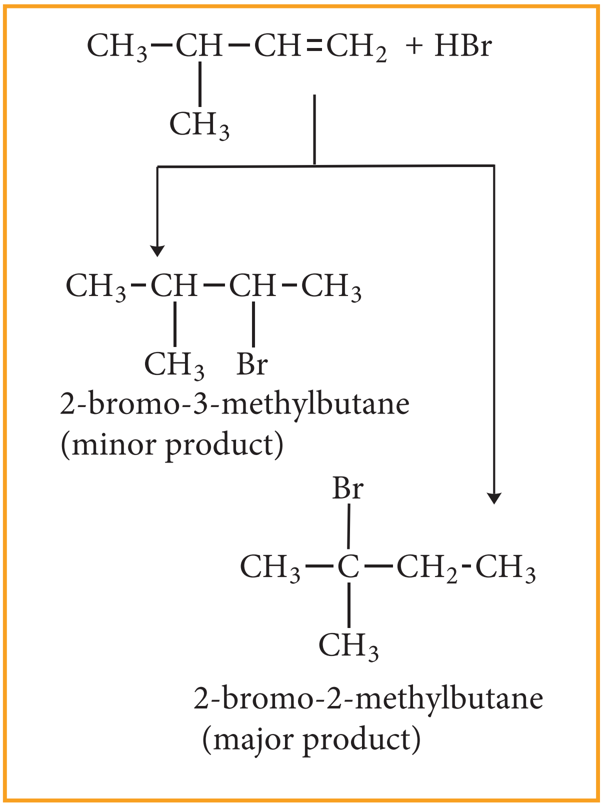
In H-Br, Br is more electronegative than H. When bonded electron moves toward Br, polarity is developed and creates an electrophile H^+ which attaches the double bond to form carbocation, as shown below.



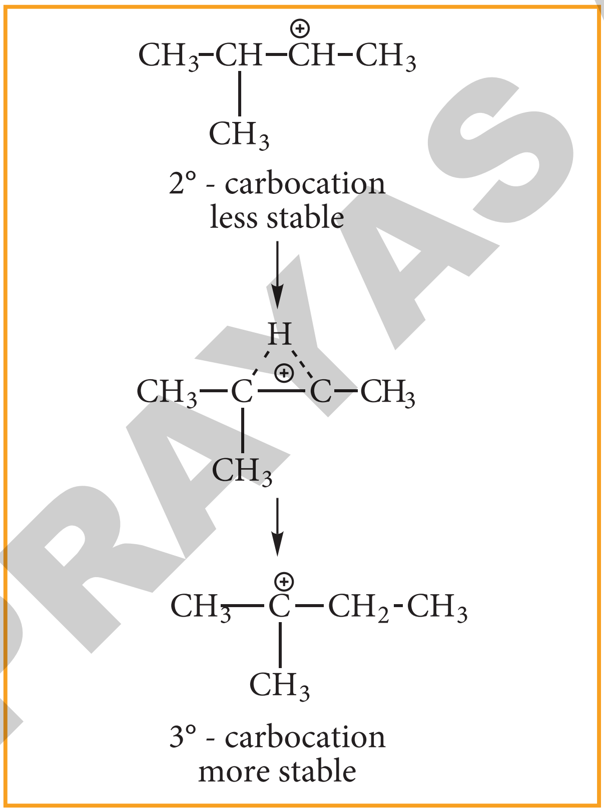
Step:2 Secondary carbocation is more stable than primary carbocation and it predominates over a the primary carbocation.

Step:3 The Br^-ion attack the 2° carbocation to from 2-Bromobutane, the major product.

Consider addition of HBr to 3-methyl-1-butene. Here the expected product according to markovnikoff's rule is 2-bromo-3-methyl butane but the actual major product is 2-Bromo-2-methyl butane. This is because, the secondary carbocation formed during the reaction rearranged to more stable tertiary carbocation. Attack of Br^- on this tertiary carbocation gives the major product 2-bromo-2-methyl butane.

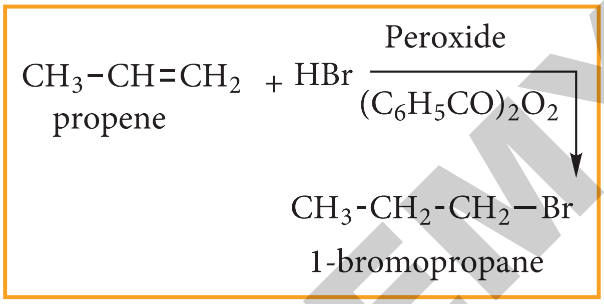


Carbocation rearrangement



Anti-Markovnikoff's Rule (Or) Peroxide Effect (Or) KharaschAddition

The addition of HBr to an alkene in the presence of organic peroxide, gives the anti Markovnikoff's product. This effect is called peroxide effect.

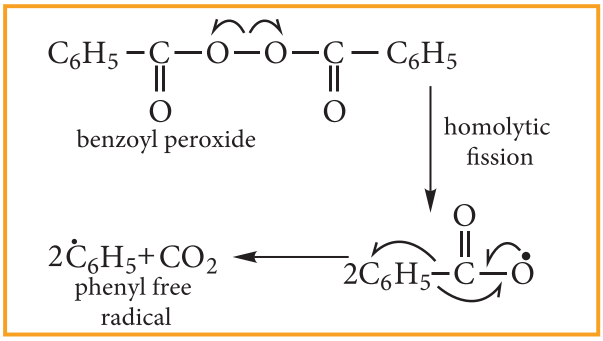


Mechanism:

The reaction proceeds via free radical mechanism.

Step:1

The weak O-O single bond linkages of peroxides undergoes homolytic cleavage to generate free radical.



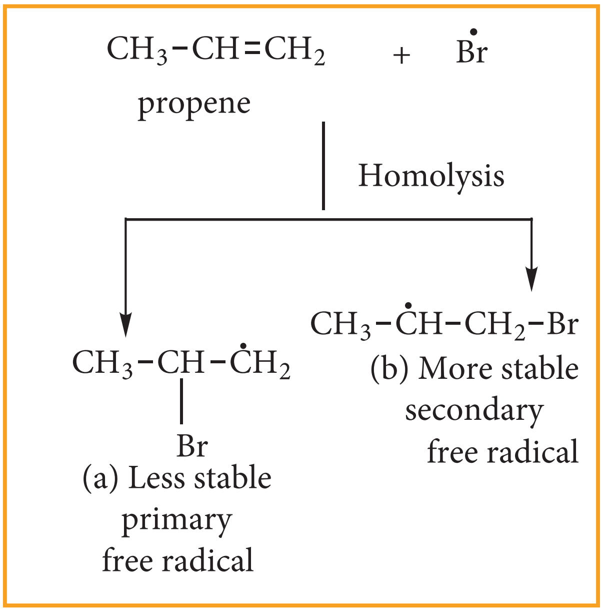
Step:2

The radicals abstracts a hydrogen from HBr thus generating bromine radical.

$$\dot{C}_6H_5 + HBr \longrightarrow C_6H_6 + \dot{Br}$$

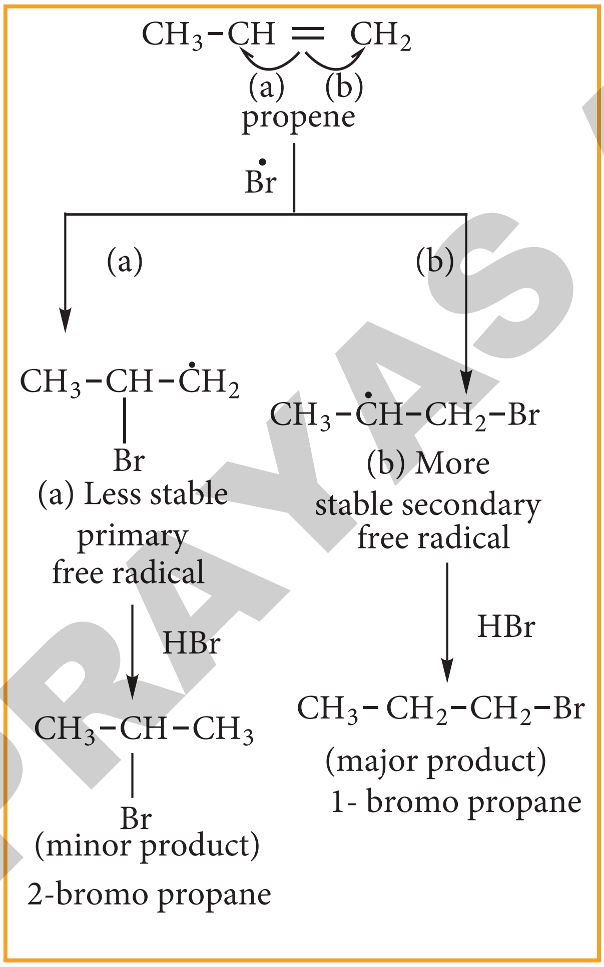
Step:3

The Bromine radical adds to the double bond in the way to form more stable alkyl free radical.



Step:4

Addition of HBr to secondary free radical



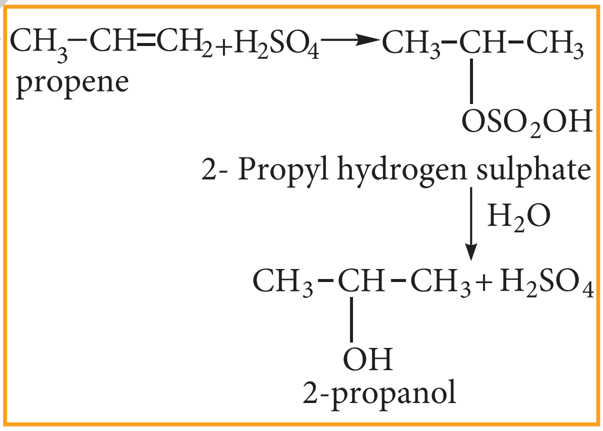
The H-Cl bond is stronger (430.5 $kJmol^{-1}$) than H-Br bond (363.7 $kJmol^{-1}$), thus H-Cl is not cleaved by the free radical. The H-I bond is weaker (296.8 kJ mol^{-1}), than H-Cl bond. Thus H-I bond breaks easily but iodine free radicals combine to form iodine molecules instead of adding to the double bond and hence peroxide effect is not observed in HCl& HI.

Kharasch Addition

Metal catalysed free radical addition of $CXCl_3$ Compounds to alkene is called Kharash addition reaction

(v) Addition of sulphuric acid to alkenes

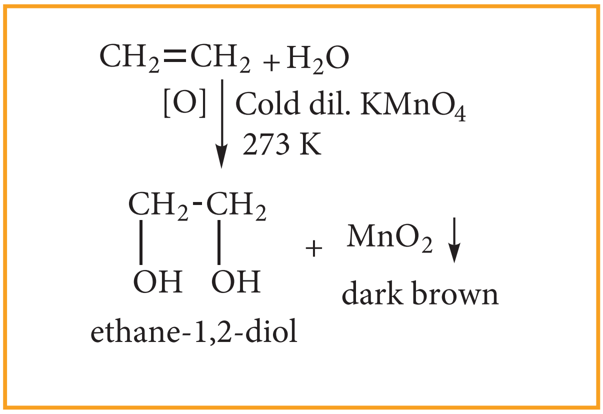
Alkenes react with cold and concentrated sulphuric acid to form alkyl hydrogen sulphate accordance with Markownikoff 's rule. Further hydrolysis yields alcohol.



(2) Oxidation:

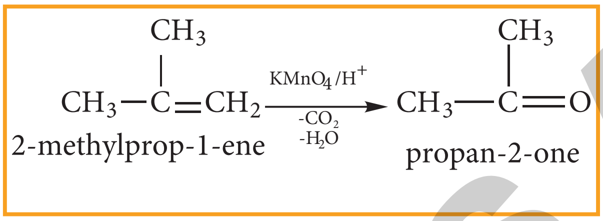
(i) With cold dilute alkaline KMnO4 solution (Baeyer's Reagent)

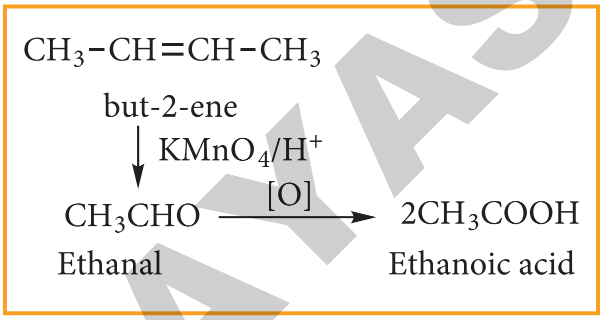
Alkenes react with Baeyer's reagent to form vicinal diols. The purple solution (Mn^{2+}) becomes dark green (Mn^{6+}), and then produces a dark brown precipitate (Mn^{4+}).



(ii) With acidified $KMnO_4$ Solution:

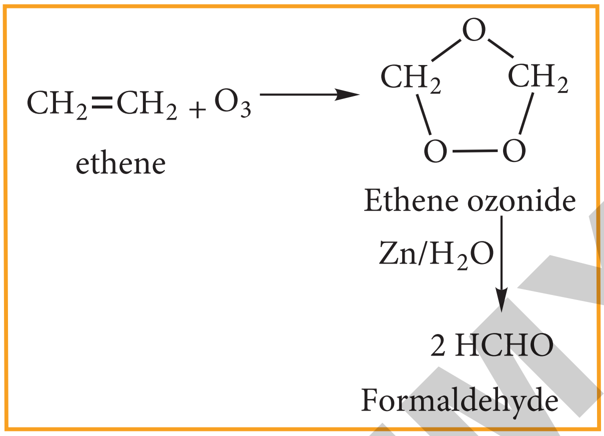
Alkenes react with acidified $KMnO_4$ solution and are oxidised to ketones or carboxylic acid depends on the substituent at the olefinic carbon atom.. The purple solution becomes colourless. This is one of the test for unsaturation.

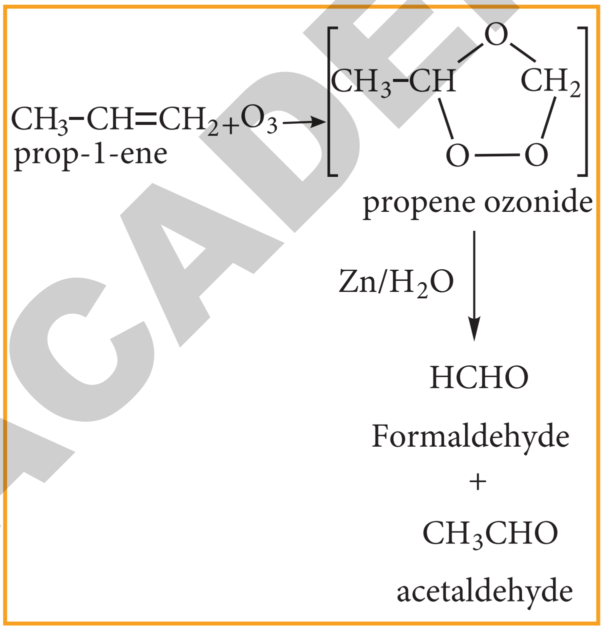




(iii) Ozonolysis:

Ozonolysis is a method of oxidative cleavage of alkenes or alkynes using ozone and forms two carbonyl compounds. Alkenes react with ozone to form Ozonide and it is cleaved by Zn/H_2O to form smaller molecules. This reaction is often used to identify the structure of unknown alkene or alkyne by detecting the position of double or triple bond.





Evaluate Yourself

13) How ozone reacts with 2-methyl propene?

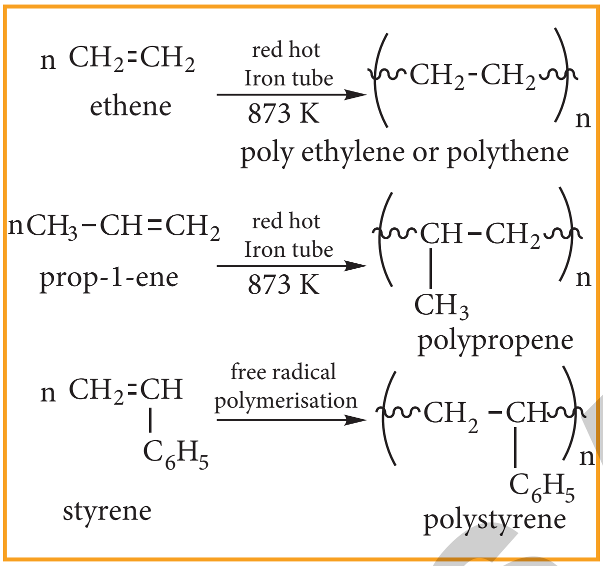
14) An organic compound (A) on ozonolysis gives only acetaldehyde. (A) reacts with Br_2/CCl_4 to give compound (B) Identify the compound (A) and (B). Write the IUPAC name of (A) and (B). Give the Geomatrical isomers of (A)

15) An organic compund (A) C_2H_4 decolourises bromine water. (A) on reaction with chlorine gives (B) A reacts with HBr to give (C).identify (A),(B),(C), Explain the reactions.

(iv) Polymerisation:

A polymer is a large molecule formed by the combination of larger number of small molecules. The process in known as polymerisation. Alkenes undergo polymerisation at high temperature and pressure, in the presence of a catalyst.

for example



$$n\,CH_2{=}CH_2 \xrightarrow[873\,K]{\text{red hot Iron tube}} \left(\sim CH_2{-}CH_2\sim\right)_n$$

ethene

poly ethylene or polythene

$$nCH_3{-}CH{=}CH_2 \xrightarrow[873\,K]{\text{red hot Iron tube}} \left(\sim \underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_2\sim\right)_n$$

prop-1-ene

polypropene

$$n\,CH_2{=}\underset{\displaystyle C_6H_5}{\underset{|}{CH}} \xrightarrow{\text{free radical polymerisation}} \left(\sim CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}\sim\right)_n$$

styrene

polystyrene

Recycling plastics

Extensive use of polymers clogs up landfills and polute the environment. Because of diversity of polymers in consumer products, recycling requires sorting the polymers into various sub-types, labels with codes and symbols, which are then recycled separately.

Table shows the codes and symbols used in recycling of ethene-based additionpolymers.

(Lower the number, greater the ease of recycling the material)

CODE	TYPE	NAME	EXAMPLES
PET	♳	Polyethylene terephthalate	Soft drinks bottles, jars, vegetable oil bottle.
HDPE	♴	High-density polyethylene	Milk, water and juice containers
PVC	♵	Polyvinyl chloride	Shampoo bottles, plastic pipes
CDPE	♶	Low density polyethylene	Sandwich bags, grocery bags
PP	♷	Polypropylene	Straws, diaper, toys
PS	♸	Polystyrene	Disposable utensil, foam cups
Other	♹	Multilayer plastics	Various flexible item.

13.3.4. Uses of Alkenes

1) Alkenes find many diverse applications in industry. They are used as starting materials in the synthesis of alcohols, plastics, liquors, detergents and fuels

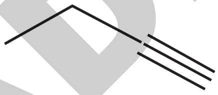
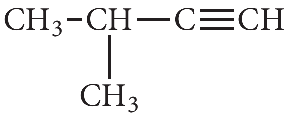
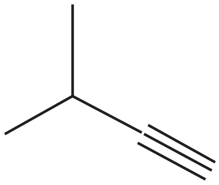
2) Ethene is the most important organic feed stock in the polymer industry. E.g. PVC, Sarans and polyethylene. These polymer are used in the manufacture of floor tiles, shoe soles, synthetic fibres, raincoats, pipes etc.,

13.4.Alkenes:

Alkynes are unsaturated hydrocarbons that contain carbon-carbon triple bonds in their molecules. Their general formula is $C_nH_{2n-2.}$ The first member of alkyne series is Ethyne popularly known as acetylene. Oxyacetylene torch is used in welding.

Nomenclture of alkynes:

Let us write the IUPAC name for the below mentioned alkynes by applying the general rules of nomenclature that we already discussed in unit No.11

Structure	IUPAC name	Carbon Skeleton Formula
$CH_3-C\equiv CH$	Propyne	
$CH_3\text{-}CH_2-C\equiv CH$	1-butyne	
$CH_3-C\equiv C-CH_3$	2-butyne	
 $CH_3-\underset{CH_3}{\underset{\vert}{CH}}-C\equiv CH$	2-methyl-1-butyne	

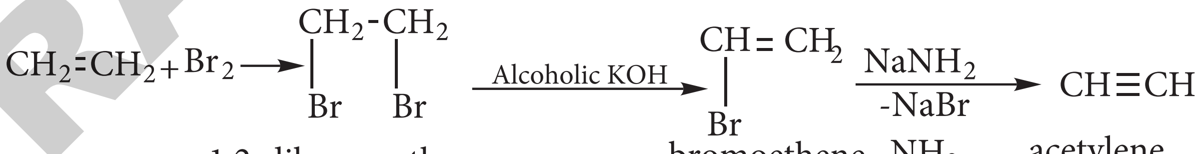
13.4.1. General Methods Of Preparation Of Alkynes

1. Preparation of alkynes from alkenes:

This process involves two steps:

(i) Halogenation of alkenes to form vicinal dihalides

(ii) Dehalogenation of vicinal dihalides to form alkynes.

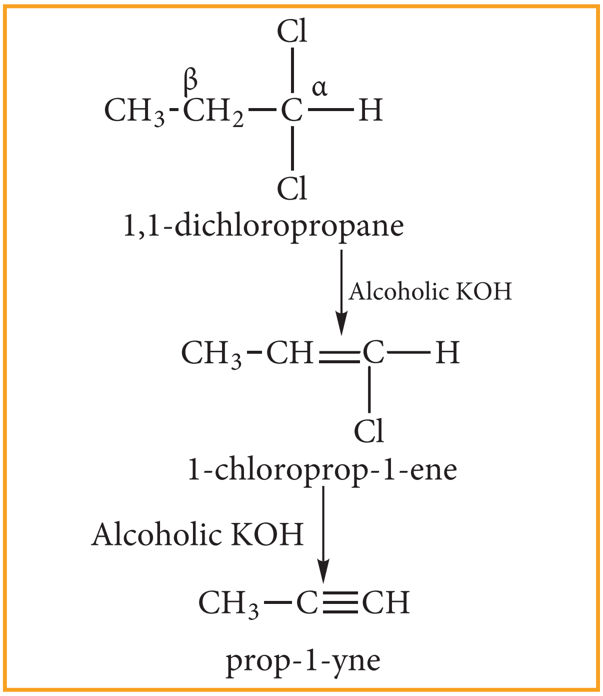


$$CH_2{=}CH_2 + Br_2 \longrightarrow \underset{Br}{\underset{\vert}{CH_2}}\text{-}\underset{Br}{\underset{\vert}{CH_2}} \xrightarrow{\text{Alcoholic KOH}} \underset{Br}{\underset{\vert}{CH}}{=}CH_2 \xrightarrow[\text{-NaBr}]{NaNH_2} CH\equiv CH$$

1,2-dibromoethane bromoethene $-NH_3$ acetylene

2. Preparation of alkene from gem dihalides:

A compound containing two halogen atoms on the same carbon atom is called gem dihalide (Latin word 'Gemini' means twins). On heating with alcoholic KOH, gem dihalides give alkynes.



$$CH_3\text{-}\overset{\beta}{C}H_2-\overset{\alpha}{C}(Cl)_2-H \xrightarrow{\text{Alcoholic KOH}} CH_3-CH=C(Cl)-H \xrightarrow{\text{Alcoholic KOH}} CH_3-C\equiv CH$$

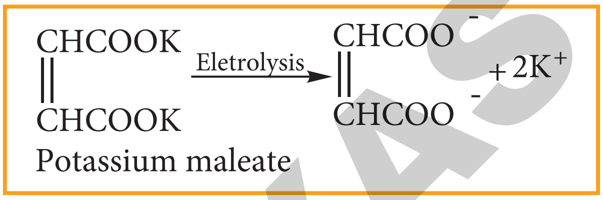
1,1-dichloropropane

1-chloroprop-1-ene

prop-1-yne

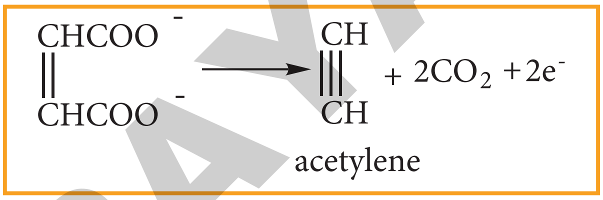
3. Preparation Of Alkenes From Electrolysis Of Salts Of Unsaturated Dicarboxylic Acids. (Kolbe's Electrolytic Method)

Electrolysis of sodium or potassium salt of maleic or fumaric acid yields alkynes.



$$\begin{matrix} CHCOOK \\ \| \\ CHCOOK \end{matrix} \xrightarrow{\text{Eletrolysis}} \begin{matrix} CHCOO^- \\ \| \\ CHCOO^- \end{matrix} + 2K^+$$

Potassium maleate

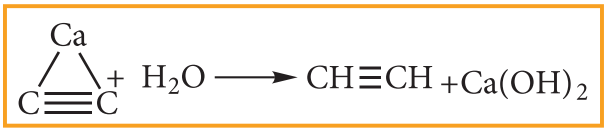


$$\begin{matrix} CHCOO^- \\ \| \\ CHCOO^- \end{matrix} \longrightarrow \begin{matrix} CH \\ ||| \\ CH \end{matrix} + 2CO_2 + 2e^-$$

acetylene

4. Industrial prefaration of ethyne:

Ethyne can be manufactured in large scale by action of calcium carbide with water.



$$CaC_2 + H_2O \longrightarrow CH\equiv CH + Ca(OH)_2$$

Calcium carbide required for this reaction is prepared by heating quick lime and coke in an electric furance at 3273 K

$$CaO + 3C \xrightarrow{3273\ K} CaC_2 + CO$$

Evaluate Yourself

16) Prepare propyne from its corresponding alkene.

17) Write the products A & B for the following reaction.

$$Cl-CH_2-CH_2-Cl \xrightarrow[\text{-HCl}]{\text{Alcoholic KOH}} (A) \xrightarrow[\text{-HCl}]{\text{Alcoholic KOH}} (B)$$

13.4.2. Physical properties of alkynes:

1. The first three members are gases, next eight are liquids and the higher alkynes are solids. They are all colourless and odourless except acetylene which h as a garlic odour.

2. They are slightly soluble in water but dissolve readily in organic solvents like benzene, acetone and ethyl alcohol

13.4.3. Chemical properities of alkynes

Terminal Alkynes are acidic in nature. It undergoes polymerization and addition reaction.

1. Acidic nature of alkynes:

An alkyne shows acidic nature only if it contains terminal hydrogen. This can be explained by considering sp hybrid orbitals of carbon atom in alkynes. The percentage of S-character of sp hybrid orbital (50%) is more than sp^2 hybrid orbital of alkene (33%) and sp^3 hybrid orbital of alkane (25%). Because of this, Carbon becomes more electronegative facilitating donation of H^+

ions to bases. So hydrogen attached to triply bonded carbon atoms is acidic.

$$\underset{\text{1-butyne}}{CH_3\text{-}CH_2-C\equiv CH} + 2AgNO_3 + 2NH_4OH \longrightarrow \underset{\text{Silver butynide}}{CH_3\text{-}CH_2-C\equiv C-Ag\downarrow} + 2\,NH_4NO_3 + 2H_2O$$

$$\underset{\text{1-butyne}}{CH_3\text{-}CH_2-C\equiv CH} + Cu_2Cl_2 + 2NH_4OH \longrightarrow \underset{\text{Copper butynide}}{CH_3\text{-}CH_2-C\equiv C-Cu\downarrow} + 2\,NH_4NO_3 + 2H_2O$$

$$\underset{\text{2-butyne}}{CH_3-C\equiv C-CH_3} + 2AgNO_3 + 2NH_4OH \longrightarrow \text{No Raection due to absence of acidic hydrogen}$$

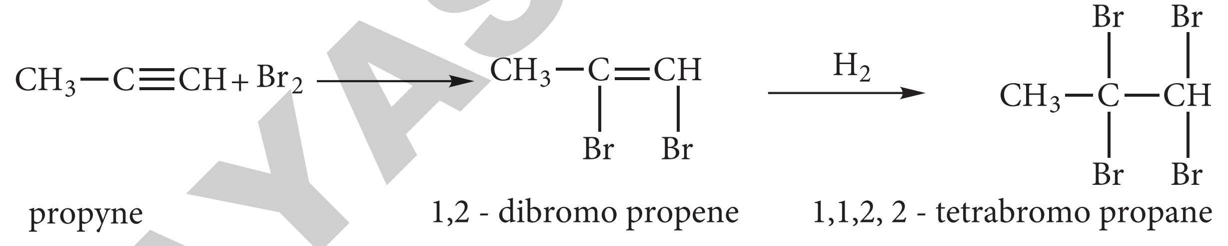
2. Addition reactions of alkynes

i) addition of hydrogen

$$\underset{\text{acetylene}}{CH\equiv CH} + H_2 \xrightarrow{Pt} \underset{\text{ethylene}}{CH_2=CH_2} \xrightarrow{H_2} \underset{\text{ethane}}{CH_3\text{-}CH_3}$$

ii) Addition Of Halogens:

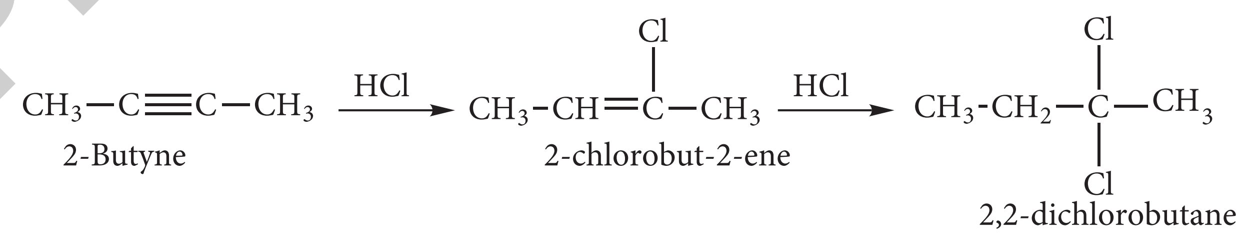
When Br_2 in CCl_4 (Reddishbrown) is added to an alkyne, the bromine solution is decolourised. This is the test for unsaturation.



$$\underset{\text{propyne}}{CH_3-C\equiv CH} + Br_2 \longrightarrow \underset{\text{1,2 - dibromo propene}}{CH_3-\underset{Br}{C}=\underset{Br}{CH}} \xrightarrow{H_2} \underset{\text{1,1,2, 2 - tetrabromo propane}}{CH_3-\overset{Br}{\underset{Br}{C}}-\overset{Br}{\underset{Br}{CH}}}$$

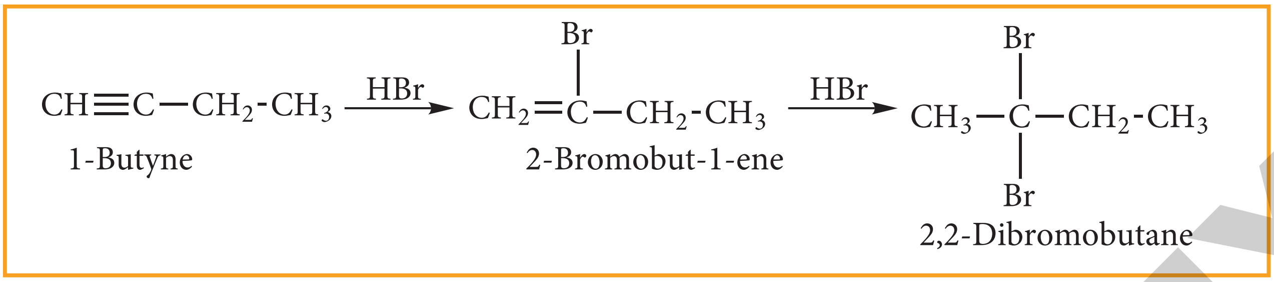
iii) Addition Of Hydrogen Halides:

Reaction of hydrogen halides to symmetrical alkynes is electrophilic addition reaction. This reaction also follows Markovnikoff's rule.



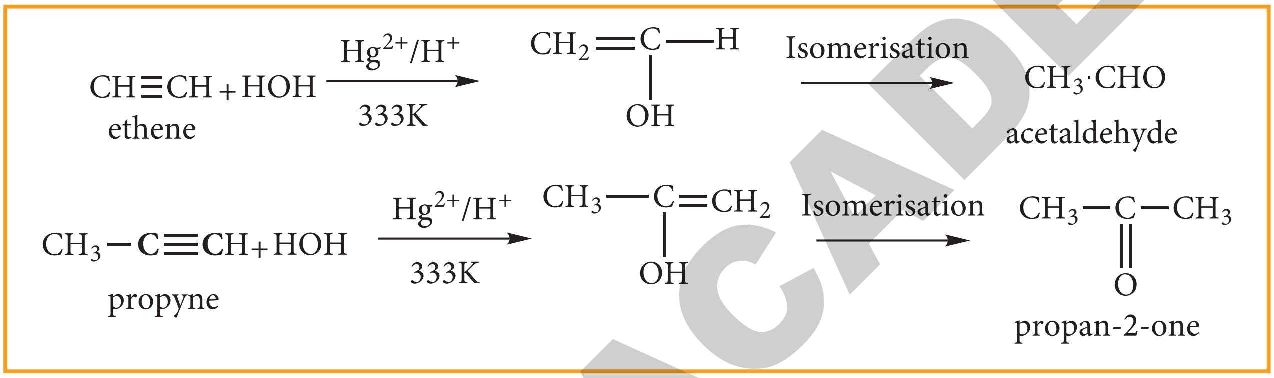
$$\underset{\text{2-Butyne}}{CH_3-C\equiv C-CH_3} \xrightarrow{HCl} \underset{\text{2-chlorobut-2-ene}}{CH_3\text{-}CH=\overset{Cl}{C}-CH_3} \xrightarrow{HCl} \underset{\text{2,2-dichlorobutane}}{CH_3\text{-}CH_2-\overset{Cl}{\underset{Cl}{C}}-CH_3}$$

Addition of HBr to unsymmetrical alkene follows Markownikoff's rule.



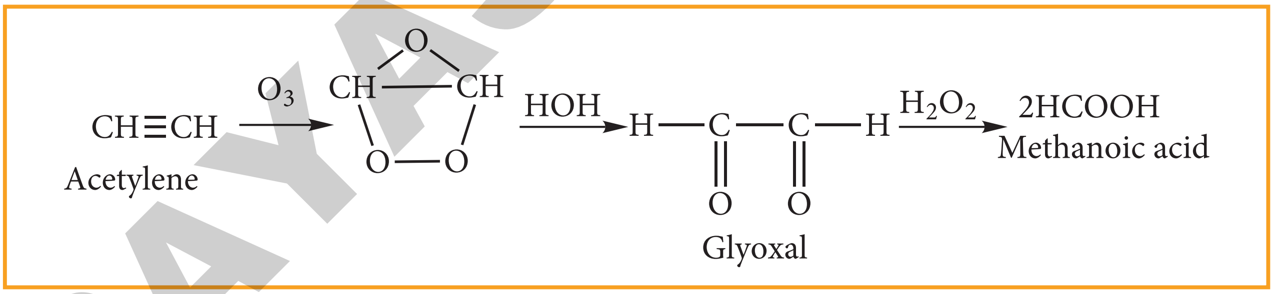
iv) Addition Of Water:

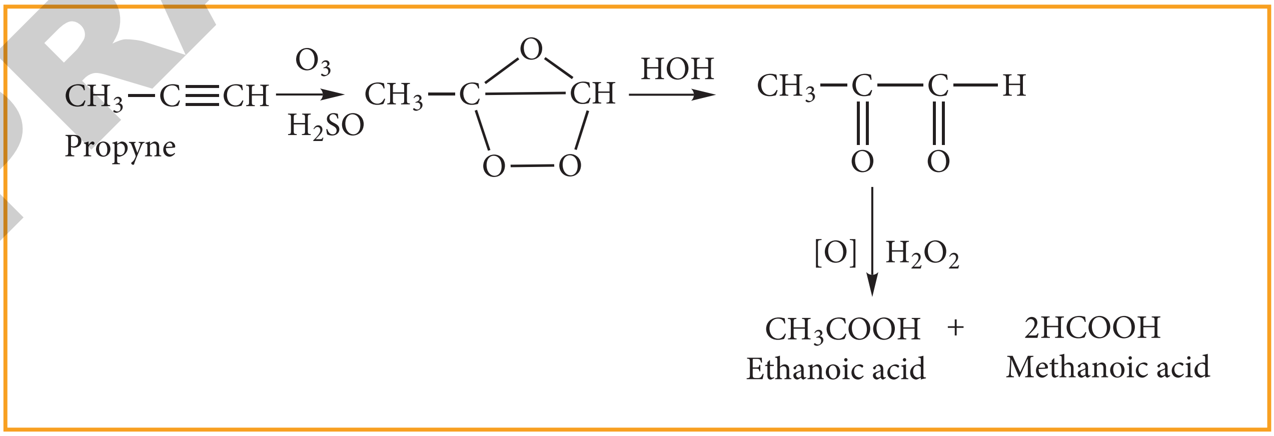
Alkynes undergo hydration on warming with mercuric sulphate and dilute H_2SO_4 at 333K to form carbonyl compounds.



3. Ozonolysis:

Ozone adds to carbon-carbon triple bond of alkynes to form ozonides. The ozonides are hydrolyzed by water to form carbonyl compounds. The hydrogen peroxide (H_2O_2) formed in the reaction may oxidise the carbonyl compound to carboxylic acid.



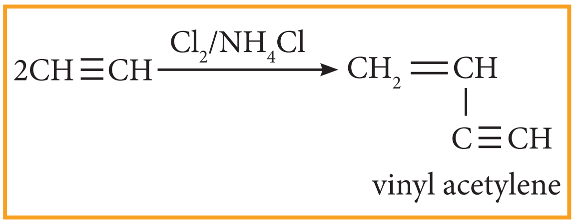


4. Polymerisation:

Alkyne undergoes two types of polymerisation reaction

(i) Linear Polymerisation:

Ethyne forms linear polymer, when passed into a solution of cuprous chloride and ammonium chloride.

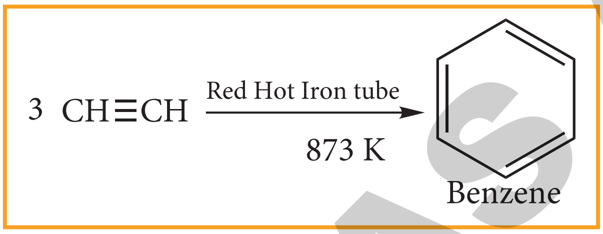


$$2CH\equiv CH \xrightarrow{Cl_2/NH_4Cl} \underset{\underset{C\equiv CH}{|}}{CH_2=CH}$$

vinyl acetylene

(ii) Cyclic Polymerisation:

Ethyne undergoes cyclic polymerization on passing through red hot iron tube. Three molecules of ethynepolymerises to benzene.



13.4.4 Uses of Alkynes

1) Acetylene is used in oxy acetylene torch used for welding and cutting metals.

2) It is used for manufacture of PVC, polyvinyl acetate, polyvinyl ether, orlon and neoprene rubbers.

Evaluate Yourself

18) $CH\equiv C-CH_3 + H_2 \xrightarrow{Pt} ? \xrightarrow{H_2} ?$

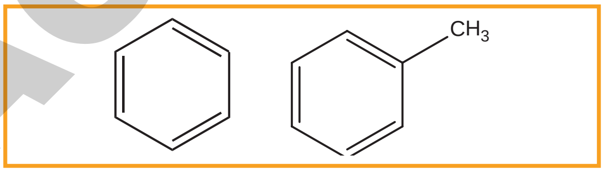
13.5. Aromatic Hydrocarbons

Take a moment and think of substances that have a strong fragrance. What kind of things come to your mind?

Perfume, Vanila or cinnamon? They smell differently, they have something in common. These substances are made of aromatic compounds [Greek: Aroma-Pleasant smelling]. However, some compounds are chemically aromatic but do not have distinct smell. The aromatic hydrocarbons are classified depending upon number of rings present in it.

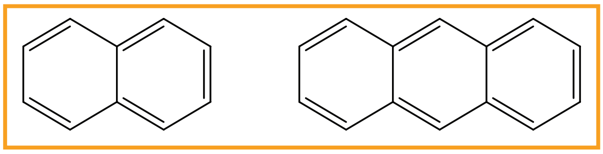
(i) Monocyclic aromatic hydrocarbon (MAH)

(Ex) Benzene (C_6H_6) and Toluene (C_7H_8)



(ii) Polycyclic aromatic hydrocarbon(PAH)

(Ex) Naphthalene ($C_{10}H_8$) and Anthracene ($C_{14}H_{10}$)



Evaluate Yourself

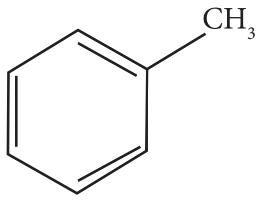
19) Calculate the number of rings present in $C_{18}H_{12}$.

13.5.1. Nomenclature and Isomerism

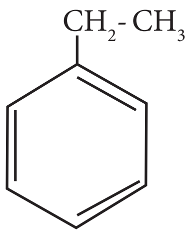
- We have already discussed about nomenclature of aromatic hydrocarbons in Unit:11. The first member of aromatic hydrocarbon is benzene (C_6H_6)

represented by a regular hexagon with a circle inscribed in it.

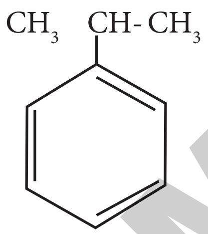
- Since, all the six hydrogen atom in benzene are equivalent, it can give only one mono-substituted compound (Ex) methyl benzene (C_6H_5-CH_3) which named as toluene.



tolune

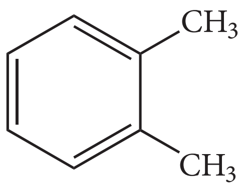


ethylbenzene

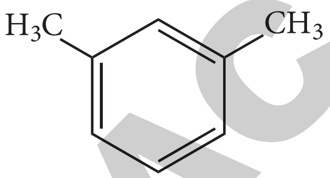


cumene
isopropylbenzene

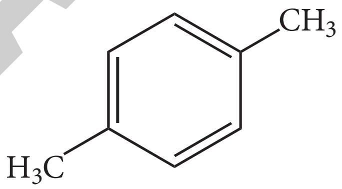
- When di substitution occurs either by a similar monovalent atom or two different atoms or groups in benzene, then three different position isomers are possible. Their relative positions are indicated as ortho (1,2), meta (1,3) and para (1,4). For example, consider dimethyl benzene which is named as xylene.



o-xylene
1,2-dimethylbenzene



m-xylene
1,3-dimethyl benzene



p-xylene
1,4-dimethyl benzene

Evaluate Yourself

20) write all possible isomers for an aromatic benzenoid compound having the molecular formula C_8H_{10}

21) write all possible isomers for a monosubstituted aromatic benzenoid compound having the molecular formula C_9H_{12}

13.5.2. Aromaticity

Huckel proposed that aromaticity is a function of electronic structure. A compound may be aromatic, if it obeys the following rules

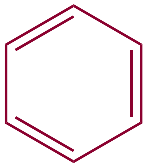
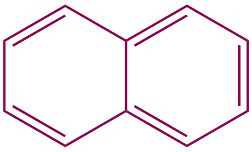
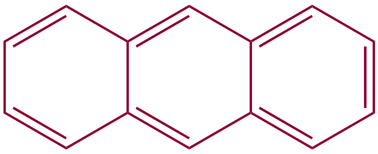
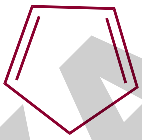
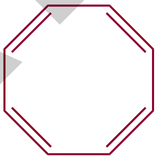
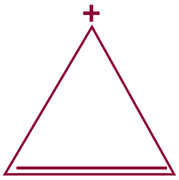
(i) The molecule must be co-planar

(ii) Complete delocalization of π electron in the ring

(iii) Presence of (4n+2) π electrons in the ring where n is an integer (n=0,1,2….)

This is known as Huckel's rule.

Some of the examples for Huckel rule

1.	 **Benzene**	(i) The benzene is a planar molecule (ii) It has six deloclaised π electorns (iii) $4n + 2 = 6$ $4n = 6- 2$ $4n = 4$ $n = 1$ it obeys Huckel's $(4n+2)$ π electron rule with $n = 1$ hence, benzene is aromatic.
2.	 **Naphthalene**	(i)Naphthalene has a planar ring structure (ii) It has 10 delocalised π electrons (ii) $4n + 2 = 10$ $4n = 10- 2$ $4n = 8$ $n = 8/4 = 2$ hence, naphthalene is aromatic.
3.	 **Anthracene**	It has a planar ring structure with 14 delocalised π electrons. Applying Huckel's rule $4n+2=14\pi$ electrons. $n=3$ Hence it is an aromatic compound
4.	 **Cyclo penta diene**	(i) It has planar structure (ii) It has four π electron but the π electrons are not delocalised and hence it is not an aromatic compound
5.	 **Cyclooctatetraene**	molecule is non planar and hence it is not an aromatic compund
6	 **Cyclopropenylcation**	(i) cyclopropenyl cation has planar structure (ii) It has 2 delocalised π electron. (ii) $4n + 2 = 2$ $4n = 0$ $n = 0$ (an interger) and hence it is aromatic compound.

13.5.3. Structure of benzene:

1. Molecular formula:v

Elemental Analysis and molecular weight determination have proved that the molecular formula of benzene is C_6H_6. This indicates that benzene is a highly unsaturated compound.

2. Straight chain structure not possible:

Benzene could be constructed as a straight chain or ring compound but it not feasible since it does not show the properties of alkenes or alkynes.for example, it did not decolourise bromine in carbon tetrachloride or acidified $KMnO_4$. It did not react with water in the presence of acid.

3. Evidence of cyclic structure:

I) substitution of benzene:

Benzene reacts with bromine in the presence of $AlCl_3$ to form mono bromobenzene.

$$C_6H_6 + 3Br_2 \xrightarrow{AlCl_3} C_6H_5Br + HBr$$

bromobenzene

Formation of only one monobromo compound indicates that all the six hydrogen atoms in benzene were identical. This is possible only if it has a cyclic structure of six carbons each containing one hydrogen.

Ii) addition of hydrogen:

Benzene can add on to three moles of hydrogen in the presence of nickel catalyst to give cyclohexane.

$$C_6H_6 + 3H_2 \xrightarrow{\text{Raney Ni}} C_6H_{12} + HBr$$

cyclohexane

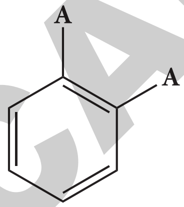
This confirms cyclic structure of benzene and the presence of three carbon-carbon double bond.

4. Kekule's structure of benzene:

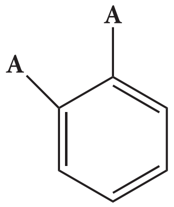
In 1865, August Kekule suggested that benzene consists of a cyclic planar structure of six carbon with alternate single and double bonds.

There were two objections:

(i) Benzene forms only one orthodisubstituted products whereas the Kekule's structure predicts two o-di substituted products as shown below.

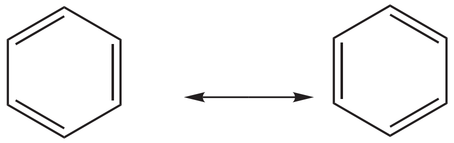


Presence of double bond between the substituents



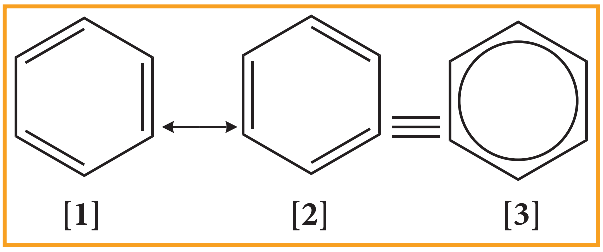
Presence of single bond between the substituents

(ii) Kekule's structure failed to explain why benzene with three double bonds did not give addition reactions like other alkenes.To overcome this objection, Kekule suggested that benzene was mixture of two forms (1 and 2)which are in rapid equilibrium.



5. Resonance description of benzene:

The phenomenon in which two or more structures can be written for a substance which has identical position of atoms is called resonance. The actual structure of the molecule is said to be resonance hybrid of various possible alternative structures. In benzene, Kekule's structures I & II represented the resonance structure, and structure III is the resonance hybrid of structure I &II



The structures 1 and 2 exist only in theory. The actual structure of benzene is the hybrid of two hypothetical resonance structures.

6. Spectrosscopic measurments:

Spectroscopic measurements show that benzene is planar and all of its carbon-carbon bonds are of equal length 1.40A°. This value lies between carbon-carbon single bond length 1.54A° and carbon-carbon double bond length 1.34A°.

7. Molecular orbital structre:

The structure of benzene is best described in terms of the molecular orbital theory. All the six carbon atoms of benzene are sp^2 hybridized. Six sp^2 hybrid orbitals of carbon leanerly overlap with six one is orbitals of hydrogen atoms to form six C - H sigma bonds. Overlap between the remaining sp^2 hybrid orbitals of carbon forms six C-C sigma bonds.

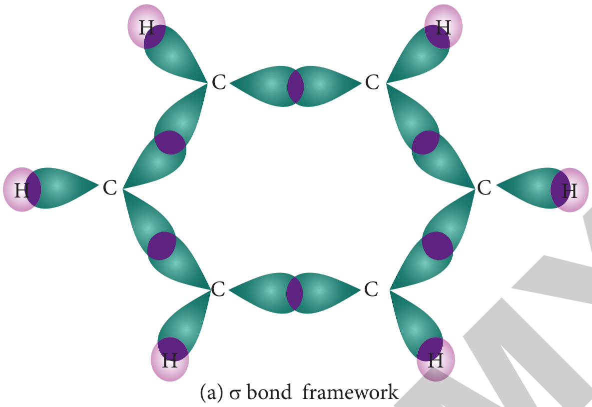


Figure13.6. Formation of Sigma bond in benzene

All the σ bonds in benzene lie in one plane with bond angle 120°. Each carbon atom in benzene possess an un hybridized p-orbital containing one electron. The lateral overlap of their p-orbital produces 3 π- bond The six electrons of the p-orbitals cover all the six carbon atoms and are said to be delocalised. Due to delocalization, strong π-bond is formed which makes the molecule stable. Hence unlike alkenes and alkynes benzene undergoes substitution reactions rather addition reactions under normal conditions.

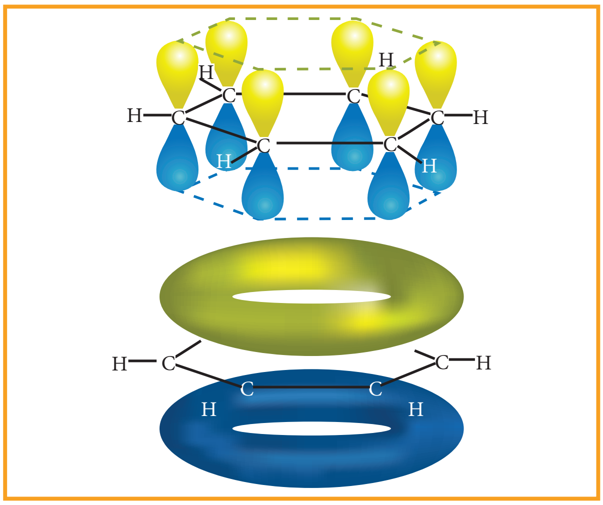
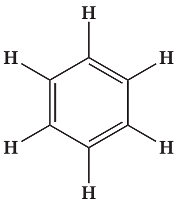


Figure 13.7. All carbon atoms have The delocalized π Mo is formed by

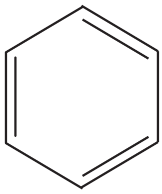
p orbitals the overlap of six p-orbitals

8. Representation of benzene:

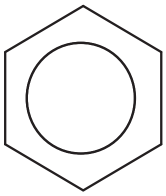
Hence, there are three ways in which benzene can be represented.



Expanded form



Kekule structure



Short hand representation

Benzene and its homologous series

Benzene and its homologous series are colorless liquids with pleasant odour .They are lighter than water and insoluble in it. Their vapours are highly flammable, and volatile and toxic in nature.

13.5.4. Sources of aromatic compound:

- Benzene and other aromatic compound are obtained from coal tar and petroleum
- It can also be prepared in laboratory using some simple aliphatic compounds

1. Preparation of benzene

(i) industrial preparation of benzene from coal tar :

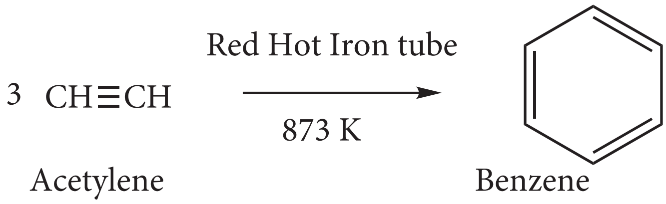
Coal tar is a viscous liquid obtained by the pyrolysis of coal. During fractional distillation, coal tar is heated and distills away its volatile compounds namely benzene, toluene, xylene in the temperature range of 350 to 443 K. These vapours are collected at the upper part of the fractionating column (Table 13.5.)

TABLE.13.5COMPENENTS OF DISTILLATION OF COAL TAR

NAME OF THE FRACTION	TEMPERATURE RANGE	NAME OF THE COMPENENTS
1. Crude light oil	350 - 443 K	Benzene, Toluene, Xylenes
2. Middle oil	443 - 503 K	Phenol, Naphthalene
3. Heavy oil	503 - 543 K	Naphthalene, Cresol
4. Green oil	543 - 633 K	Anthracene
5. Pitch	Alone 633 K	Residue

(ii) from acetylene.

Acetylene on passing through a red –hot tube trimerises to give benzene. We have already studied this concept in polymerization of alkynes.



(iii) Laboratory Methods Of Preparing Benzene And Toluene

(a) Decarboxylaation Of Aromatic Acid.

When sodium benzoate in heated with sodalime, benzene vapours distil over.

$$\underset{\text{sodium benzoate}}{C_6H_5COONa} + NaOH \xrightarrow{CaO} \underset{\text{benzence}}{C_6H_6} + Na_2CO_3$$

(b) Preparation Of Benzene From Phenol

When phenol vapours are passed over zinc dust, then it is reduced to benzene.

$$\underset{\text{phenol}}{C_6H_5OH} + Zn \longrightarrow C_6H_6 + ZnO$$

(c) Wurtz – Fittig Reaction:

When a solution of bromo benzene and iodo methane in dry ether is treated with metallic sodium, toluene is formed.

$$\underset{\text{bromo benzene}}{C_6H_5Br} + 2Na + \underset{\text{iodo methane}}{ICH_3} \xrightarrow{ether} \underset{\text{toluene}}{C_6H_6CH_3} + NaBr + NaI$$

(d) Friedel Craft's Reaction:

When benzene is treated with methyl chloride in the presence of anhydrous aluminium chloride, toluene is formed.

$$\underset{\text{Benzene}}{C_6H_6} + \underset{\text{chloromethane}}{CH_3Cl} \xrightarrow{\text{anhydrous } AlCl_3} \underset{\text{toluene}}{C_6H_5CH_3} + HCl$$

Evaluate Yourself

22) How benzene can be prepared by Grignard Reagent

13.4. Physical Properties:

- Benzene is a colourless liquid, insoluble in water and solution alcohol, ether and chloroform.

- It bums with luminous sooty flame in contrast to alkanes and alkenes which usually burn with bluish flame.
- Their vapours are highly toxic which an inhalation produce loss of consciousness.

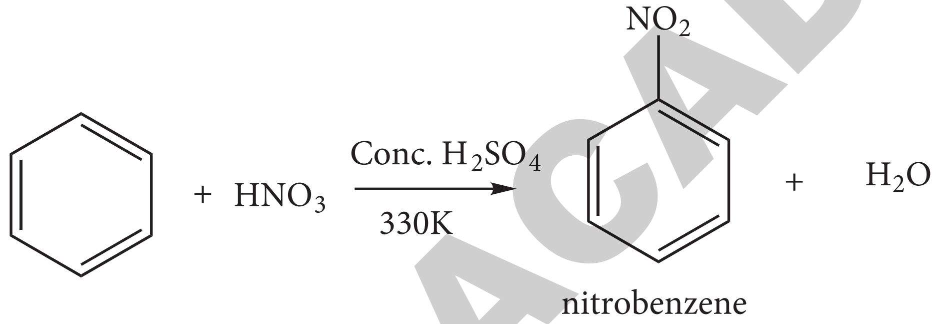
13.5. Chemical Properties:

1. Benzene contains delocalized π-electrons which make the ring to act as an electro rich centre. So electrophilic substitution reaction occurs in benzene.
2. Benzene ring is stabilized by delocalized π electrons. Though it is highly stable, it undergoes addition and oxidation reaction under specific conditions.

1. Electrophilic Substitution Reaction

(a) Nitration:

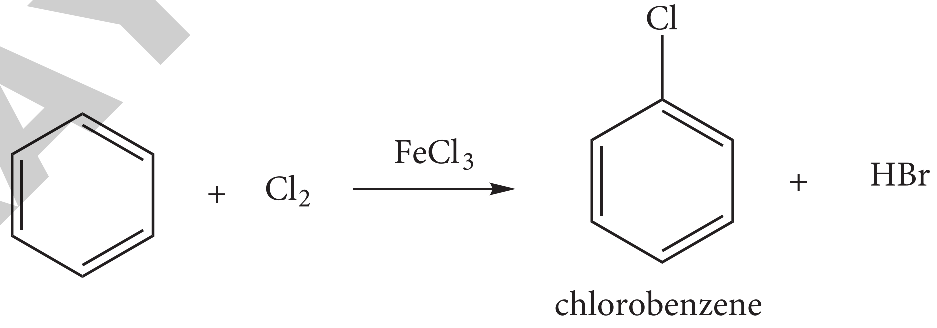
When benzene is heated at 330K with a nitrating mixture (Con. HNO_3 + Con. H_2SO_4), nitro benzene is formed by replacing are hydrogen atom by nitronium ion NO^{2+}(electrophile)



Concentrated H_2SO_4 is added to produce nitronium ion NO^{2+}

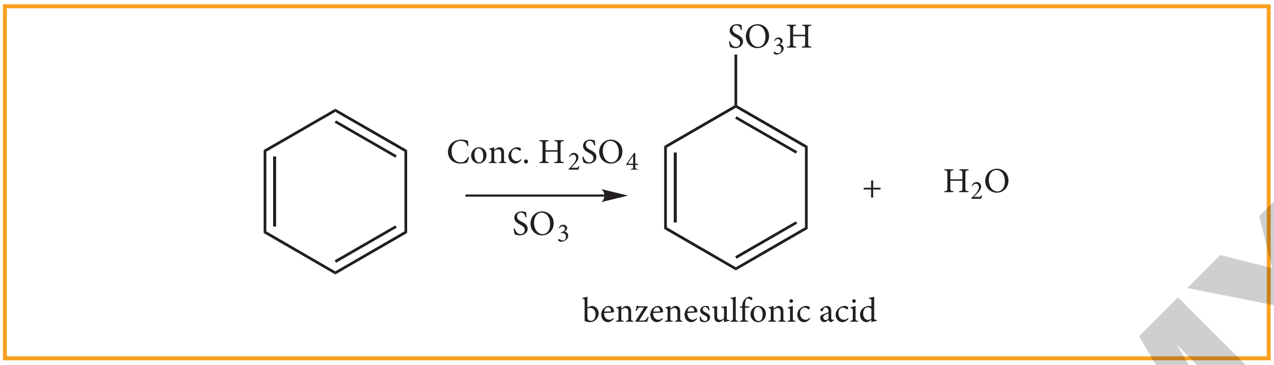
(b) Halogenation:

Benzene reacts with halogens (X_2=Cl_2, Br_2,) in the presence of Lewis acid such as $FeCl_3$, $FeBr_3$ or $AlCl_3$ and give corresponding halo benzene. In the absence of catalyst, Fluorine reactsvigoursly with benzene even in the absence of catalyst. However iodine is very inactive even in the presence of catalyst



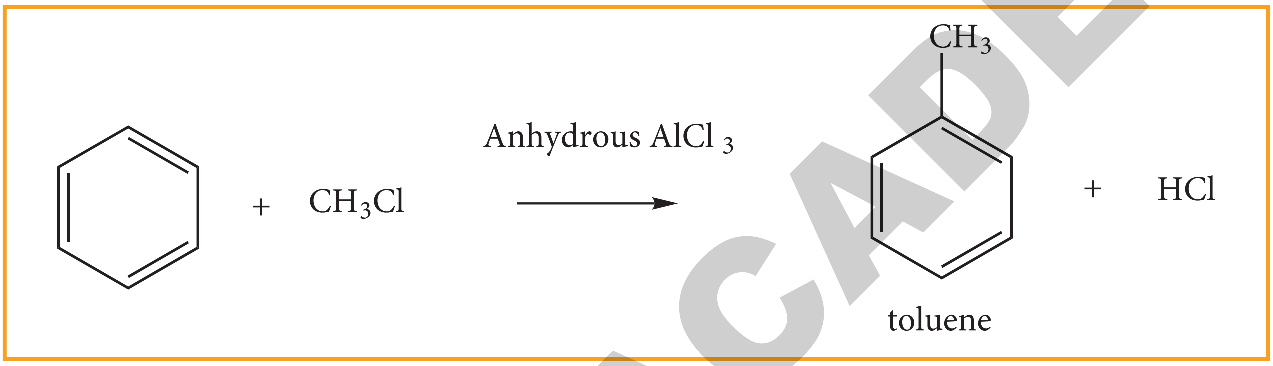
(c) Sulphonation:

Benzene reacts with fuming sulphuric acid (Con H_2SO_4 + SO_3) and gives benzene sulphonic acid. The electrophile SO_3 is a molecule. Although it does not have positive charge, it is a strong electrophile. This is because the octet of electron around the sulphur atom is not reached. The reaction is reversible and desulphonation occurs readily in aqueous medium.



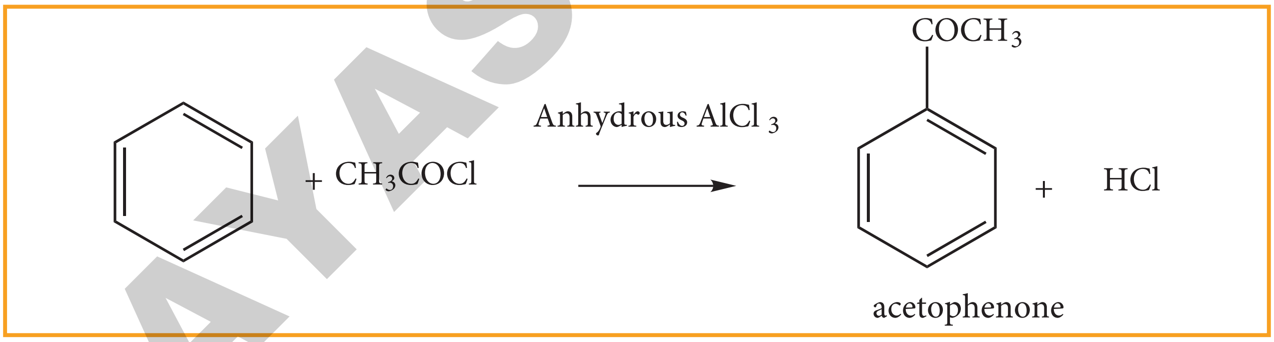
(d) Friedel Craft's Alkylation: (Methylation)

When benzene is treated with analkyl halide in the presence of only AlCl3, alkyl benzene is formed.



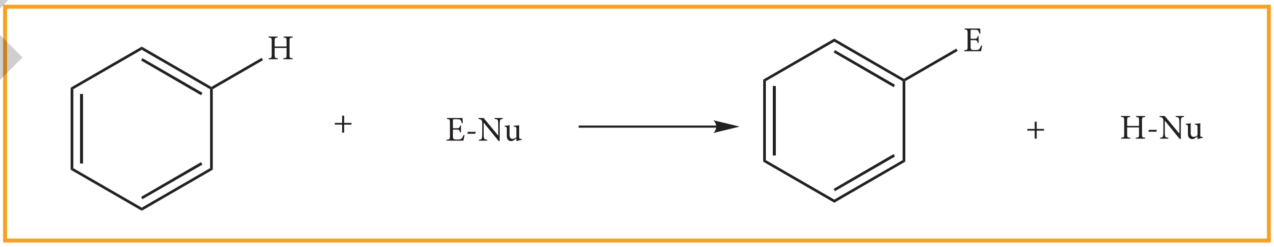
(e) Friedel Craft's Acylation : Acetylation

When benzene is treated withacetylchloride in the presence of AlCl3, acyl benzene is formed.



(f) Electrophilic Subitution Reactions: Mechanism

Benzene undergoes electrophilic substitution reaction because it is an electron-rich system due to delocalised π electron. So it a easily attacked by electrophilies and gives substituted products.



Mechanism:

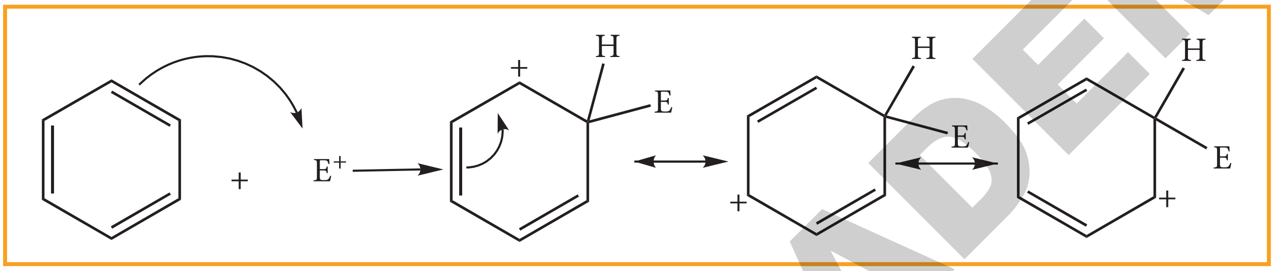
Step: 1

Formulation of the electrophile

$$E - Nu + Catalyst \longrightarrow E^{+} + Nu\text{-}Catalyst$$

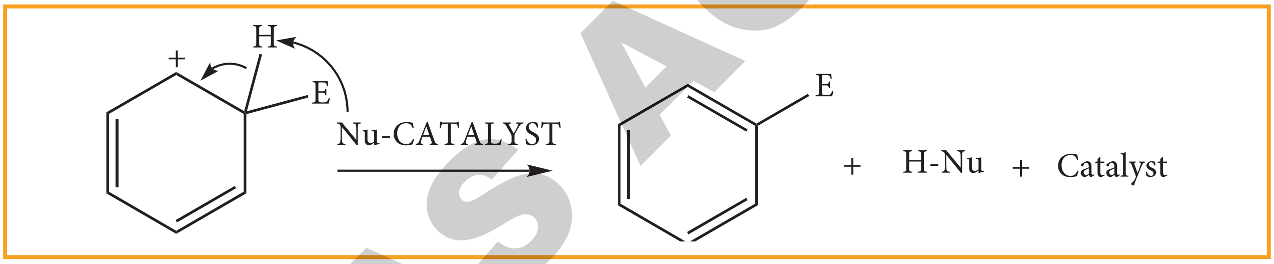
Step:2

The electrophile attacks the aromatic ring to form a carbocation intermediate which is stabilized by resonance.



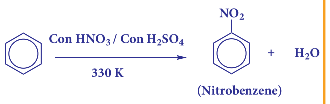
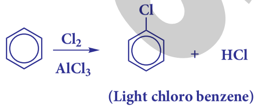
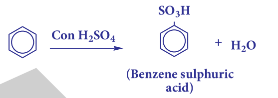
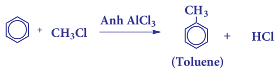
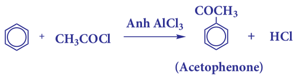
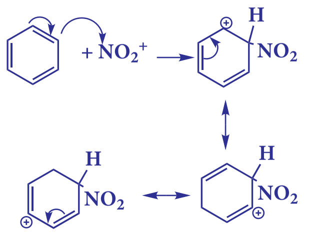
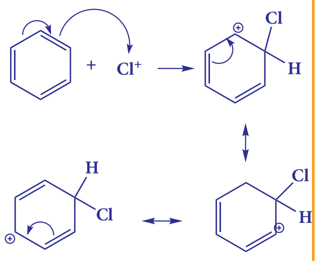
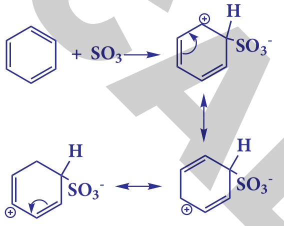
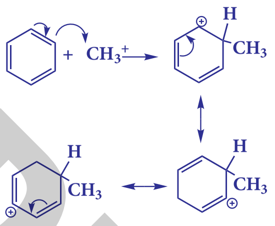
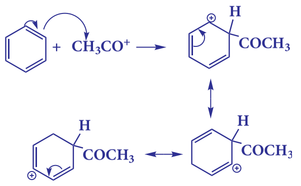
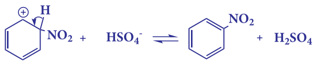
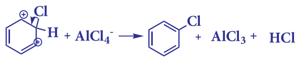
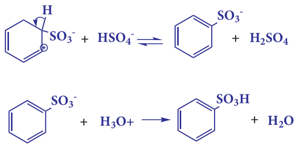
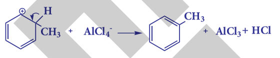
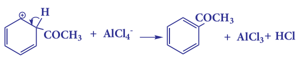
Step: 3

Loss of proton gives the substitution product.



Evaluate Yourself

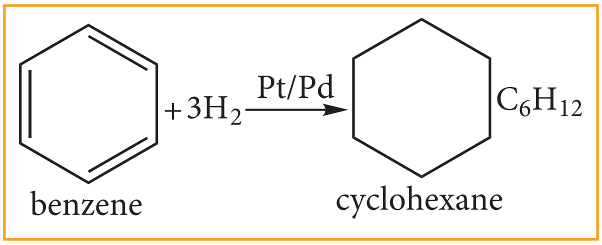
21) Why benzene undergoes electrophilic substitution reaction where asalkenes undergoes addition reaction?

Types of reaction	NITRATION	HALOGENATION	SULPHONATION	FRIEDEL CRAFT'S ALKYLATION	FRIEDEL CRAFT'S ACYLATION
Reagents	Con HNO_3 + Con H_2SO_4	X_2 / Al X_3	Fuming H_2SO_4 $CH_2SO_4 + SO_3$	CH_3Cl + anhydrous $AlCl_3$	CH_3COCl + anhydrous $AlCl_3$
Electro-phile	$-NO_2^+$	$-X^+$ (X = Cl, Br)	$-SO_3$ (Neutral electrophile)	$-\overset{\oplus}{C}H_2$	$-\overset{\oplus}{C}OCH_3$
Over all reaction	 (Nitrobenzene)	 (Light chloro benzene)	 (Benzene sulphuric acid)	 (Toluene)	 (Acetophenone)
Mechanism Step 1	$NO_3+H_2SO_4 \longrightarrow \overset{\oplus}{N}O_2+HSO_4+H_2O$	$AlCl_3 + Cl_2 \longrightarrow \overset{+}{Cl} + \overset{-}{A}lCl_4^-$	$2H_2SO_4 \longrightarrow \overset{+}{H_3}O+SO_3+H\overset{-}{S}O_4$	$AlCl_3+CH_3Cl \rightarrow \overset{+}{C}H_3 + \overset{-}{A}lCl_4$	$AlCl_3+CH_3COCl \rightarrow CH_3\overset{+}{C}O + \overset{-}{A}lCl_4$
Step 2					
STEP 3					

(ii) Addition Reaction:

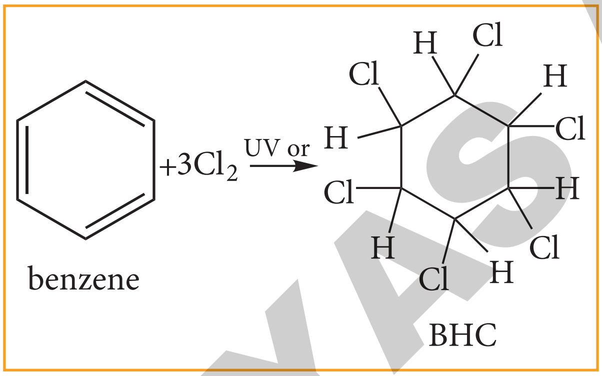
a. Hydrogenation of benzene:

Benzene reacts with hydrogen in the presence of Platinum or Palladium to yield Cyclohexane. This is known as hydrogenation.



b. Chlorination of Benzene:

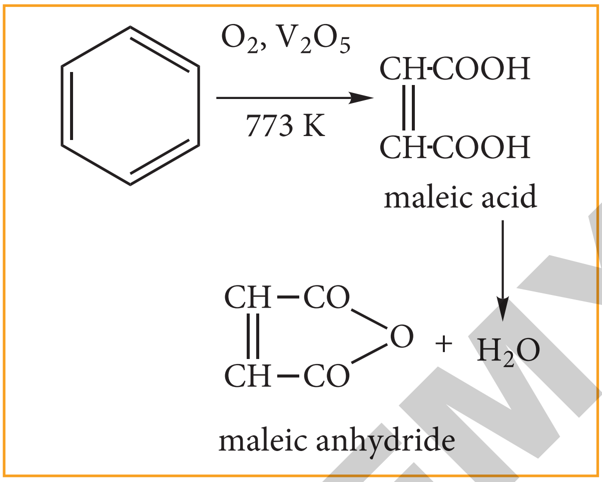
Benzene reacts with three molecules of Cl_2 in the presence of sun light or UV light to yield Benzene Hexa Chloride (BHC) $C_6H_6Cl_6$. This is known as gammaxane or Lindane which is a powerful insecticide.



(Iii) Oxidation:

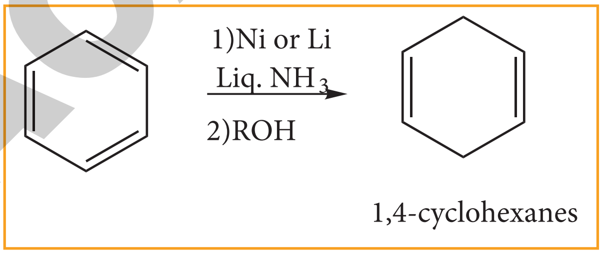
a. Vapour – phase oxidation:-

Although benzene is very stable to strong oxidizing agents, it quickly undergoes vapour phase oxidation by passing its vapour mixed with oxygen over V_2O_5 at 773k. The ring breaks to give maleic anhydride.



b. Birch reduction:

Benzene can be reduced to 1, 4-cyclohexadiene by treatment with Na or Li in a mixture of liquid ammonia and alcohol. It is the convenient method to prepare cyclic dienes.



Evaluate Yourself

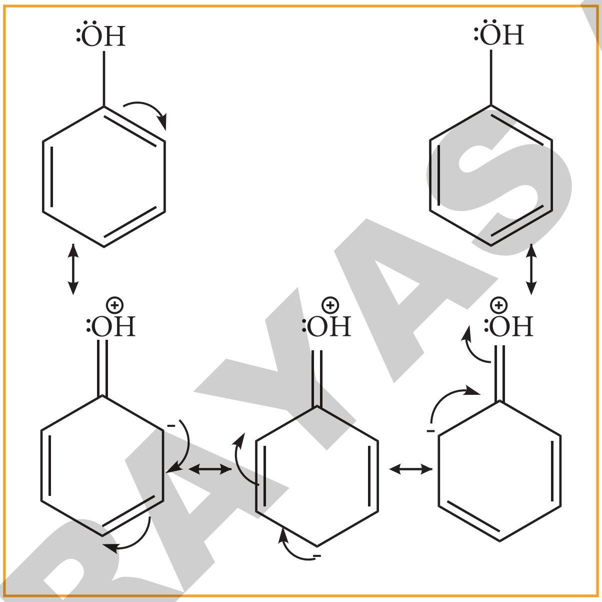
24) Convert Ethyne to Benzene and name the process.

13.5.1 directive influence of a functional group in monosubtituted benzene:

When mono substituted benzene undergoes an electrophilic substitution reaction, the rate of the reaction and the site of attack of the incomeing electrophile depends on the functional group already attached to it. Some groups increase the reactivity of benzene ring and are known as activating groups. While others which decrease the reactivity are known as deactivating groups. We further divide these groups into two categories depending on the way they influence the orientation of attack by the incoming groups. Those which increases electron density at 'ortho' and 'para' position are known as ortho-para directors while those which increase electron density at 'meta' position is known as meta-directors. Some examples of directive influence of functional groups in mono-substituted benzene are explained below.

Ortho and para directing groups

All the activating groups are 'ortho-para' directors. Example –OH, -NH_2, -NHR, -$NHCOCH_3$, -OCH_3-CH_3 – C_2H_5 etc. Let us consider the directive influences of phenolic (-OH) group. Phenol is the resonance hybrid of following structures.

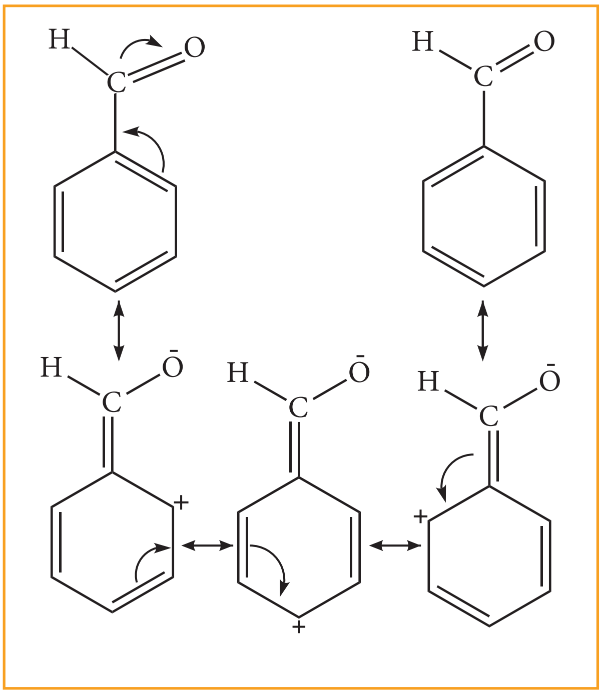


In these resonance structures, the (-) charge residue is present on ortho and para position of ring structure. It is quite evident that the lone pair of electron on the atom which is attached to the ring involves in resonance and makes the ring more electron rich than benzene. The electron density at ortho and parapositions increases as compared to the meta position. Therefore phenolic group activates the benzene ring for electrophilic attack at 'ortho' and 'para positions and hence –OH group is an ortho-para director and activator.

In aryl halides, the strong –I effect of the halogens (electron withdrawing tendency) decreases the electron density of benzene ring, thereby deactivating for electrophilic attack. However the presence of lone pair on halogens involved in the resonance with pi electrons of benzene ring, increases electron density at ortho and para position. Hence the halogen group is an ortho-para director and deactivator.

META DIRECTING GROUPS

Generally all deactivating groups are meta-directors. For example –NO_2, -CN, -CHO, -COR, -COOH, -COOR, -SO_3H etc. Let us consider the directive influence of aldehyde (-CHO) group. Benz aldehyde is the resonance hybrid of following structures.



In these resonance structures, the (+) charge residues is present on the ring structure. It is quite evident that resonance delocalizes the positive charge on the atoms of the ring, making the ring less electron rich than benzene. Here overall density of benzene ring decreases due to –I effect of –CHO group there by deactivating the benzene for electrophilic attack. However resonating structure shows that electron density is more in meta position. Compared to o & p-position. Hence –CHO group is a meta-director and deactivator.

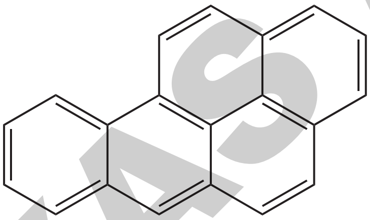
Evaluate Yourself

25) Toluene undergoes nitration easily than benzene.Why?

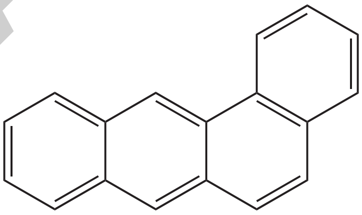
13.5.2. Carcinogenity and toxicity

Benzene and polycyclic aromatic hydrocarbons (PAH) are ubiquitous environmental pollutants generated during incomplete combustion of coal oil, petrol and wood. Some PAH originate from open burning, natural seepage of petroleum and coal deposits and volcanic activities. They are toxic, mutagenic and carcinogenic. It has hematological. immunological and neurological effect on humans. They are radiomimetic and prolonged exposure leads to genetic damage.Some of the examples of PAH are.

"L" shaped polynuclear hydrocarbons are much more toxic & carcinogenic

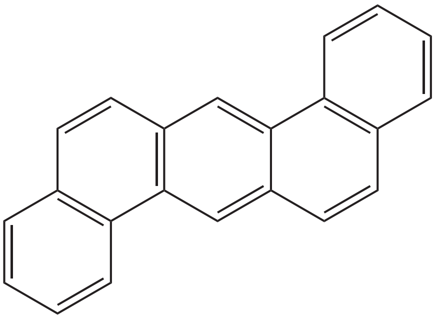


1,3- Benzpyrene



1,3- Benzanthracine

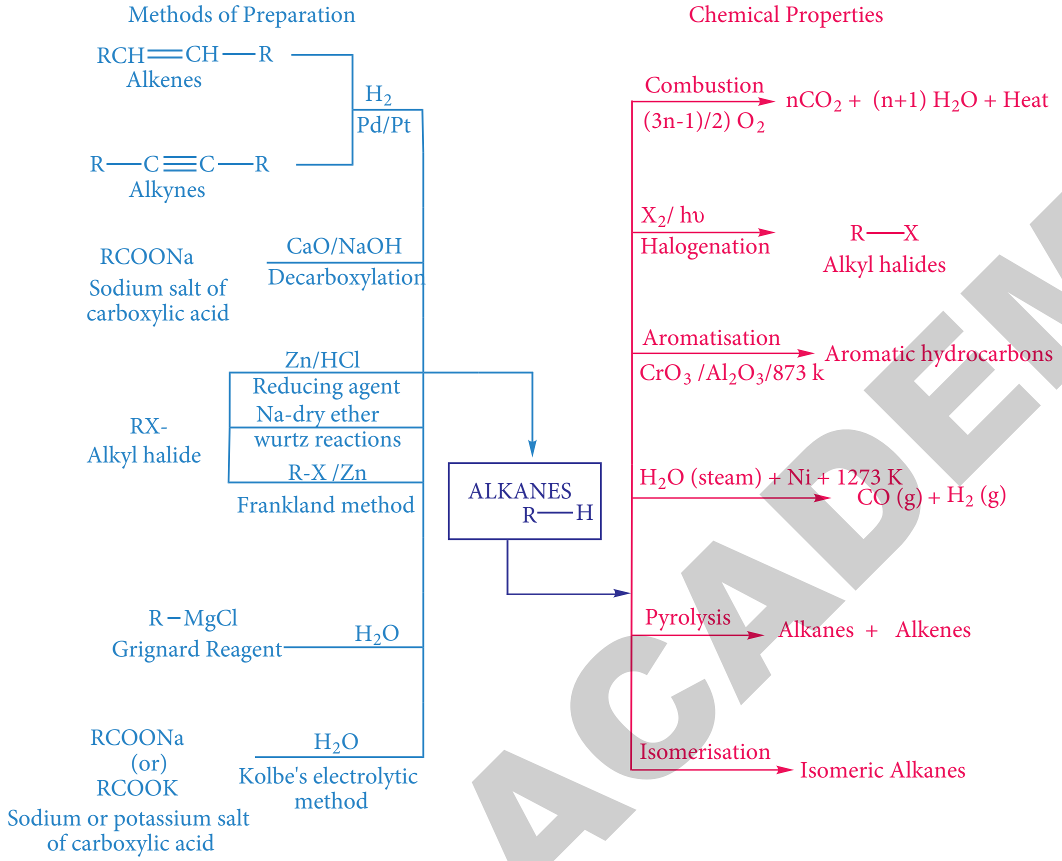
Found in cigarette smoke Found in tobacco and cigarette and charcoal boiled food

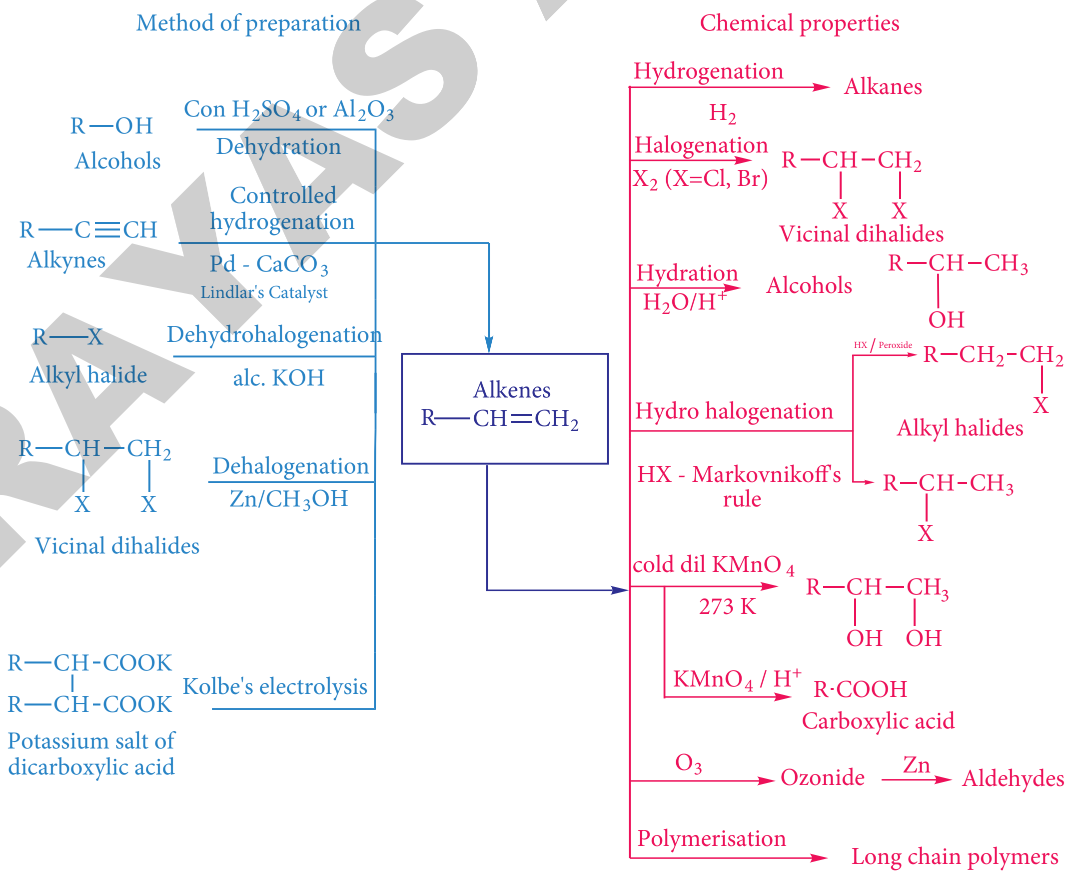


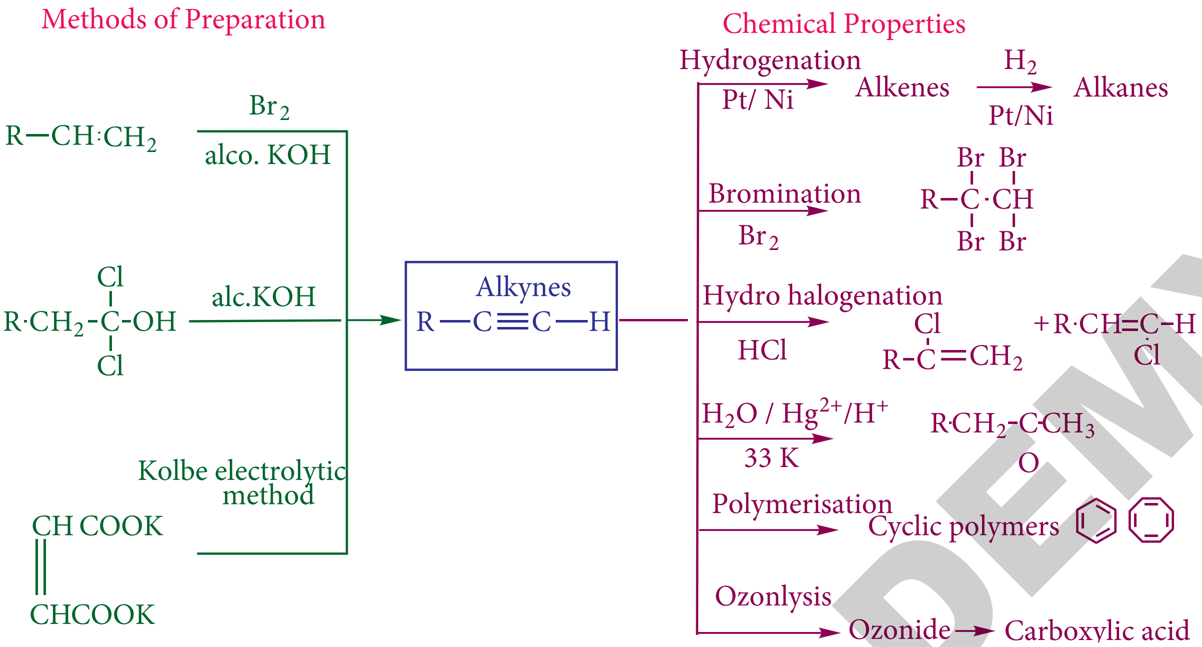
1,2,5,6 dibenzanthracene

Found in gasoline exhaust and barbaccued food

FLOWCHART AND REACTION SUMMARY OF HYDROCARBON






Methods of Preparation
R—CH:CH₂
Br₂
alco. KOH
Cl
R·CH₂-C-OH
Cl
alc.KOH
Kolbe electrolytic method
CH COOK
CHCOOK
Alkynes
R—C≡C—H
Chemical Properties
Hydrogenation
Pt/ Ni
Alkenes
H₂
Pt/Ni
Alkanes
Bromination
Br₂
Br Br
R—C·CH
Br Br
Hydro halogenation
HCl
Cl
R-C=CH₂
+R·CH=C-H
Cl
H₂O / Hg²⁺/H⁺
33 K
R·CH₂-C-CH₃
O
Polymerisation
Cyclic polymers
Ozonlysis
Ozonide
Carboxylic acid

Evaluation

1. The correct statement regarding the comparison of staggered and eclipsed conformations of ethane, is (NEET)

   a) the eclipsed conformation of ethane is more stable than staggered conformation even though the eclipsed conformation has torsional strain.

   b) the staggered conformation of ethane is more stable than eclipsed conformation, because staggered conformation has no torsional strain.

   c) the staggered conformation of ethane is less stable than eclipsed conformation, because staggered conformation has torsional strain.

   d) the staggered conformation of ethane is less stable than eclipsed conformation, because staggered conformation has no torsional strain.

2. $C_2H_5\ Br + 2Na \xrightarrow{\text{dry ether}} C_4H_{10} + 2NaBr$ The above reaction is an example of which of the following

   a) Reimer Tiemann reaction

   b) Wurtz reaction

   c) Aldol condensation

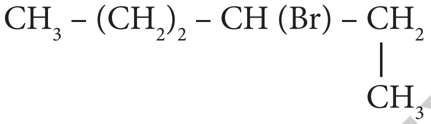
   d) Hoffmann reaction

3. An alkyl bromide (A) reacts with sodium in ether to form 4, 5– diethyloctane, the compound (A) is

   a) $CH_3\ (CH_2)_3\ Br$

   b) $CH_3(CH_2)_5\ Br$

   c) $CH_3(CH_2)_3\ CH(Br)CH_3$

   d) 

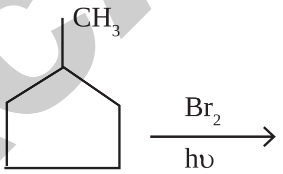
   $CH_3-(CH_2)_2-CH(Br)-\underset{CH_3}{\underset{|}{CH_2}}$

4. The C – H bond and C – C bond in ethane are formed by which of the following types of overlap

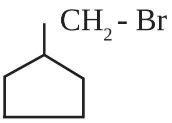
   a) $sp^3 - s$ and $sp^3 - sp^3$
   b) $sp^2 - s$ and $sp^2 - Sp^2$

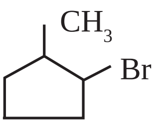
   c) sp – sp and sp – sp
   d) p – s and p – p

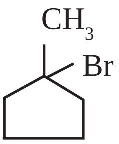
5. In the following reaction,

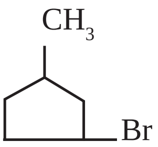


The major product obtained is

a) 

b) 

c) 

d) 

6. Which of the following is optically active

   a) 2 – methyl pentane

   b) citric acid

   c) Glycerol

   d) none of of these

7. The compounds formed at anode in the electrolysis of an aquous solution of potassium acetate are

a) CH_4 and H_2

b) CH_4 and CO_2

c) C_2H_6 and CO_2

d) C_2H_4 and Cl_2

8. The general formula for cyclo alkanes

a) C_nH_n b) C_nH_{2n}

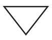
c) $C_n H_{2n-2}$ d) $C_n H_{2n+2}$

9. The compound that will react most readily with gaseous bromine has the formula (NEET)

a) C_3H_6 b) C_2H_2

c) C_4H_{10} d) C_2H_4

10. Which of the following compounds shall not produce propene by reaction with HBr followed by elemination (or) only direct elimination reaction (NEET)

a) 

b) $CH_3 - CH_2 - CH_2 - OH$

c) $H_2C = C = 0$

d) $CH_3 - CH_2 - CH_2Br$

11. Which among the following alkenes on reductive ozonolysis produces only propanone ?

a) 2 – Methyl propene

b) 2 – Methyl but – 2 - ene

c) 2, 3 – Dimethyl but – 1 – ene

d) 2, 3 – Dimethyl but – 2 – ene

12. The major product formed when 2 – bromo – 2 – methyl butane is refluxed with ethanolic KOH is

a) 2 – methylbut – 2 – ene

b) 2 – methyl butan – 1 – ol

c) 2 – methyl but – 1 – ene

d) 2 – methyl butan – 2 – ol

13. Major product of the below mentioned reaction is,

$(CH_3)_2 C = CH_2 \xrightarrow{ICl}$

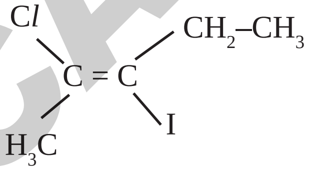
a) 2–chloro –1– iodo – 2 – methyl propane

b) 1–chloro–2–iodo–2–methylpropane

c) 1,2 – dichloro – 2 – methyl propane

d) 1, 2 – diiodo – 2 – methyl propane

14. The IUPAC name of the following compound is



a) trans–2–chloro–3–iodo – 2 – pentane

b) cis–3 – iodo – 4 – chloro – 3 – pentane

c) trans–3–iodo–4–chloro – 3 – pentene

d) cis–2 – chloro – 3 – iodo – 2 – pentene

15. Cis – 2 – butene and trans – 2 – butene are

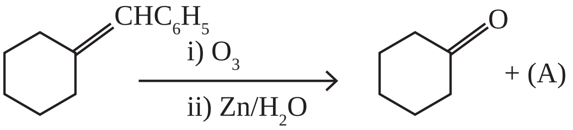
a) conformational isomers

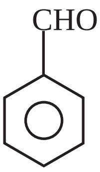
b) structural isomers

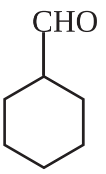
c) configurational isomers

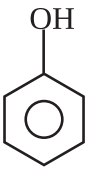
d) optical isomers

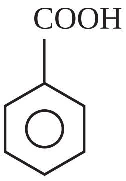
16. Identify the compound (A) in the following reaction

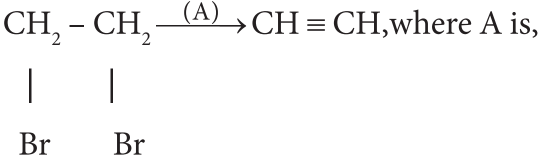


a) 

b) 

c) 

d) 

17. 
$\underset{Br}{CH_2}-\underset{Br}{CH_2}\xrightarrow{(A)}CH\equiv CH$, where A is,

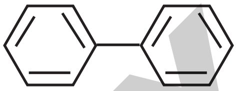
a) Zn
b) Conc H_2SO_4
c) alc. KOH
d) dil H_2SO_4

18. Consider the nitration of benzene using mixed con H_2SO_4 and HNO_3 if a large quantity of $KHSO_4$ is added to the mixture, the rate of nitration will be

a) unchanged
b) doubled
c) faster
d) slower

19. In which of the following molecules, all atoms are co-planar

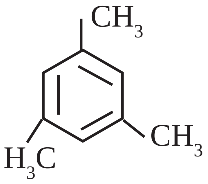
a) 

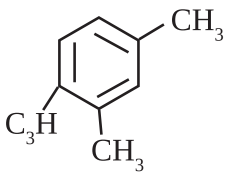
b) 

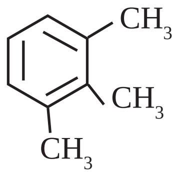
c) 

d) both (a) and (b)

20. Propyne on passing through red hot iron tube gives

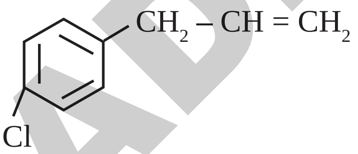
a) 

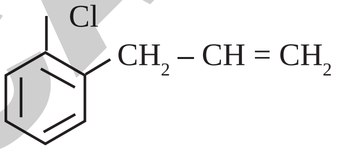
b) 

c) 

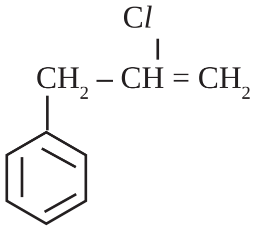
d) none of these

21. 

a) 

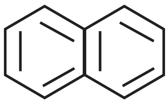
b) 

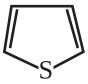
c) both (a) and (b)

d) 

22. Which one of the following is non aromatic ?

a) 

b) 

c) 

d) 

23. Which of the following compounds will not undergo Friedal – crafts reaction easily ? (NEET)

a) Nitro benzene

b) Toluene

c) Cumene

d) Xylene

24. Some meta-directing substituents in aromatic substitution are given. Which one is most deactivating ?

a) – COOH
b) – NO_2
c) – $C\equiv N$
d) – SO_3H

25. Which of the following can be used as the halide component for friedal - crafts reaction ?

a) Chloro benzene

b) Bromo benzene

c) chloro ethene

d) isopropyl chloride

26. An alkane is obtained by decarboxylation of sodium propionate. Same alkane can be prepared by

a) Catalytic hydrogenation of propene

b) action of sodium metal on iodomethane

c) reduction of 1 – chloro propane

d) reduction of bromomethane

27. Which of the following is aliphatic saturated hydrocarbon

a) C_8H_{18}
b) C_9H_{18}
c) C_8H_{14}
d) All of these

28. Identify the compound 'Z' in the following reaction

$$C_2H_6O \xrightarrow[623\ K]{Al_2O_3} X \xrightarrow{O_3} Y \xrightarrow{Zn/H_2O} (Z)$$

a) Formaldehyde

b) Acetaldehyde

c) Formic acid
d) none of these

29. Peroxide effect (Kharasch effect) can be studied in case of

a) Oct – 4 – ene
b) hex – 3 – ene
c) pent – 1 – ene
d) but – 2 – ene

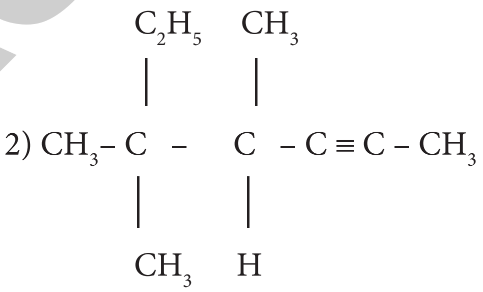
30. 2 – butyne on chlorination gives

a) 1 – chloro butane
b) 1, 2 – dichloro butane

c) 1, 1, 2, 2 – tetrachlorobutane
d) 2, 2, 3, 3 – tetra chloro butane

31. Give IUPAC names for the following compounds

1) $CH_3–CH=CH–CH=CH–C\equiv C–CH_3$



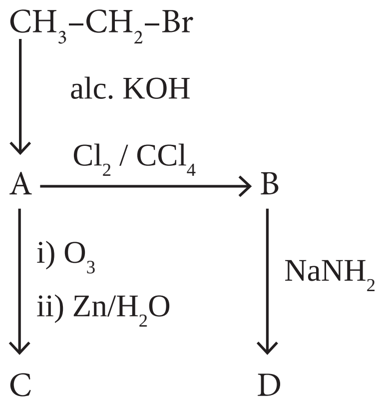
2) $CH_3-\overset{C_2H_5}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{H}{C}}-C\equiv C-CH_3$

3) $(CH_3)_3C-C\equiv C-CH(CH_3)_2$

4) ethyl isopropyl acetylene

5) $CH\equiv C-C\equiv C-C\equiv CH$

32. Identify the compound A, B, C and D in the following series of reactions



Write short notes on ortho, para directors in aromatic electrophilic substitution reactions.

33. How is propyne prepared from an alkyene dihalide ?

34. An alkylhalide with molecular formula $C_6H_{13}Br$ on dehydro halogenation gave two isomeric alkenes X and Y with molecular formula C_6H_{12}. On reductive ozonolysis, X and Y gave four compounds CH_3COCH_3, CH_3CHO, CH_3CH_2CHO and $(CH_3)_2$ CHCHO. Find the alkylhalide.

35. Describe the mechanism of Nitration of benzene.

36. How does Huckel rule help to decide the aromatic character of a compound.

37. Suggest the route for the preparation of the following from benzene.

1) 3 – chloro nitrobenzene

2) 4 – chlorotoluene

3) Bromo benzene

4) m - dinitro benzene

38. Suggest a simple chemical test to distinguish propane and propene.

39. What happens when isobutylene is treated with acidified potassium permanganate ?

40. How will you convert ethyl chloride in to

i) ethane ii) n – butane

41. Describe the conformers of n - butane.

42. Write the chemical equations for combustion of propane.

43. Explain Markow nikoff's rule with suitable example.

44. What happens when ethylene is passed through cold dilute alkaline potassium permanganate.

45. Write the structures of folowing alkanes.

1) 2, 3 – Dimethyl – 6 – (2 – methyl propyl) decane

2) 5 – (2 – Ethyl butyl) – 3, 3 – dimethyldecane

3) 5 – (1, 2 – Dimethyl propyl) – 2 – methylnonane

46. How will you prepare propane from a sodium salt of fatty acid ?

47. $CH_3 - CH\,(CH_3) - CH\,(OH) - CH_3$

$$\Big\downarrow \; H^+/\text{heat}$$

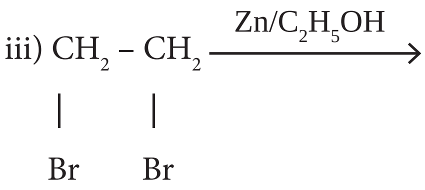
$$(A)\ \text{major product} \xrightarrow{HBr} (B)\ \text{major product}$$

Identify A and B

48. Complete the following :

i) 2 – butyne $\xrightarrow{\text{Lindlar Catalyst}}$

ii) $CH_2 = CH_2 \xrightarrow{I_2}$

iii) 

$$\underset{Br}{\underset{|}{CH_2}} - \underset{Br}{\underset{|}{CH_2}} \xrightarrow{Zn/C_2H_5OH}$$

iv) $CaC_2 \xrightarrow{H_2O}$

49. How will you distinguish 1 – butyne and 2 – butyne?

Unit 14 Haloalkanes and Haloarenes

Francois Auguste Victor Grignard

He a French chemist was awarded the noble prize for chemistry in 1912. He prepared and realised the usefulness of organo magnesium compounds. He took maths degree and eventually switched over organic chemistry while attempting to find the catalyst for the process of Methylation.

Learning Objectives

After learning this unit, students will be able to

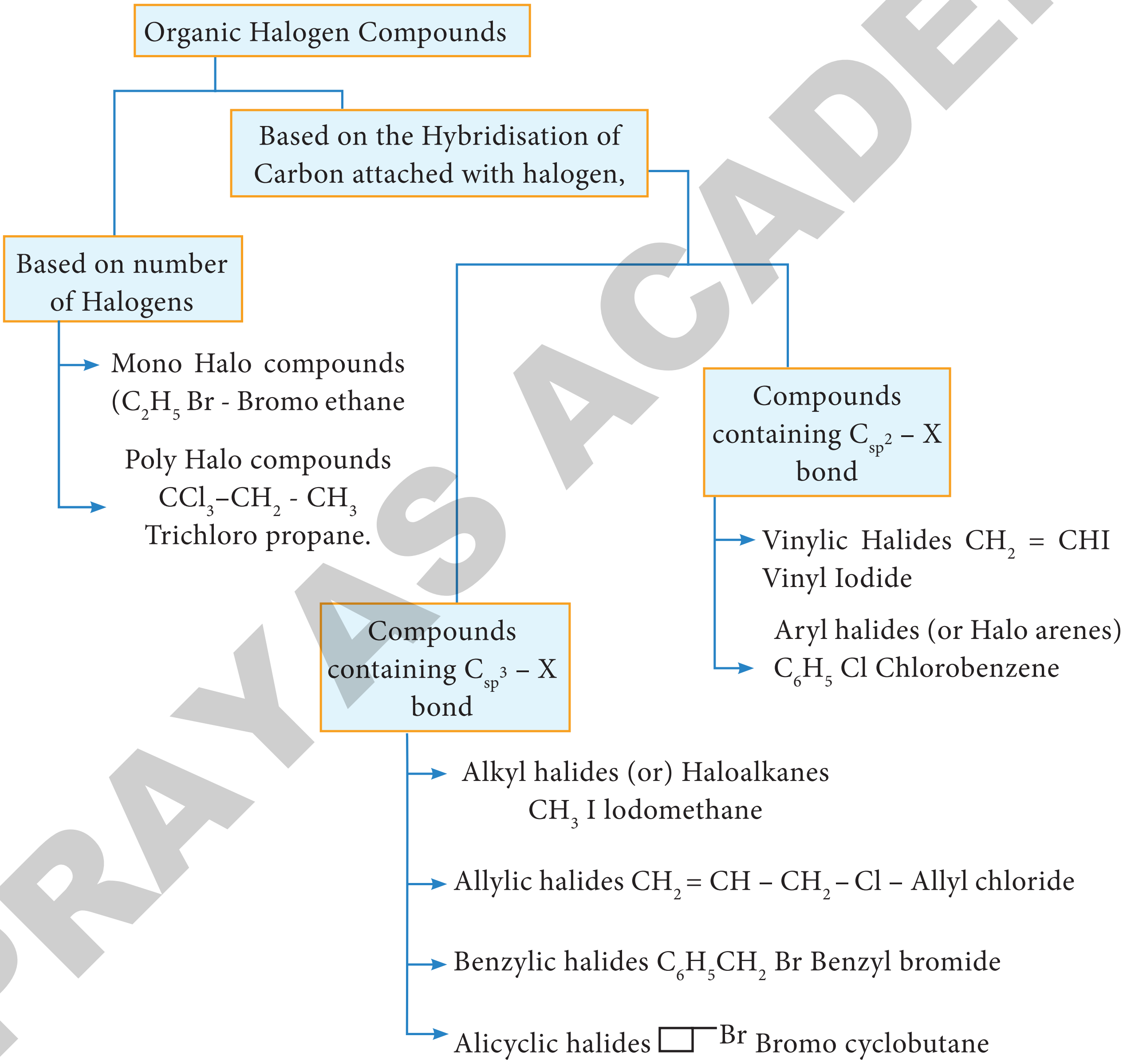
- classify the various organic halo compounds.
- name the organic halo compounds according to IUPAC system.
- recognise the nature of C-X bond.
- describe the general methods of preparation of haloalkanes and haloarenes
- explain the physical and chemical properties of haloalkanes and haloarenes.
- describe the mechanism of nucleophilic substitution and elimination reactions of halo organics
- explain the preparation and synthetic uses of grignard reagent.
- highlight the uses of poly halogen compounds.
- comprehend the environmental effect of poly halogen compounds.

14.1 INTRODUCTION

In the previous unit we learnt about the chemistry of hydrocarbons. In this unit us learn about organic compounds containing halogens. When one or more hydrogen atoms of aliphatic or aromatic hydrocarbons are replaced by the corresponding number of halogens like fluorine, chlorine, bromine or iodine, the resultant compounds are called either haloalkanes or halo arenes. They serve as starting materials for many organic synthesis.

Halogen substituted organic compounds are widely spread in nature and find application in our day to day life as well as in industry. Certain compounds like chloramphenicol produced by soil microbes are used in the treatment of typhoid; chloroquine is used in the treatment of malaria, halothane is used as an anesthetic, and halogenated solvents like trichloroethylene are used for cleaning electronic equipments.

14.2 Classification of organic halogen compounds

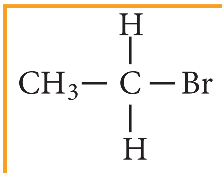


14.3 Haloalkanes

Mono halogen derivatives of alkanes are called haloalkanes. Haloalkanes are represented by general formula R – X, Where, R is an alkyl group (C_nH_{2n+1}) – and X is a halogen atom (X=F, Cl, Br or I). Haloalkanes are further classified into primary, secondary, tertiary haloalkane on the basis of type of carbon atom to which the halogen is attached.

Primary haloalkane

Examples:

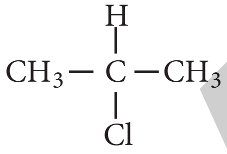


$$CH_3-\underset{\substack{|\\H}}{\overset{\substack{H\\|}}{C}}-Br$$

Bromoethane

(a 1° Haloalkane)

Secondary haloalkane

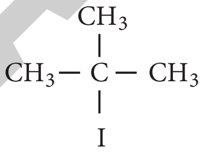


$$CH_3-\underset{\substack{|\\Cl}}{\overset{\substack{H\\|}}{C}}-CH_3$$

2- Chloro propane
(Iso propylchloride)

(a 2° Haloalkane)

Tertiary haloalkane



$$CH_3-\underset{\substack{|\\I}}{\overset{\substack{CH_3\\|}}{C}}-CH_3$$

2- Iodo - 2- methyl propane
(tert- Butyl iodide)

(a 3° Haloalkane)

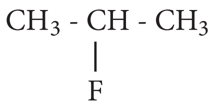
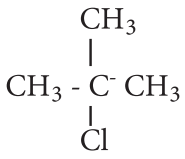
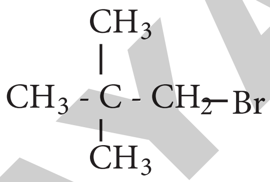
14.3.1 Nomenclature

Common system

In the common system, haloalkanes are named as alkyl halides. It is derived by naming the alkyl group followed by the halide.

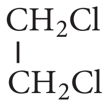
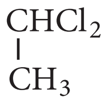
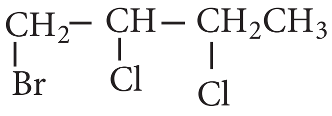
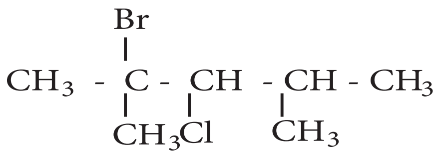
IUPAC system

Let us write the IUPAC name for the below mentioned haloalkanes by applying the general rules of nomeclature that are already discussed in Unit no : 11

S.No	Structural formula	Common name	IUPAC name
1	CH_3I	methyl iodide	Iodomethane
2	CH_3CH_2Br	ethyl bromide	Bromoethane
3	$CH_3CH_2CH_2F$	n-propyl fluoride	1-Fluoropropane
4	 $CH_3 - \underset{F}{CH} - CH_3$	iso - propyl fluoride	2- Fluoropropane
5	$CH_3 - CH_2 - CH_2 - CH_2 - Cl$	n- butyl chloride	1-Chlorobutane
6	 $CH_3 - \underset{CH_3}{CH} - CH_2 - Cl$	iso butyl chloride	1- Chloro-2-methyl propane
7	 $CH_3 - \underset{Cl}{CH} - CH_2 - CH_3$	sec-butyl chloride	2-Chlorobutane
8	 $CH_3 - \overset{CH_3}{\underset{Cl}{C}}{}^{-} CH_3$	tert-butyl chloride	2- Chloro -2- methyl propane
9	 $CH_3 - \overset{CH_3}{\underset{CH_3}{C}} - CH_2 - Br$	neo-pentyl bromide	1-Bromo-2, 2- dimethylpropane
10	$CH_2 = CH - Cl$	vinyl chloride	Chloroethene
11	$CH_2 = CH - CH_2 - Br$	allyl bromide	3-Bromopropene

Poly halogen Compounds:

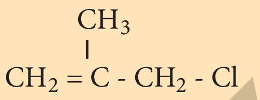
The common and IUPAC name of polyhalogen compounds are give below

S.No	Structural formula	Common name	IUPAC name
12	 CH_2Cl-CH_2Cl	Ethylene chloride (or) Ethylene dichloride	1,2- Dichloroethane
13	 $CHCl_2-CH_3$	Ethylidene chloride (or) Ethylidene dichloride	1,1- Dichloroethane
14.	 $CH_2(Br)-CH(Cl)-CH(Cl)CH_3$	–	1- Bromo-2, 3-dichloro butane
15	 $CH_3-C(Br)(CH_3)-CH(Cl)-CH(CH_3)-CH_3$	–	2-Bromo -3- Chloro -2, 4-dimethyl pentane

Evaluate Yourself

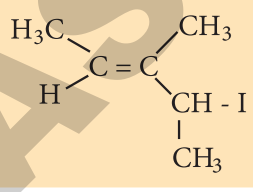
1) Write the IUPAC name of the following

i)

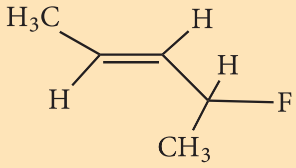


$CH_2=C(CH_3)-CH_2-Cl$

ii)



iii)



Evaluate Yourself

2) Write the structure of the following compounds

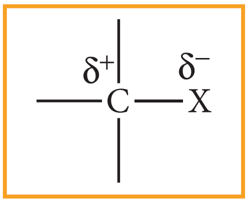
i) 1-Bromo-4-ethyl cyclohexane

ii) 1,4 – Dichlorobut – 2 – ene

iii) 2- Chloro – 3- methyl pentane

14.3.2 Nature of C – X bond in haloalkane

Carbon halogen bond is a polar bond as halogens are more electro negative than carbon. The carbon atom exhibits a partial positive charge (δ+) and halogen atom a partial negative charge (δ-)



The C –X bond is formed by overlap of sp^3 orbital of carbon atom with half filled p-orbital of the halogen atom. The atomic size of halogen increases from fluorine to iodine, which increases the C – X bond length. Larger the size, greater is the bond length, and weaker is the bond formed. The bond strength of C – X decreases from C – F to C – I in CH_3X. The changes in the value of bond length, bond enthalpy and bond polarity, as we more from C –F to C –I, is given in the table.

Table showing carbon – halogen bond length, bond enthalpy and polarity of bond.

Bond	Bond length (pm)	Bond Enthalpy ($kJmol^{-1}$)	Polarity of bond in terms of dipole moment (Debye)
$CH_3 – F$	139	452	1.847
$CH_3 – Cl$	178	351	1.860
$CH_3 – Br$	193	293	1.830
$CH_3 – I$	214	234	1.636

14.3.3 Methods of preparation

Haloalkanes are prepared by the following methods

1) From alcohols

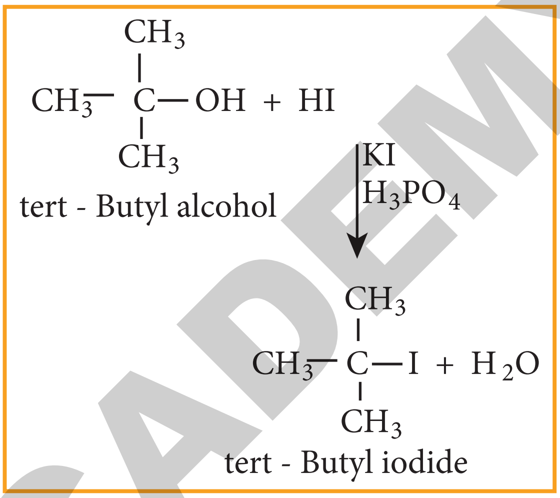
Alcohols can be converted into halo alkenes by reacting it with any one of the following reagent 1. hydrogen halide 2. Phosphorous halides 3. Thionyl chloride

a)Reaction with hydrogen halide

$$CH_3CH_2OH + HCl \xrightarrow[\Delta]{\text{Anhydrous } ZnCl_2} CH_3CH_2Cl + H_2O$$

Ethanol　　　　　　　　Chloroethane

Mixture of con.HCl and anhydrous $ZnCl_2$ is called **Lucas reagent.**



The order of reactivity of halo acids with alcohol is in the order HI > HBr > HCl. The order of reactivity of alcohols with halo acid is tertiary > secondary > primary.

b)Reaction with phosphorous halides

Alcohols react with PX_5 or PX_3 to form haloalkane. PBr_3 and PI_3 are usually generated in situ (produced in the reaction mixture) by the reaction of red phosphorus with bromine and iodine, respectively.

Example

$$CH_3CH_2OH + PCl_5 \longrightarrow CH_3CH_2Cl + POCl_3 + HCl$$

Ethanol　　　　Chloro ethane

$$3CH_3CH_2OH + PCl_3 \longrightarrow 3CH_3CH_2Cl + H_3PO_3$$

Ethanol　　　　Chloro ethane

c) Reaction with thionyl chloride (Sulphonyl chloride)

Example

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + SOCl_2 \xrightarrow{\text{Pyridine}} \underset{\text{Chloroethane}}{CH_3CH_2Cl} + SO_2\uparrow + HCl\uparrow$$

This reaction is known as **Darzen's halogenation**

2) From alkenes

Alkenes react with halogen acids (HCl, HBr, HI) to give haloalkane. The mode of addition follows Markovnikov's rule.

3) From alkanes

Alkanes react with halogens (Cl_2 or Br_2) in the presence of ultra violet light to form haloalkane. This reaction is a free radical substitution reaction and gives a mixture of mono, di or poly substituted haloalkane.

Example

Chlorination of methane gives different products which have differences in the boiling points. Hence, these can be separated by fractional distillation.

$$\underset{\text{Methane}}{CH_4} \xrightarrow[- HCl]{Cl_2 / \text{light}} \underset{\text{Chloromethane}}{CH_3Cl} \xrightarrow[- HCl]{Cl_2} \underset{\text{Dichloromethane}}{CH_2Cl_2} \xrightarrow[- HCl]{Cl_2} \underset{\text{Trichloro methane}}{CHCl_3} \xrightarrow[- HCl]{Cl_2} \underset{\text{Tetrachloro methane}}{CCl_4}$$

4) Halogen exchange reactions

a) Finkelstein reaction

Chloro or bromoalkane on heating with a concentrated solution of sodium iodide in dry acetone gives iodo alkanes. This reaction is called Finkelstein reaction, (S_N2 reaction).

$$\underset{\text{Bromoethane}}{CH_3CH_2Br} + NaI \xrightarrow[\Delta]{\text{Acetone}} \underset{\text{Iodoethane}}{CH_3CH_2I} + NaI$$

b) Swarts reaction

Chloro or bromo alkanes on heating with metallic fluorides like AgF, SbF_3 or Hg_2F_2 gives fluoro alkanes. This reactions is called Swarts reaction.

Example

$$\underset{\text{Bromo ethane}}{CH_3CH_2Br} + AgF \xrightarrow{\Delta} \underset{\text{Fluoro ethane}}{CH_3CH_2F} + AgBr$$

5) From silver salts of fatty acids (Hunsdiccker reaction)

Silver salts of fatty acids when refluxed with bromine in CCl_4 gives bromo alkane

$$\underset{\text{Silver propionate}}{CH_3CH_2COOAg} + Br_2 \xrightarrow[\text{reflux}]{CCl_4} \underset{\text{Bromo ethane}}{CH_3CH_2Br} + CO_2 + AgBr$$

$$\underset{\text{Silver propionate}}{CH_3CH_2COOAg} + Br_2 \xrightarrow[\text{reflux}]{CCl_4} \underset{\text{Bromo ethane}}{CH_3CH_2Br} + CO_2 + AgBr$$

14.3.4 Physical Properties

1. Pure haloalkanes are colourless. Bromo and iodo alkanes are coloured in the presence of light.

2. Haloalkanes having one, two or three carbon atoms are in the gaseous state at normal temperature. Haloalkanes having more than three carbon atoms are liquids or solids.

3). Boiling point and Melting point

i) Haloalkanes have higher boiling point and melting point than the parent alkanes having the same number of carbons because the intermolecular forces of attraction (dipole – dipole interaction and vander Waals forces) are stronger in haloalkane.

ii) The boiling point and melting point of haloalkanes decreases with respect to the helogen in the following order.

Example

$CH_3I > CH_3Br > CH_3Cl > CH_3F$

iii) The boiling points of chloro, bromo and iodo alkanes increase with the increase in the number of halogen atoms.

For Example:

$CCl_4 > CHCl_3 > CH_2Cl_2 > CH_3Cl$

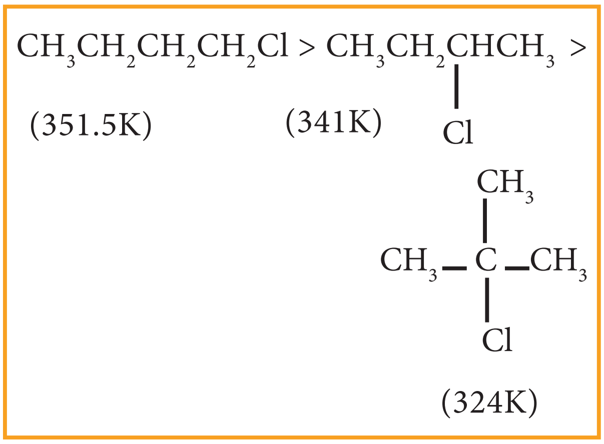
iv) The boiling point and melting point of mono haloalkane increase with the increase in the number of carbon atoms.

Example

$CH_3CH_2CH_2Cl > CH_3CH_2Cl > CH_3Cl$

v) Among isomeric alkyl halides the boiling point decreases with the increase in branching in the alkyl group; with increase in branching, the molecule attains spherical shape with less surface area. As a result the inter molecular forces become weak, resulting in lower boiling points.

Example



$$\underset{(351.5K)}{CH_3CH_2CH_2CH_2Cl} > \underset{(341K)}{CH_3CH_2CH(Cl)CH_3} > \underset{(324K)}{(CH_3)_3CCl}$$

4. Solubility

Haloalkanes are polar covalent compounds soluble in organic solvents, but insoluble in water because they cannot form hydrogen bonds with water molecules

5. Density

The density of liquid alkyl halides are higher than these of hydrocarbons of comparable molecular weight.

Evaluate Yourself

3) Write all possible chain isomers with molecular formula $C_5H_{11}Cl$

14.3.5 Chemical properties

Haloalkanes are one of the most reactive classes of organic compounds. Their reactivity is due to the presence of polar carbon – halogen bond in their molecules. The reactions of haloalkane may be divided into the following types

i) Nucleophilic substitution reactions

ii) Elimination reactions

iii) Reaction with metals

iv) Reduction

1) Nucleophilic substitution reactions

We know that the $C^{\delta+}$ - $X^{\delta-}$ present in halo alkane is polar and hence the nucleophilic reagents are attracted by partially positively charged carbon atoms resulting in substitution reactions.

Reaction with aqueous alkali or moist silver oxide.(Hydrolysis)

Haloalkane reacts with aqueous solution of KOH or moist silver oxide (Ag_2O/H_2O) to form alcohols.

Example

$$CH_3-CH_2-Br + KOH\,(aq) \xrightarrow{boil} CH_3-CH_2-OH + KBr$$

Bromoethane

Ethyl alcohol

$$CH_3-CH_2-Br + AgOH \xrightarrow{boil} CH_3-CH_2-OH + AgBr$$

Bromoethane

Moist silver oxide

Ethanol

i) Reaction with alcoholic ammonia (Ammonolysis)

Haloalkanes react with alcoholic ammonia solution to form alkyl amines.

Example

$$CH_3-CH_2-Br + H-NH_2 \longrightarrow CH_3-CH_2-NH_2 + HBr$$

Bromo ethane

ammonia

Ethyl amine

However, with excess of halo alkane, secondary and tertiary amines along with quartenary ammonium salts are obtained

$$CH_3CH_2NH_2 \xrightarrow[-HBr]{CH_3CH_2Br} (CH_3CH_2)_2NH$$

Ethyl amine (1)

Diethyl amine (2)

$$(CH_3CH_2)_2NH \xrightarrow[-HBr]{CH_3CH_2Br} (CH_3CH_2)_3N$$

Triethyl amine (3)

$$(CH_3CH_2)_3N \xrightarrow[-HBr]{CH_3CH_2Br} (CH_3CH_2)_4N^+Br^-$$

Tetra ethyl ammonium bromide

Ambident Nucleophiles

Nucleophiles such as cyanide and nitrite ion which can attack nucleophilic centre from two sides are called ambident nucleophiles. These nucleophiles can attack with either of the two sides depending upon the reaction conditions and the reagent used.

ii) Reaction with alcoholic KCN

Haloalkanes react with alcoholic KCN solution to form alkyl cyanides.

Example

$$\underset{\text{Bromoethane}}{CH_3-CH_2-Br}+KCN \rightarrow \underset{\text{Ethyl cyanide}}{CH_3-CH_2-CN}+KBr$$

iii) Reaction with alcoholic AgCN

Haloalkanes react with alcoholic AgCN solution to form alkyl isocyanide.

Example

$$\underset{\text{Bromoethane}}{CH_3CH_2Br} + AgCN \longrightarrow \underset{\text{Ethyl isocyanide}}{CH_3CH_2NC}+AgBr$$

iv) Reaction with sodium or potassium nitrite

Haloalkanes react with alcoholic solution of $NaNO_2$ or KNO_2 to form alkyl nitrites.

Example

$$\underset{\text{Bromoethane}}{CH_3CH_2Br} + KNO_2 \rightarrow \underset{\text{Ethyl nitrite}}{CH_3CH_2-O-N=O}+KBr$$

v) Reaction with silver nitrite

Haloalkanes react with alcoholic solution of $AgNO_2$ to form nitro alkanes.

Example

$$\underset{\text{Bromo ethane}}{CH_3CH_2Br}+AgNO_2 \rightarrow \underset{\text{Nitro ethane}}{CH_3CH_2NO_2}+ AgBr$$

vi) Reaction with sodium or potassium hydrogen sulphide

Haloalkanes react with sodium or potassium hydrogen sulphide to form thio alcohols.

Example

$$\underset{\text{Bromo ethane}}{CH_3CH_2Br}+NaSH \xrightarrow[\Delta]{\text{alcohol/}H_2O} \underset{\text{Ethane thiol}}{CH_3CH_2SH}+NaBr$$

vii) Williamson ether synthesis

Haloalkane, when boiled with sodium alkoxide gives corresponding ethers.

Example

This method can be used to prepare mixed (unsymmetrical) ethers also.

$$\underset{\text{Bromo ethane}}{CH_3CH_2Br}+\underset{\text{Sodium ethoxide}}{NaOCH_2CH_3}$$
$$\downarrow \Delta$$
$$\underset{\text{diethyl ether}}{CH_3CH_2OCH_2CH_3}+NaBr$$

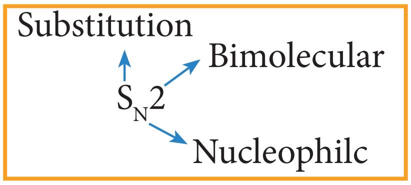
Mechanism of Nucleophilic substitution reaction

The mechanism of nucleophilic substitution reaction is classified as

a) Bimolecular Nucleophilic substitution reaction (SN_2)

b) Unimolecular Nucleophilic substitution reaction (SN_1)

S_N2 Mechanism



The rate of S_N2 reaction depends upon the concentration of both alkyl halide and the nucleophile.

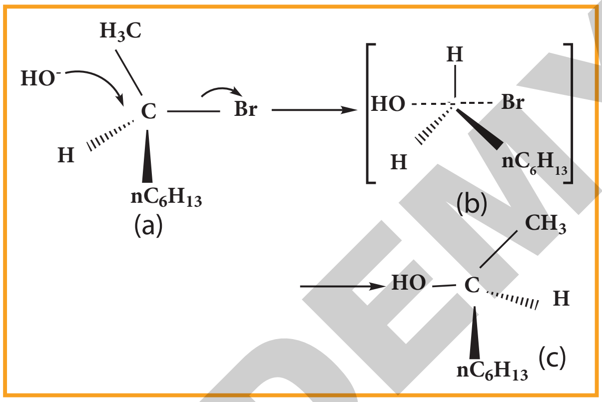
Rate of reaction = k_2 [alkylhalide] [nucleophile]

It follows second order kinetics and occurs in one step.

This reaction involves the formation of a transition state in which both the reactant molecules are partially bonded to each other. The attack of nucleophile occurs from the back side (i.e opposite to the side in which the halogen is attacked). The carbon at which substitution occurs has inverted configuration during the course of reaction just as an umbrella has tendency to invert in a wind storm. This inversion of configuration is called Walden inversion; after paul walden who first discovered the inversion of configuration of a compound in S_N2 reaction.

S_N2 reaction of an optically active haloalkane is always accompanied by inversion of configuration at the asymmetric centre. Let us consider the following example

When 2 - Bromooctane is heated with sodium hydroxide, 2 – octanol is formed with invesion of configuration. (-) – 2 – Bromo octane is heated with sodium hydroxide (+) – 2 – Octanol is formed in which – OH group occupies a position opposite to what bromine had occupied,



(a) (-) 2 – Bromo octane

(b) Transition State

(c) (+) 2 – Octanol (product)

S_N1 Mechanism

S_N1 stands for unimolecular nucleophilic substitution

'S' stands for substitution

'N' stands for nucleophilic

'1' stands for unimolecular (one molecule is involved in the rate determining step)

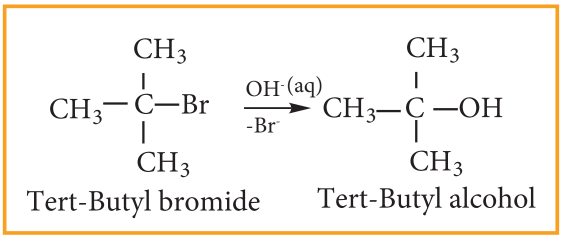
The rate of the following S_N1 reaction depends upon the concentration of alkyl halide (RX) and is independent of the concentration of the nucleophile (OH^-).

Hence Rate of the reaction = k[alkyl halide]

$$R–Cl + OH^- \longrightarrow R – OH + Cl^-$$

This S_N1 reaction follows first order kinetics and occurs in two steps.

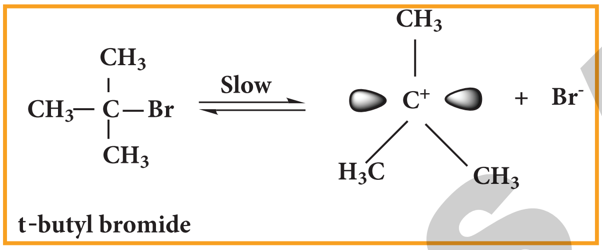
We understand S_N1 reaction mechanism by taking a reaction between tertiary butyl bromide with aqueous KOH.



This reaction takes place in two steps as shown below

Step - 1 Formation of carbocation

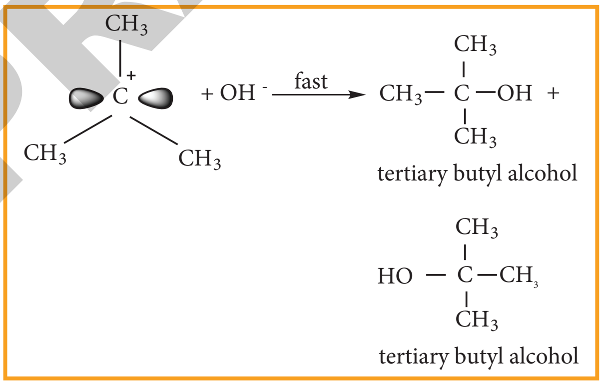
The polar C - Br bond breaks forming a carbocation and bromide ion. This step is slow and hence it is the rate determining step.



The carbocation has 2 equivalent lobes of the vacant 2p orbital, so it can react equally rapidly from either face

Step - 2

The nucleophile immediately reacts with the carbocation. This step is fast and hence does not affect the rate of the reactions.



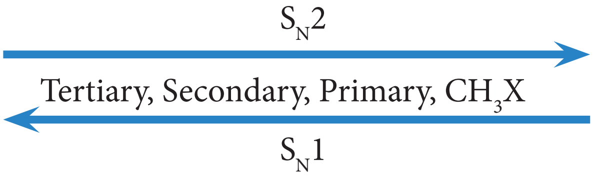
As shown above, the nucleophilic reagent OH^- can attack carbocation from both the sides.

In the above example the substrate tert-butyl bromide is not optically active, hence the obtained product is optically inactive. If halo alkane substrate is optically active then, the product obtained will be optically inactive racemic mixture. As nucleophilic reagent OH^- can attack carbocation from both the sides, to form equal proportion of dextro and levorotatory optically active isomers which results in optically inactive racemic mixture.

Example

Hydrolysis of optically active 2 - bromo butane gives racemic mixture of ± butan-2-ol

The order of reactivity of haloalkanes towards S_N1 and S_N2 reaction is given below.
S_N2 reaction



Evaluate Yourself

4) neo-pentyl bromide undergoes nucleophilic substitution reactions very slowly - justify.

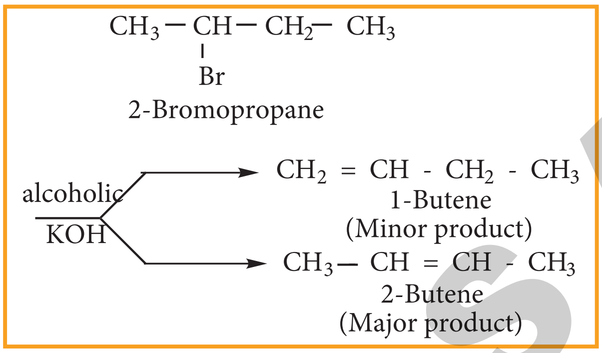
2) Elimination reactions

When a haloalkene containing a hydrogen on β carbon is treated with an ethanolic solution of potassium hydroxide, an alkene is formed. In this reaction a double bond between α and β carbon is formed by releasing a halogen attached to a α carbon and a hydrogen to a β carbon of halo alkane. This reaction is called β elimination reaction. (dehydrohalogenation).

$$CH_3CH_2Br + KOH \xrightarrow{\text{ethanol}} \underset{\text{Ethylene}}{CH_2{=}CH_2} + KBr + H_2O$$

Some haloalkanes yield a mixture of olefins in different amounts. It is explained by Saytzeff's Rule, which states that 'In a dehydrohalogenation reaction, the preferred product is that alkene which has more number of alkyl groups attached to the doubly bonded carbon (more substituted double bond is formed)

Example



Elimination reactions may proceed through two different mechanisms namely E_1 and E_2

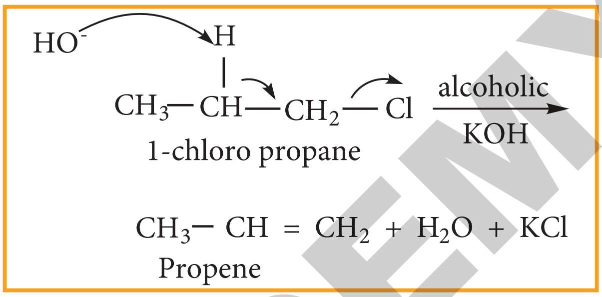
E_2 reaction mechanism

E_2 → Elimination
→ bimolecular
(Second order)

The rate of E_2 reaction depends on the concentration of alkyl halide and base

$$\text{Rate} = k\,[\text{alkyl halide}]\,[\text{base}]$$

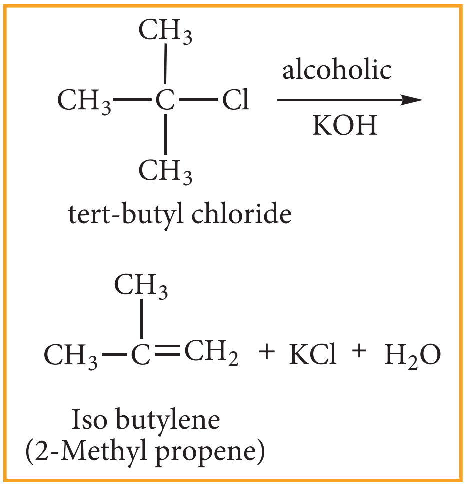
It is therefore, a second order reaction. Generally primary alkyl halide undergoes this reaction in the presence of alcoholic KOH. It is a one step process in which the abstraction of the proton from the β carbon and expulsion of halide from the ∝ carbon occur simultaneously. The mechanism is shown below.



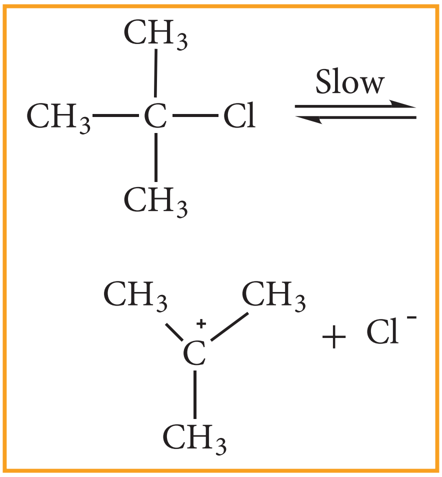
E_1 reaction mechanism

E_1 → Elimination
→ Unimolecular

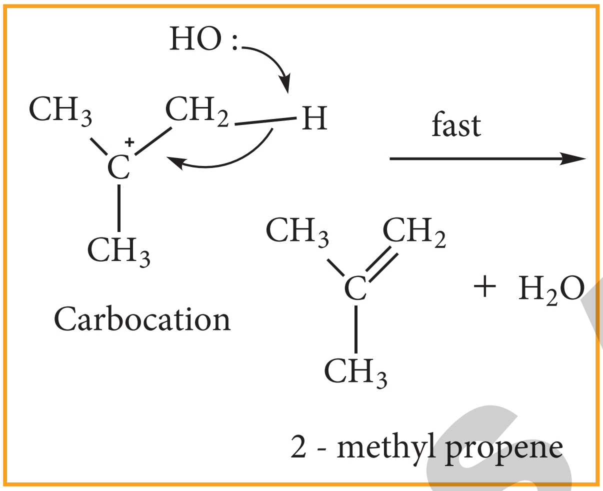
Generally, tertiary alkyl halide which undergoes elimination reaction by this mechanism in the presence of alcoholic KOH. It follows first order kinetics. Let us consider the following elimination reaction.



Step - 1 Heterolytic fission to yield a carbo-cation



Step - 2 Elimination of a proton from the β - carbon to produce an alkene



3) Reaction with metals

Haloalkane reacts with metals, to form a compound containing carbon - metal bond known as organometallic compounds.

a) Grignard reaction

When a solution of halo alkane in ether is treated with magnesium, we get alkyl magnesium halide known as Grignard reagent.

Example

$CH_3CH_2Br + Mg \xrightarrow{\text{Dry ether}} CH_3CH_2MgBr$

Ethyl bromide Ethyl magnesium bromide

b) Reaction with active metals like sodium, lead etc

Haloalkane reacts with active metals like sodium, lead etc in the presence of dry ether to form organo metallic compounds.

$CH_3CH_2Br + 2Li \xrightarrow{\text{Dry ether}} CH_3CH_2Li + LiBr$

Ethyl bromide Ethyl Lithium

$4CH_3CH_2Br + 4Na/Pb \longrightarrow (CH_3CH_2)_4Pb + 4NaBr + 3Pb$

Ethyl bromide Sodium - lead alloy Tetra ethyl lead (TEL)

4) Reduction reactions

Haloalkanes are reduced to alkanes by treating with H_2 in the presence of metal catalyst like nickel, palladium etc or with hydroiodic acid in the presence of red phosphorous.

$CH_3CH_2Br + H_2 \xrightarrow[523\ K]{Ni(or)Pd} CH_3\text{-}CH_3 + HBr$

Bromo ethane Ethane

$CH_3CH_2I + HI \xrightarrow{\text{Red P}} CH_3\text{ - }CH_3 + I_2$

Iodo ethane Ethane

The chemistry of haloalkane can be well understood by the following flowchart.

14.3.6 Uses of haloalkane

Chloroform: As a solvent in pharmaceutical industry and for producing pesticides and drugs As an anaesthetic.

As a preservative for anatomical specimens.

Iodoform: Iodoform is used as an antiseptic for dressing wounds.

Carbon tetrachloride: Carbon tetrachloride is used as dry cleaning agent

It is used as a solvent for oils, fats and waxes

As the vapour of CCl_4 is non – combustible, it is used under the name pyrene for extinguishing the fire in oil or petrol.

14.4 Organo metallic Compounds

Organo metallic compounds are organic compounds in which there is a direct carbon –metal bond

Example

CH_3 Mg I - Methyl magnesium iodide

CH_3 CH_2 Mg Br - Ethyl magnesium bromide

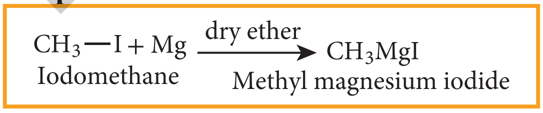
The carbon - magnesium bond in Grignard reagent is covalent but highly polar. The carbon atom is more electro negative than magnesium. Hence, the carbon atom has partial negative charge and the magnesium atom has partial positive charge

$\delta-$ $\delta+$ R ----- MgX

14.4.1. Preparation

When a solution of alkyl halide in ether is allowed to stand over pieces of magnesium metal, the metal gradually dissolves and alkyl magnesium halide (Grignard reagent) is formed. All the reagents used should be pure and dry

Example



$$CH_3-I + Mg \xrightarrow{\text{dry ether}} CH_3MgI$$

Evaluate Yourself

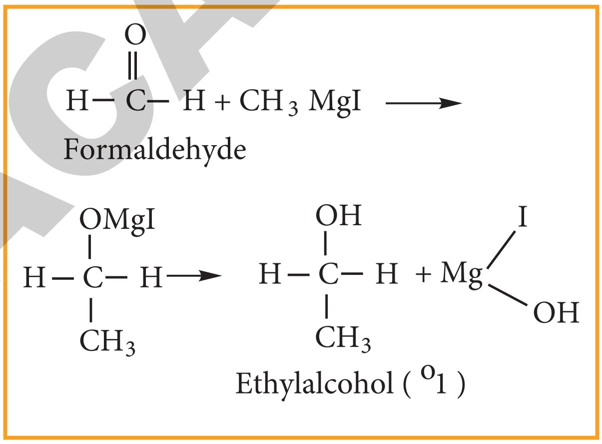
5) Why Grignard reagent should be prepared in anhydrous condition?

14.4.2. Uses of Grignard reagent

Grignard reagents are synthetically very useful compounds. These reagents are converted to various organic compounds like alcohols, carboxylic acids, aldehydes and ketones. The alkyl group being electron rich acts as a carbanion or a nucleophile. They would attack polarized molecules at a point of low electron density. The following reactions illustrate the synthetic uses of Grignard reagent.

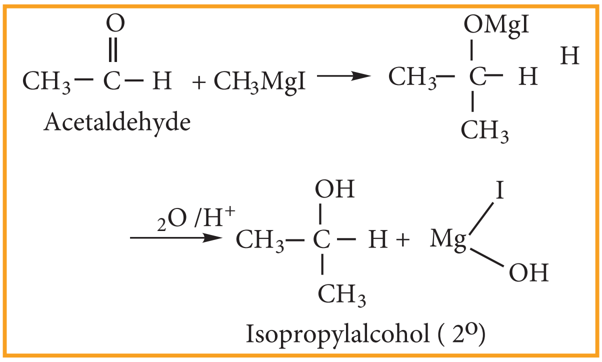
(1) Preparation of primary alcohol

Formaldehyde reacts with Grignard reagent to give addition products which on hydrolysis yields primary alcohol.



2) Preparation of secondary alcohol

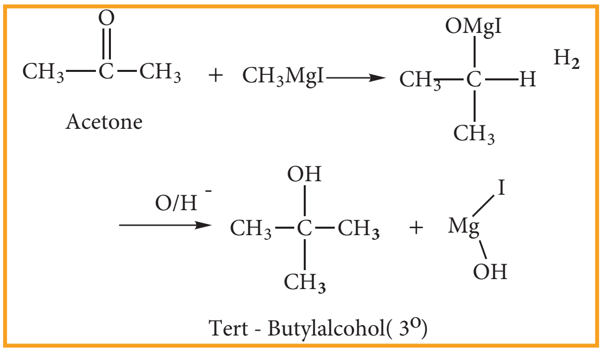
Aldehydes other than formaldehyde, react with Grignard reagent to give addition product which on hydrolysis yields secondary alcohol.



3) Preparation of Tertiary alcohol

Ketone reacts with Grignard reagent to give an addition product which on hydrolysis yields tertiary alcohols.

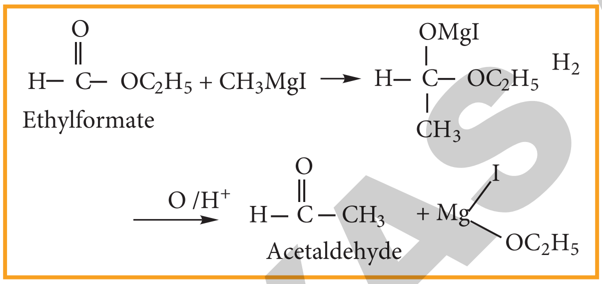
Example



(4) Preparation of aldehyde

Ethyl formate reacts with Grignard reagent to form aldehyde. However, with excess of Grignard reagent it forms secondary alcohol.

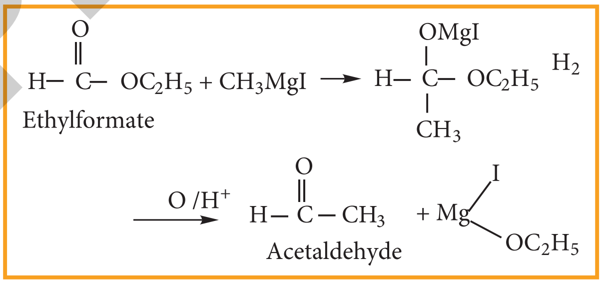
Example



(5) Preparation of ketone

Acid chloride reacts with Grignard reagent to form ketones. However, with excess of Grignard reagent it forms tertiary alcohol.

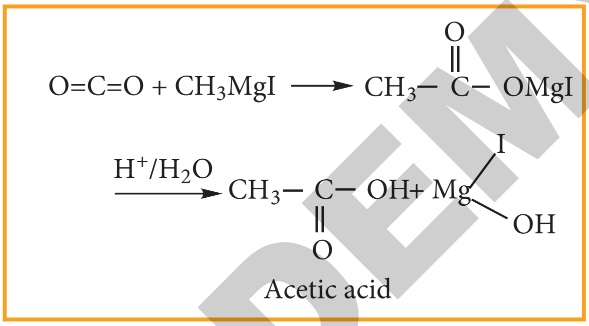
Example



6) Preparation of carboxylic acids

Solid carbon dioxide reacts with Grignard reagent to form addition product which on hydrolysis yields carboxylic acids.

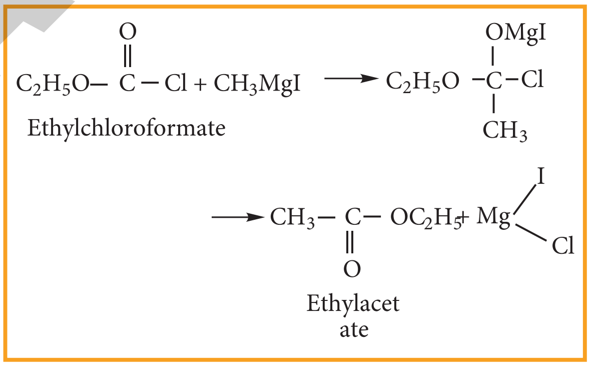
For Example



7) Preparation of esters

Ethylchloroformate reacts with Grignard reagent to form esters.

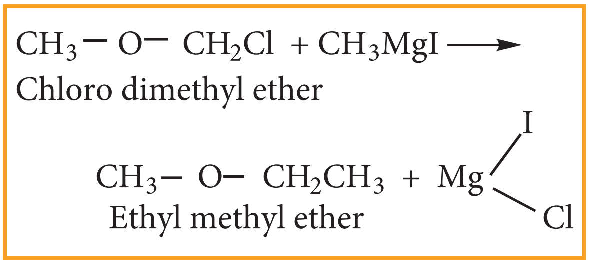
Example



8) Preparation of higher ethers

Lower halogenated ether reacts with Grignard reagent to form higher ethers.

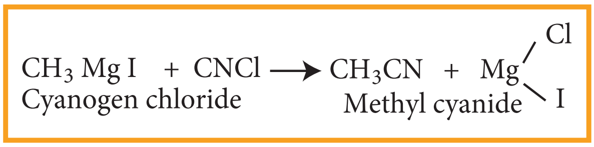
Example



9) Preparation of alkyl cyanide

Grignard reagent reacts with cyanogen chloride to from alkyl cyanide

Example



$$\underset{\text{Cyanogen chloride}}{CH_3MgI + CNCl} \longrightarrow \underset{\text{Methyl cyanide}}{CH_3CN} + Mg\begin{matrix}Cl\\I\end{matrix}$$

10) Preparation of Alkanes

Compounds like water, alcohols and amines which contain active hydrogen atom react with Grignard reagents to form alkanes.

Example

$$CH_3MgI + HO-H \longrightarrow CH_4 + MgI(OH)$$

$$CH_3MgI + \underset{\text{Ethyl alcohol}}{C_2H_5OH} \xrightarrow{\Delta} \underset{\text{methane}}{CH_4} + MgI(OC_2H_5)$$

14.5 Haloarenes

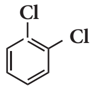
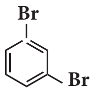
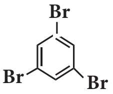
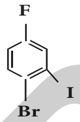
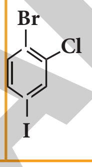
Haloarenes are the compounds in which the halogen is directly attached to the benzene ring.

14.5.1. Nomenclature of haloarenes

In the IUPAC nomenclature, the halo arenes are named by adding prefix halo before the name of the aromatic hydrocarbon. For naming disubstituted arenes, the relative position of the substituent 1,2; 1,3 and 1,4 are indicated by the prefixes ortho, meta and para, respectively.

For poly haloarenes the numbering should be done in such a way that the lowest possible number should be given to the substituents and the name of the halogens are arranged in alphabetic order.

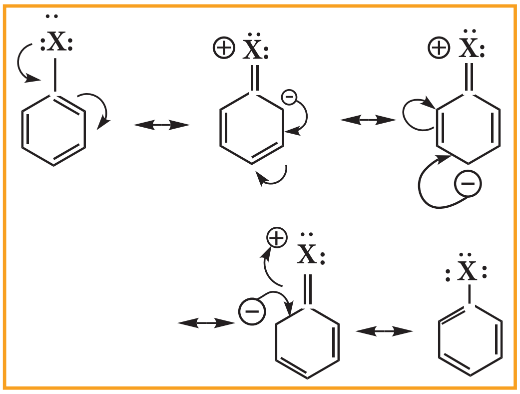
Nomenclature can be well understood from the following examples.

Compound	IUPAC NAME
1	 1, 2 - Dichlorobenzene
2	 1, 3- Dibromobenzene
3	 1,3,5-tri bromobenzene
4	 1- Bromo - 4- fluoro -2- iodobenzene
5	 1- Bromo -2- chloro-4- iodobenzene

14.5.2 Nature of C- X bond in haloarenes

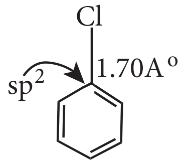
In halo arenes the carbon atom is sp^2 hybridised. The sp^2 hybridised orbitals are shorter and holds the electron pair of bond more tightly.

Halogen atom contains P-orbital with lone pair of electrons which interacts with π-orbitals of benzene ring to form extended conjugated system of π- orbitals. The delocalisation of these electrons give double bond character to C – X bond. The resonance structure of halobenzene is given as



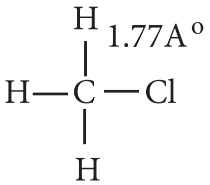
Due to this double bond character of C- X bond in haloarenes ,the C-X bond is shorter in length and stronger than in halo alkanes.

Example



Chloro benzene

sp3 hybridisation

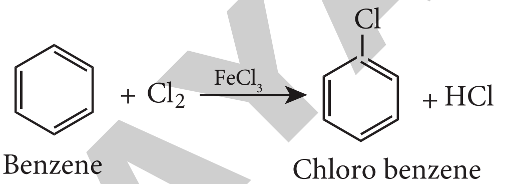


Chloro methane

14.5.3 Methods of preparation

1) Direct halogenation

Chlorobenzene is prepared by the direct chlorination of benzene in the presence of lewis acid catalyst like $FeCl_3$

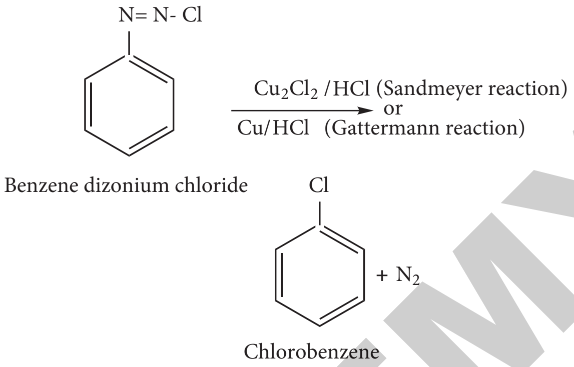


2) From benzene diazonium chloride

Chloro benzene is prepared by Sandmeyer reaction or Gattermann reaction using benzene diazonium chloride.

(i) Sandmeyer reaction

When aqueous solution of benzene diazonium chloride is warmed with Cu_2Cl_2 in HCl gives chloro benzene



3) Preparation of iodobenzene

Iodobenzene is prepared by warming benzene diazonium chloride with aqueous KI solution.

$$C_6H_5N_2Cl + KI \xrightarrow{warm} C_6H_5I + N_2 + KCl$$

Benzene diazonium chloride Iodo benzene

4) Preparation of fluorobenzene

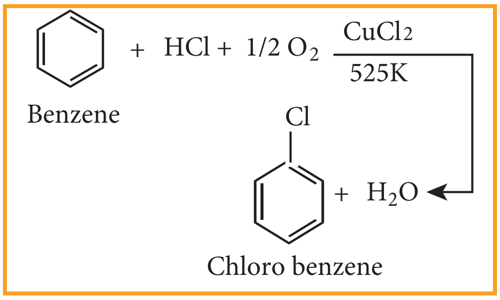
Fluoro benzene is prepared by treating benzenediazonium chloride with fluoro boric acid. This reaction produces diazonium fluoroborate which on heating produces fluorobenzene. This reaction is called Balz – schiemann reaction.

$$C_6H_5N_2Cl + HBF_4 \xrightarrow[-HCl]{} C_6H_5N_2^+ BF^- \xrightarrow{heat} C_6H_5F + BF_3 + N_2$$

Benzene diazonium chloride Fluorobenzene

5) Commercial preparation of chloro benzene (Raschig process)

Chloro benzene is commercially prepared by passing a mixture of benzene vapour, air and HCl over heated cupric chloride .This reaction is called Raschig process.



14.5.4 Physical properties

1. Melting and boiling points

The boiling points of monohalo benzene which are all liquids follow the order

Iodo > Bromo > Chloro

The boiling points of isomeric dihalobenzene are nearly the same

The melting point of para isomer is generally higher than the melting points of ortho and meta isomers. The higher melting point of p-isomer is due to its symmetry which leads to more close packing of its molecules in the crystal lattice and consequently strong intermolecular attractive force which requires more energy for melting

p –Dihalo benzene > o- Dichloro benzene > m-Dichloro benzene

2. Solubility

Haloarenes are insoluble in water because they cannot form hydrogen bonds with water ,but are soluble in organic solvents

3. Density

Halo arenes are all heavier than water and their densities follow the order.

Iodo benzene > Bromo benzene > Chloro benzene

14.5.5 Chemical properties

A. Reactions invoving halogen atom

1. Aromatic nucleophilic substitution reaction

Halo arenes do not undergo nucleophilic substitution reaction readily. This is due to C–X bond in aryl halide is short and strong and also the aromatic ring is a centre of high electron density.

The halogen of haloarenes can be substituted by OH^- , NH_2^-, or CN^- with appropriate nucleophilic reagents at high temperature and pressure.

For Example

$$C_6H_5Cl + NaOH \xrightarrow[300\ atm]{350^0C} C_6H_5OH + NaCl$$

Chlorobenzene Pheno1

This reaction is known as Dow's Process

$$C_6H_5Cl + 2NH_3 \xrightarrow[50\ atm]{250^0C} C_6H_5NH_2 + NH_4Cl$$

Chlorobenzene Aniline

$$C_6H_5Cl + CuCN \xrightarrow[Pyridine]{250^0C} C_6H_5CN + CuCl$$

Chlorobenzene Phenyl cyanide

2. Reaction with metals

a) Wurtz Fittig reaction

Halo arenes reacts with halo alkanes when heated with sodium in ether solution to form alkyl benzene. This reaction is called wurtz fittig reaction.

$$C_6H_5Cl + 2Na + ClC_2H_5 \xrightarrow[\Delta]{Ether} C_6H_5\,C_2H_5 + 2NaBr$$

Chlorobenzene chloroethane ethyl benzene

b) Fittig reaction

Haloarenes react with sodium metal in dry ether, two aryl groups combine to give biaryl products. This reaction is called fittig reaction

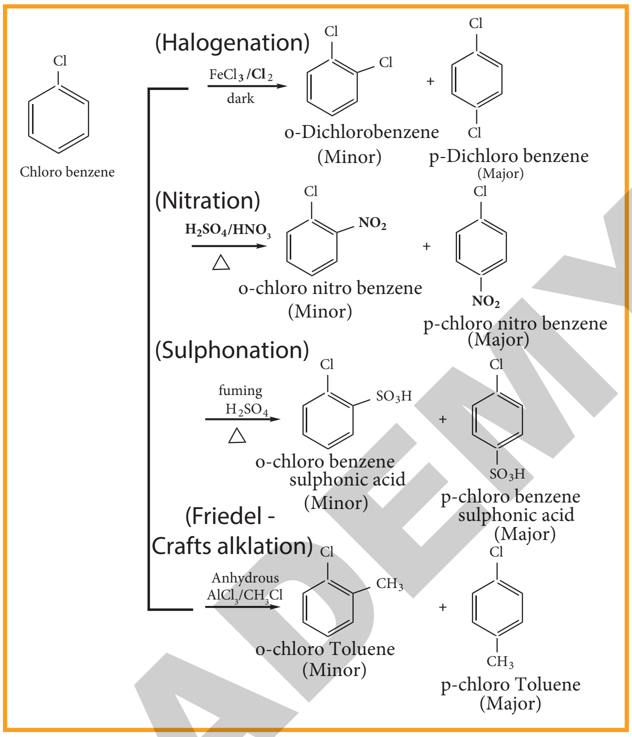
$$C_6H_5Cl + 2Na + Cl\text{-}C_6H_5 \xrightarrow[\Delta]{Ether} C_6H_5-C_6H_5 + 2NaCl$$

Chlorobenzene Biphenyl

B) Reaction involving aromatic ring

3. Electrophilic substitution reaction

Haloarenes undergo aromatic electrophilic substitution reactions. The rate of eleclophilic substitution of halobenzene is lower than that of benzene. halogen is deactivating due to - I effect of halogen. The lone pair of electrons on the chlorine involves in resonance with the ring. It increases the electron density at ortho and para position (refer figure no 14.1). The halogen attached to the benzine ring with draw electron and thereby and hence the halogen which is attached to the benzene directs the incoming, electrophile either to ortho or to para position in electrophilie substitution reaction



Toluenes.

4) Reduction

Haloarenes on reduction with Ni-Al alloy in the presence of NaOH gives corresponding arenes.

$$C_6H_5Cl + 2(H) \xrightarrow[NaOH]{Ni\text{-}Al} C_6H_6 + HCl$$

Chloro benzene Benzene

5) Formation of Grignard reagent

Haloarenes reacts with magnesium to form Grignard reagent in tetra hydrofuran (THF).

$$C_6H_5Cl + Mg \xrightarrow{THF} C_6H_5MgCl$$

Chloro benzene Phenyl magnesium chloride

14.5.6 Uses of Chloro benzene

i) Chloro benzene is used in the manufacture of pesticides like DDT

ii) It is used as high boiling solvent in organic synthesis.

iii) It is used as fibre - swelling agent in textile processing.

Evaluate Yourself

6) Haloalkanes undergo nucleophilic substitution reaction whereas haloarenes undergo electrophilic substitution reaction. comment.

14.6 Poly halogen compounds

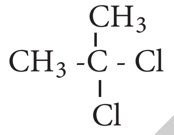
Carbon compounds containing more than one halogen atoms are called poly halogen compounds. Some of the important poly halogen compounds are described below.

They are classified as

a) gem – dihalides

CH_3CHCl_2

Ethylidene chloride
1,1 - Dichloro ethane

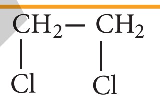


$$CH_3-\underset{Cl}{\overset{CH_3}{C}}-Cl$$

Isopropylidene chloride (or)
Isopropylidene dichloride
2,2-Dichloropropane

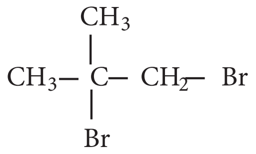
b) vic - dihalides

For Example



$$\underset{Cl}{CH_2}-\underset{Cl}{CH_2}$$

Ethylene dichloride (or) Ethylene chloride
1, 2 -Dichloro ethane



$$CH_3-\underset{Br}{\overset{CH_3}{C}}-CH_2-Br$$

Isobutylene dibromide (or) Isobutylene bromide
1, 2-Dibromo-2-methyl propane

14.6.1 Preparation

a) gem- Dihalides

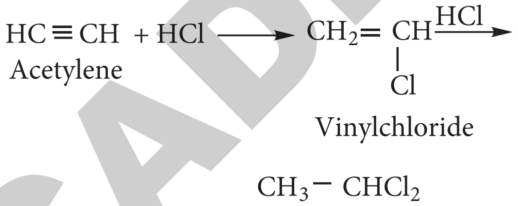
Ethylidene dichloride (1, 1 - Dichloro ethane) is prepared by

(i) Treating acetaldehyde with PCl_5

$CH_3CHO + PCl_5 \longrightarrow CH_3CHCl_2 + POCl$

Acetaldehyde — Ethylidene dichloride

(ii) Adding hydrogen chloride to acetylene



$$HC\equiv CH + HCl \longrightarrow CH_2=\underset{Cl}{CH} \xrightarrow{HCl} CH_3-CHCl_2$$

Acetylene

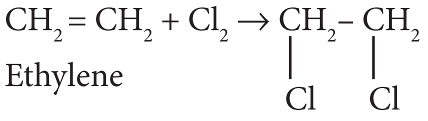
Vinylchloride

Ethylidene dichloride

b) vic- Dihalides

Ethylene dichloride (1, 2 - Dichloro ethane) is prepared by the following methods.

i) Addition of chlorine to ethylene

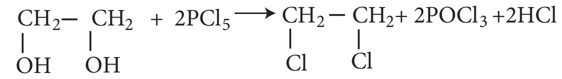


$$CH_2=CH_2+Cl_2\rightarrow \underset{Cl}{CH_2}-\underset{Cl}{CH_2}$$

Ethylene

Ethylene dichloride

ii) Action of PCl_5 (or HCl) on ethylene glycol



$$\underset{OH}{CH_2}-\underset{OH}{CH_2} + 2PCl_5 \longrightarrow \underset{Cl}{CH_2}-\underset{Cl}{CH_2} + 2POCl_3 + 2HCl$$

Ethylene glycol — Ethylene dichloride

Properties

Physical Properties

i) They are sweet smelling, colourless liquids having relatively high boiling points.

ii) The boiling point of ethylidene chloride is less than that of ethylene dichloride.

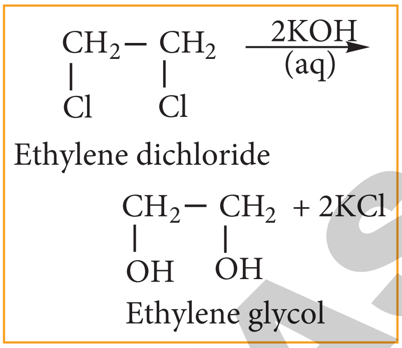
Chemical properties

1) Hydrolysis with aqueous NaOH or KOH

gem-Dihalides, on hydrolysis with aqueous KOH give an aldehyde or a ketone vic-Dihalides, on hydrolysis with aqueous KOH gives glycols.

$$CH_3-CHCl_2 \xrightarrow[-2KCl]{2KOH} [CH_3CH(OH)_2] \xrightarrow[-H_2O]{} CH_3CHO$$

Ethylene dichloride   unstable   Acetaldehyde



$$\underset{\text{Cl}}{\underset{|}{CH_2}}-\underset{\text{Cl}}{\underset{|}{CH_2}} \xrightarrow[\text{(aq)}]{2KOH} \underset{\text{OH}}{\underset{|}{CH_2}}-\underset{\text{OH}}{\underset{|}{CH_2}} + 2KCl$$

Ethylene dichloride

Ethylene glycol

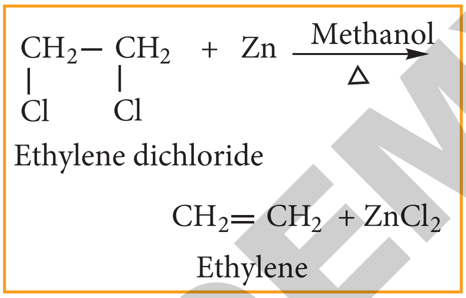
This reaction can be used to distinguish the gem- Dihalides and vic- Dihalides.

2) Reaction with Zinc (Dehalogenation)

gem- Dihalides and vic- Dihalides on treatment with zinc dust in methanol give alkenes.

$$CH_3-CHCl_2 + Zn \xrightarrow{\text{Methanol}} CH_2=CH_2 + ZnCl_2$$

Ethylidene dichloride   Ethylene



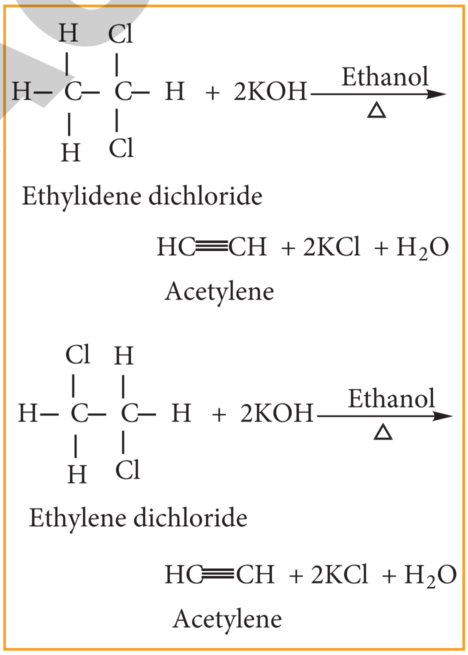
$$\underset{\text{Cl}}{\underset{|}{CH_2}}-\underset{\text{Cl}}{\underset{|}{CH_2}} + Zn \xrightarrow[\Delta]{\text{Methanol}} CH_2=CH_2 + ZnCl_2$$

Ethylene dichloride

Ethylene

3) Reaction with Alcoholic KOH (Dehydrohalogenation)

gem- Dihalides and vic- Dihalides on treatment with alcoholic KOH give alkynes.



$$H-\overset{\text{H}}{\underset{\text{H}}{\overset{|}{\underset{|}{C}}}}-\overset{\text{Cl}}{\underset{\text{Cl}}{\overset{|}{\underset{|}{C}}}}-H + 2KOH \xrightarrow[\Delta]{\text{Ethanol}} HC\equiv CH + 2KCl + H_2O$$

Ethylidene dichloride

Acetylene

$$H-\overset{\text{Cl}}{\underset{\text{H}}{\overset{|}{\underset{|}{C}}}}-\overset{\text{H}}{\underset{\text{Cl}}{\overset{|}{\underset{|}{C}}}}-H + 2KOH \xrightarrow[\Delta]{\text{Ethanol}} HC\equiv CH + 2KCl + H_2O$$

Ethylene dichloride

Acetylene

Methylene chloride (Di chloromethane)

Preparation

Methylene chloride is prepared by the following methods

1) Reduction of chloroform

a) Reduction of chloroform in the presence of Zn + HCl gives methylene chloride.

$$\underset{\text{chloro form}}{CHCl_3} \xrightarrow[2(H)]{Zn+HCl} \underset{\text{methylene chloride}}{CH_2Cl_2 + HCl}$$

b) Reduction of chloroform using H2/Ni

$$\underset{\text{chloro form}}{CHCl_3} \xrightarrow[Ni]{H_2} \underset{\text{methylene chloride}}{CH_2Cl_2 + HCl}$$

2) Chlorination of methane

Chlorination of methane gives methylene chloride

$$\underset{\text{Methane}}{CH_4} \xrightarrow[-HCl]{Cl_2/h\upsilon} \underset{\text{Methyl chloride}}{CH_3Cl}$$

$$\xrightarrow[-HCl]{Cl_2/h\upsilon} \underset{\text{Methylene chloride}}{CH_2Cl_2}$$

Uses of methylene chloride

Methylene chloride is used as

1) aerosol spray propellant
2) solvent in paint remover
3) process solvent in the manufacture of drugs
4) a metal cleaning solvent

14.6.2 Trihaloalkane

Trihaloalkanes are compounds obtained by replacing three hydrogen atoms of a hydrocarbon by three halogen atoms.

Example

$CHCl_3$	CHI_3
Chloroform	Iodoform

1) Chloroform

Chloroform is an important trihaloalkane. Dumas named $CHCl_3$ as chloroform as it gives formic acid on hydrolysis.

Preparation:

Chloroform is prepared in the laboratory by the reaction between ethyl alcohol with bleaching powderfollowed by the distillation of the product chloroform. Bleaching powder act as a source of chlorine and calcium hydroxide. This reaction is called haloform reaction. The reaction proceeds in three steps as shown below.

Step – 1: Oxidation

$$CH_3CH_2OH + Cl_2 \rightarrow CH_3CHO + 2HCl$$

Ethyl alcohol Acetaldehyde

Step – 2: Chlorination

$$CH_3CHO + 3Cl_2 \rightarrow CCl_3CHO + 3HCl$$

Acetaldehyde Trichloro acetaldehyde

Step – 3: Hydrolysis

$$2CCl_3CHO + Ca(OH)_2 \rightarrow 2CHCl_3 + (HCOO)_2\,Ca$$

Chloral chloroform

Properties

Physical properties

(i) Chloroform is a colourless liquid with peculiar sickly smell and a burning taste

(ii) The vapours of chloroform when inhaled cause unconsciousness (depress the central nervous system) and hence it is used as an anaesthetic.

Chemical properties

1) Oxidation

Chloroform undergoes oxidation in the presence of light and air to form phosgene (carbonyl chloride)

$$\underset{\text{Chloroform}}{CHCl_3} + \frac{1}{2}O_2 \xrightarrow[\text{light}]{\text{air}} \underset{\text{Phosgene}}{COCl_2} + HCl$$

Since phosgene is very poisonous, its presence makes chloroform unfit for use as anaesthetic.

2) Reduction

Chloroform undergoes reduction with zinc and HCl in the presence of ethyl alcohol to form methylene chloride.

$$\underset{\text{Chloroform}}{CHCl_3} + 2(H) \xrightarrow[\text{HCl}]{\text{Zn}} \underset{\text{Methylene chloride}}{CH_2Cl_2} + HCl$$

$$\underset{\text{Chloroform}}{CHCl_3} + 2(H) \xrightarrow[\text{HCl}]{\text{Zn}} \underset{\text{Methylene chloride}}{CH_2Cl_2} + HCl$$

3) Nitration

Chloroform reacts with nitric acid to form chloropicrin.(Trichloro nitro methane)

$$\underset{\text{Chloroform}}{CHCl_3} + HNO_3 \xrightarrow{\triangle} \underset{\text{Chloropicrin}}{CCl_3NO_2} + H_2O$$

It used as an insecticide and soil sterilising agent.

4) Carbylamine reaction

Chloroform reacts with aliphatic or aromatic primary amine and alcoholic caustic potash, to give foul smelling alkyl isocyanide (carbylamines)

$$\underset{\text{Methylamine}}{CH_3NH_2} + \underset{\text{Chloroform}}{CHCl_3} + 3KOH \longrightarrow \underset{\text{Methylisocyanide}}{CH_3NC} + 3KCl + 3H_2O$$

This reaction is used to test primary amine.

Evaluate Yourself

7) Chloroform is kept with a little ethyl alcohol in a dark coloured bottle why?

14.6.3 Tetra haloalkane

Carbon tetrachloride is a good example for tetra haloalkane

Carbon tetrachloride

Preparation

1. Chlorination of methane

The reaction of methane with excess of chlorine in the presence of sunlight will give carbon tetrachloride as the major product.

$$\underset{\text{Methane}}{CH_4} + 4Cl_2 \xrightarrow{h\gamma} \underset{\text{Carbon tetrachloride}}{CCl_4} + 4HCl$$

2. Action of carbondisulphide with chlorine gas

Carbon disulphide reacts with chlorine gas in the presence of anhydrous $AlCl_3$ as catalyst giving carbon tetrachloride

$$\underset{\text{carbon disulphide}}{CS_2 + 3Cl_2} \xrightarrow[AlCl_3]{\text{anhydrous}} \underset{\text{carbon tetrachloride}}{CCl_4} + S_2Cl_2$$

Physical properties

(i) Carbon tetrachloride is a colourless liquid with its specific smell

(ii) It is insoluble in water and soluble in organic solvents

Chemical properties

(i) Oxidation

Carbon tetrachloride reacts with hot water or with hot water vapour producing the poisonous gas, phosgene.

$$\underset{\text{carbon tetrachloride}}{CCl_4} + H_2O(g) \xrightarrow{\Delta} \underset{\text{Phosgene}}{COCl_2} + 2H_2O$$

(ii) Reduction

Carbon tetrachloride is reduced by iron powder in dilute HCl medium to form chloroform

$$\underset{\text{carbon tetrachloride}}{CCl_4} + 2(H) \xrightarrow{Fe/HCl} \underset{\text{chloroform}}{CHCl_3} + HCl$$

14.6.4 Freons (CFC)

The chloro fluoro derivatives of methane and ethane are called freons.

Nomenclature

Freon is represented as Freon-cba

Where c = number of carbon atoms – 1

b = number of hydrogen atoms + 1

a = total number of fluorine atoms

Example

Formula	C–1	H+1	F	Name
$CFCl_3$	1–1=0	0+1=1	1	Freon–11
CF_2Cl_2	1–1=0	0+1=1	2	Freon–12
$C_2F_2Cl_4$	2–1=1	0+1=1	2	Freon–112
$C_2F_3Cl_3$	2–1=1	0+1=1	3	Freon-113

Freon – 12 is prepared by the action of hydrogen fluoride on carbon tetrachloride in the presence of catalytic amount of antimony patachloride. This is called swartz reaCTION

$$\underset{\text{Carbon tetrachloride}}{CCl_4} + 2HF \xrightarrow{Sbcl_5} 2HCl + \underset{\text{Freon - 12}}{CCl_2F_2}$$

Physical properties

Freons are highly stable, unreactive, non corrosive, non toxic, easily liquefiable gases.

Uses:

(i) Freons are a used as refrigerants in refrigerators and air conditioners.

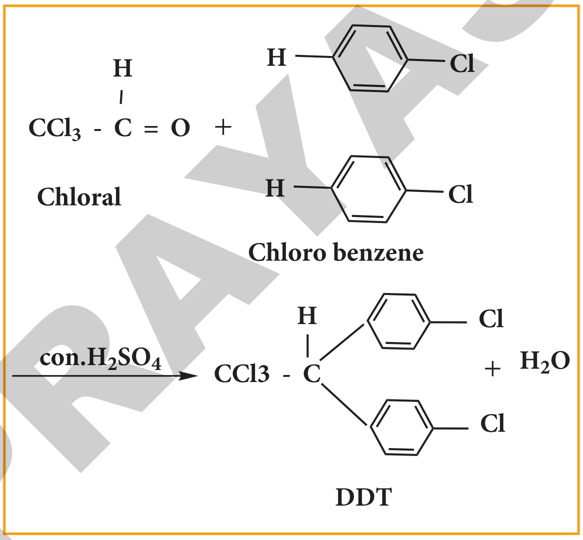
(ii) It is used as a propellant for aerosols and foams

(iii) It is used as propellant for foams to spray out deodorants, shaving creams, and insecticides.

14.6.5 DDT (p,p'-dichloro diphenyl trichloro ethane)

DDT, the first chlorinated organic pesticide was prepared in 1873, and in 1939 Paul Muller discovered the effectiveness of DDT as an insecticide. He was awarded Noble prize in medicine and physiology in 1948 for this discovery.

DDT can be prepared by heating a mixture of chlorobenzene with chloral (Trichloro acetaldehyde) in the presence of con.H_2SO_4.



Evaluate Yourself

8) What is the IUPAC name of the insecticide DDT? Why is their use banned in most of the countries?

Uses:

i) DDT is used to control certain insects which carries diseases like malaria and yellow fever

ii) It is used in farms to control some agricultural pests

iii) It is used in building construction as pest control

iv) It is used to kill various insects like housefly and mosquitoes due to its high and specific toxicity.

SUMMARY

- The compounds obtained by the substitution of hydrogen atom of alkanes by halogen atom are called haloalkane, while the compounds obtained by the substitution of hydrogen atoms of arenes by halogen atom are called haloarenes.
- Modern classification of halo compounds is based on the halogen with carbon possessing sp^3 hybridisation. In these compounds the electronegativity of halogen is more than that of carbon, hence $C\delta+ - X\delta-$ bond becomes polar.
- Haloalkane
- Haloalkanes are prepared from alkanes, alkenes or alcohols. The boiling points of haloalkane are higher than that of corresponding hydrocarbons.

- Haloalkane undergoes nucleophilic substitution and elimination reactions. Primary alkyl halides undergo S_N2 mechanism. If the reactant is chiral, the product formed exhibits inversion of stereo chemical configuration Tertiary alkyl halide undergoes S_N1 mechanism, via carbonium ion formation. If the reactant is chiral, the product formed is optically inactive due to racemisation.

- Organo metallic compound

- Haloalkane reacts with metal to form organometallic compounds like Grignard reagent. It is represented as $R^{\delta-} - Mg^{\delta+}X$. Grignard reagent reacts with variety of substances to give almost all class of organic compounds like alcohols, aldehydes, ketones, acids etc.

- Haloarenes

- Haloarenes are prepared from arenes or by decomposition of benzene diazonium chloride. Haloarenes are more stable than haloalkane. C – X bond in halo arenes is short and strong.

- Under normal conditions halo arenes do not undergo nucleophilic substitution but takes part in electrophilic substitution. Electron withdrawing inductive effect of halogen atom deactivates the benzene ring whereas resonating structure control o, p directing nature of halo arenes.

- Poly halogen compounds

- Organic compounds having two or more halogen atoms are called poly halogen compounds. These compounds are useful in our day to day life but pose environmental threat.

- Chloroform is used as an anasthetic, but because of its toxic nature it has been replaced by less toxic and safer anaesthetic like ethers.

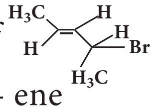
- Iodoform is used as an antiseptic, due to the liberation of free iodine. But it has been replaced by other formulation containing iodine, due to its objectional smell.

- Carbon tetrachloride is used in fire extinguishers. Freons are used as refrigerant. But both these compounds lead to adverse environmental effect.

- DDT is used an effective insecticide. Now a days it is banned because of it's long term toxic effect.

Evaluation

I. Objective type questions (MCQ)

1. The IUPAC name of  is

a) 2-Bromo pent – 3 – ene

b) 4-Bromo pent – 2 – ene

c) 2-Bromo pent – 4 – ene

d) 4-Bromo pent – 1 – ene

2. Of the following compounds, which has the highest boiling point?

a) n-Butyl chloride

b) Isobutyl chloride

c) t-Butyl chloride

d) n-propyl chloride

3. Arrange the following compounds in increasing order of their density

A) CCl_4 B) $CHCl_3$

C) CH_2Cl_2 D) CH_3Cl

a) D < C < B < A b) C > B > A > D

c) A < B < C < D d) C > A > B > D

4. With respect to the position of – Cl in the compound $CH_3 - CH = CH - CH_2 - Cl$, it is classified as

a) Vinyl b) Allyl

c) Secondary d) Aralkyl

5. What should be the correct IUPAC name of diethyl chloromethane?

a) 3 – Chloro pentane

b) 1-Chloropentane

c) 1-Chloro-1, 1, diethyl methane

d) 1 –Chloro-1-ethyl propane

6. C -X bond is strongest in

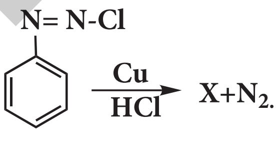
a) Chloromethane

b) Iodomethane

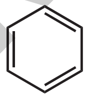
c) Bromomethane

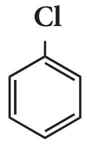
d) Fluoromethane

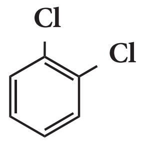
7. In the reaction

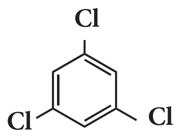


X is __________

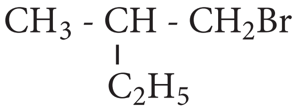
a) 

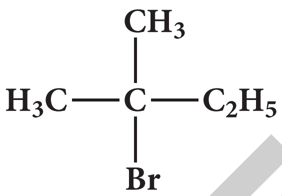
b) 

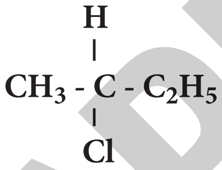
c) 

d) 

8. Which of the following compounds will give racemic mixture on nucleophilic substitution by OH- ion?

i) 
$CH_3 - \underset{C_2H_5}{\underset{|}{CH}} - CH_2Br$

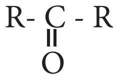
ii) 
$H_3C - \overset{CH_3}{\overset{|}{\underset{Br}{\underset{|}{C}}}} - C_2H_5$

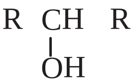
iii) 
$CH_3 - \overset{H}{\overset{|}{\underset{Cl}{\underset{|}{C}}}} - C_2H_5$

a) (i) b) (ii) and (iii)

c) (iii) d) (i) and (ii)

9. The treatment of ethyl formate with excess of RMgX gives

a) 
$R- \underset{O}{\underset{||}{C}} - R$

b) 
$R\ \underset{OH}{\underset{|}{CH}}\ R$

c) R- CHO d) R- O – R

10. Benzene reacts with Cl_2 in the presence of $FeCl_3$ and in absence of sunlight to form

a) Chlorobenzene

b) Benzyl chloride

c) Benzal chloride

d) Benzene hexachloride

11. The name of $C_2F_4Cl_2$ is ___________

a) Freon – 112

b) Freon – 113

c) Freon – 114

d) Freon – 115

12. Which of the following reagent is helpful to differentiate ethylene dichloride and ethylidene chloride?

a) Zn / methanol

b) KOH / ethanol

c) aqueous KOH

d) $ZnCl_2$ / Con HCl

13. Match the compounds given in Column I with suitable items given in Column II

	Column I (Compound)		Column II (Uses)
A	Iodoform	1	Fire extinguisher
B	Carbon tetra chloride	2	Insecticide
C	CFC	3	Antiseptic
D	DDT	4	Refrigerants

Code

a) A → 2 B → 4 C →1 D →3

b) A → 3 B → 2 C →4 D →1

c) A → 1 B → 2 C →3 D →4

d) A → 3 B → 1 C →4 D →2

14. **Assertion:** In mono haloarenes, electrophilic substitution occurs at ortho and para positions.

Reason: Halogen atom is a ring deactivator

(i) If both assertion and reason are true and reason is the correct explanation of assertion.

(ii) If both assertion and reason are true but reason is not the correct explanation of assertion.

(iii) If assertion is true but reason is false.

(iv) If both assertion and reason are false.

15. Consider the reaction,

$CH_3CH_2CH_2Br + NaCN \rightarrow CH_3CH_2CH_2CN + NaBr$

This reaction will be the fastest in

a) ethanol b) methanol

c) DMF (N, N' – dimethyl formanide)

d) water

16. Freon-12 is manufactured from tetrachloro methane by

a) Wurtz reaction

b) Swarts reaction

c) Haloform reaction

d) Gattermann reaction

17. The most easily hydrolysed molecule under SN1 condition is

a) allyl chloride

b) ethyl chloride

c) ispropylchloride

d) benzyl chloride

18. The carbo cation formed in SN1 reaction of al kyl halide in the slow step is

a) sp^3 hybridised b) sp^2 hybridised

c) sp hybridised d) none of these

19. The major products obtained when chlorobenzene is nitrated with HNO_3 and con H_2SO_4

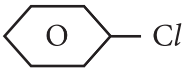
a) 1-chloro-4-nitrobenzene

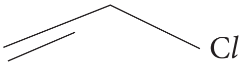
b) 1-chloro-2-nitrobenzene

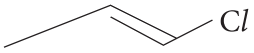
c) 1-chloro-3-nitrobenzene

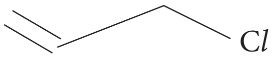
d) 1-chloro-1-nitrobenzene

20. Which one of the following is most reactive towards nucleophilic substitution reaction ?

a) 

b) 

c) 

d) 

21. Ethylidene chloride on treatment with aqueous KOH gives

a) acetaldehyde

b) ehtyleneglycol

c) formaldehyde

d) glycoxal

22. The raw material for Rasching process

a) chloro benzene b) phenol

c) benzene d) anisole

23. Chloroform reacts with nitric acid to produce

a) nitro toluene

b) nitro glycerine

c) chloropicrin

d) chloropicric acid

24. acetone $\xrightarrow[\text{ii) } H_2O / H^{-1}]{\text{i) } CH_3MgI}$ X, X is

a) 2-propanol

b) 2-methyl-2-propanol

c) 1-propanol

d) acetonol

25. Silverpropionate when refluxed with Bromine in carbontetrachloride gives

a) propionic acid

b) chloro ethane

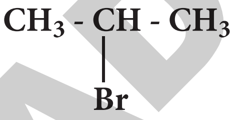
c) bromo ethane

d) chloro propane

26. Classify the following compounds in the form of alkyl, allylic, vinyl, benzylic halides

a) $CH_3 - CH = CH - Cl$

(ii) $C_6H_5CH_2I$

(iii) 

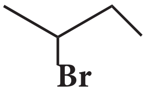
$CH_3 - \underset{\displaystyle Br}{\underset{|}{CH}} - CH_3$

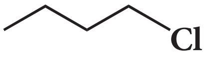
(iv) $CH_2 = CH - Cl$

27. Why chlorination of methane is not possible in dark?

28. How will you prepare n propyl iodide from n-propyl bromide?

29. Which alkyl halide from the following pair is i) chiral ii) undergoes faster S_N2 reaction?





30. How does chlorobenzene react with sodium in the presence of ether? What is the name of the reaction?

31. Give reasons for polarity of C-X bond in halo alkane.

32. Why is it necessary to avoid even traces of moisture during the use of Grignard reagent?

33. What happens when acetyl chloride is treated with excess of CH_3MgI?

34. Arrange the following alkyl halide in increasing order of bond enthalpy of RX

CH_3Br, CH_3F, CH_3Cl, CH_3I

35. What happens when chloroform reacts with oxygen in the presence of sunlight?

36. Write down the possible isomers of $C_5H_{11}Br$ and give their IUPAC and common names.

37. Mention any three methods of preparation of haloalkanes from alcohols.

38. Compare S_N1 and S_N2 reaction mechanisms.

39. Reagents and the conditions used in the reactions are given below. Complete the table by writing down the product and the name of the reaction.

Reaction	**Product**	**Name of the reaction**
$CH_3CH_2OH + SOCl_2 \xrightarrow{\text{pyridine}} ?$	--------	--------
$CH_3CH_2Br + AgF \longrightarrow ?$	--------	--------
$C_6H_5Cl + Na \xrightarrow{\text{ether}} ?$	--------	--------

40. Discuss the aromatic nucleophilic substitutions reaction of chlorobenzene.

41. Account for the following

(i) t-butyl chloride reacts with aqueous KOH by S_N1 mechanism while n-butyl chloride reacts with S_N2 mechanism.

(ii) p-dichloro benzene has higher melting point than those of o-and m-dichloro benzene.

42. In an experiment ethyliodide in ether is allowed to stand over magnesium pieces. Magnesium dissolves and product is formed

a) Name the product and write the equation for the reaction.

b) Why all the reagents used in the reaction should be dry? Explain

c) How is acetone prepared from the product obtained in the experiment.

43. Write a chemical reaction useful to prepare the following:

i) Freon-12 from Carbon tetrachloride

ii) Carbon tetrachloride from carbon disulphide

44. What are Freons? Discuss their uses and environmental effects

45. Predict the products when bromoethane is treated with the following

i) KNO_2

ii) $AgNO_2$

46. Explain the mechanism of S_N1 reaction by highlighting the stereochemistry behind it

47. Write short notes on the the following

i) Raschig process

ii) Dows Process

iii) Darzens process

48. Starting from CH_3MgI, How will you prepare the following?

i) Acetic acid

ii) Acetone

iii) Ethyl acetate

iv) Iso propyl alcohol

v) Methyl cyanide

49. Complete the following reactions

i) $CH_3 - CH = CH_2 + HBr \xrightarrow{\text{Peroxide}}$

ii) $CH_3 - CH_2 - Br + NaSH \xrightarrow[H_2O]{\text{alcohol}}$

iii) $C_6H_5Cl + Mg \xrightarrow{\text{THF}}$

iv) $CHCl_3 + HNO_3 \xrightarrow{\Delta}$

v) $CCl_4 + H_2O \xrightarrow{\Delta}$

50. Explain the preparation of the following compounds

i) DDT ii) Chloroform

iii) Biphenyl

iv) Chloropicrin

v) Freon-12

51. An organic compound (A) with molecular formula C_2H_5Cl reacts with KOH gives compounds (B) and with alcoholic KOH gives compound (C). Identify (A),(B), and (C)

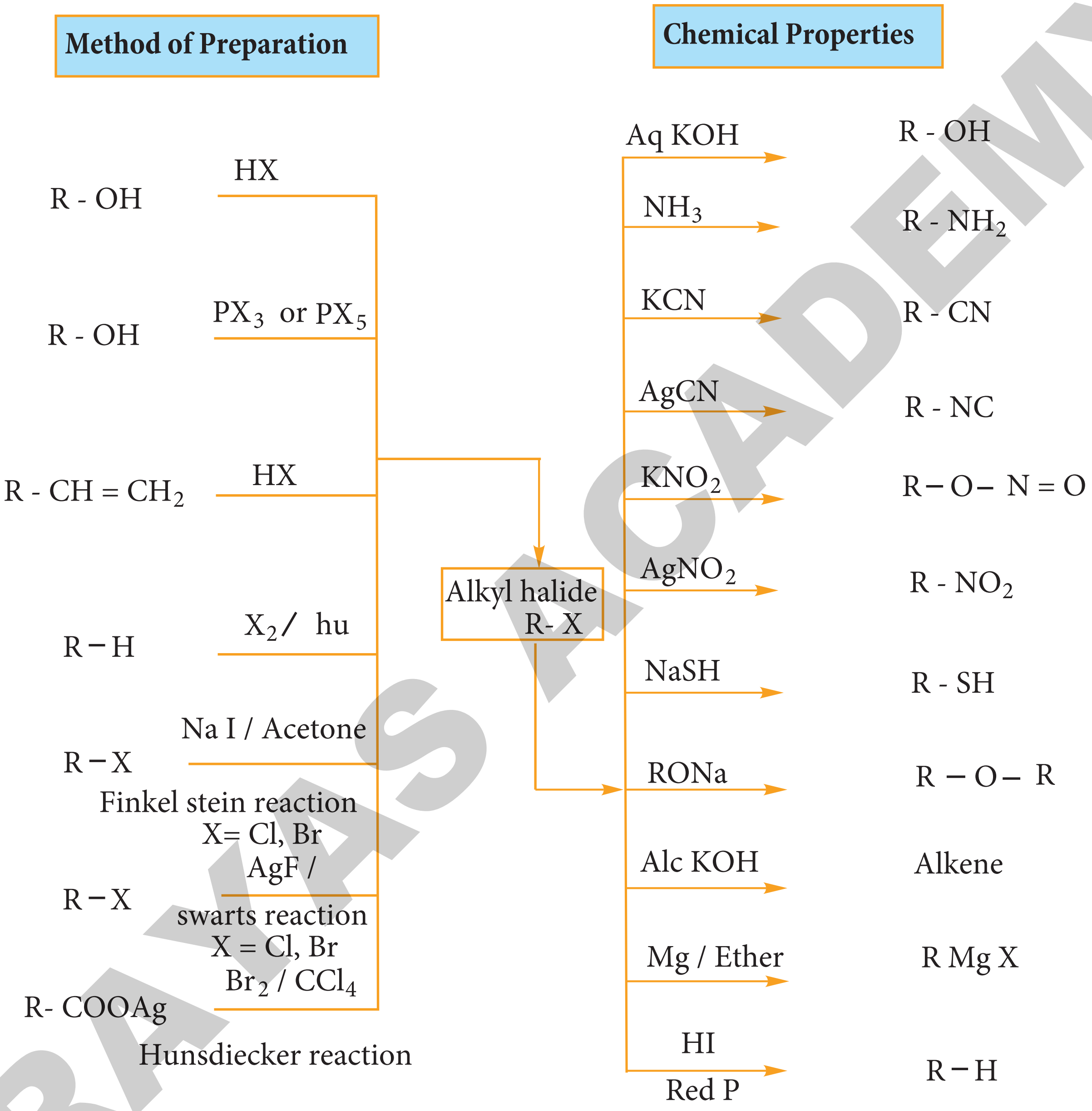
52. Simplest alkene (A) reacts with HCl to form compound (B).Compound (B) reacts with ammonia to form compound (C) of molecular formula C_2H_7N.Compound (C) undergoes carbylamine test. Identify (A), (B), and (C).

53. A hydrocarbon C_3H_6 (A) reacts with HBr to form compound (B). Compound (B) reacts with aqueous potassium hydroxide to give (C) of molecular formula C_3H_6O.what are (A) (B) and (C). Explain the reactions.

54. Two isomers (A) and (B) have the same molecular formula $C_2H_4Cl_2$. Compound (A) reacts with aqueous KOH gives compound (C) of molecular formula C_2H_4O. Compound (B) reacts with aqueous KOH gives compound (D) of molecular formula $C_2H_6O_2$. Identify (A),(B),(C) and (D).

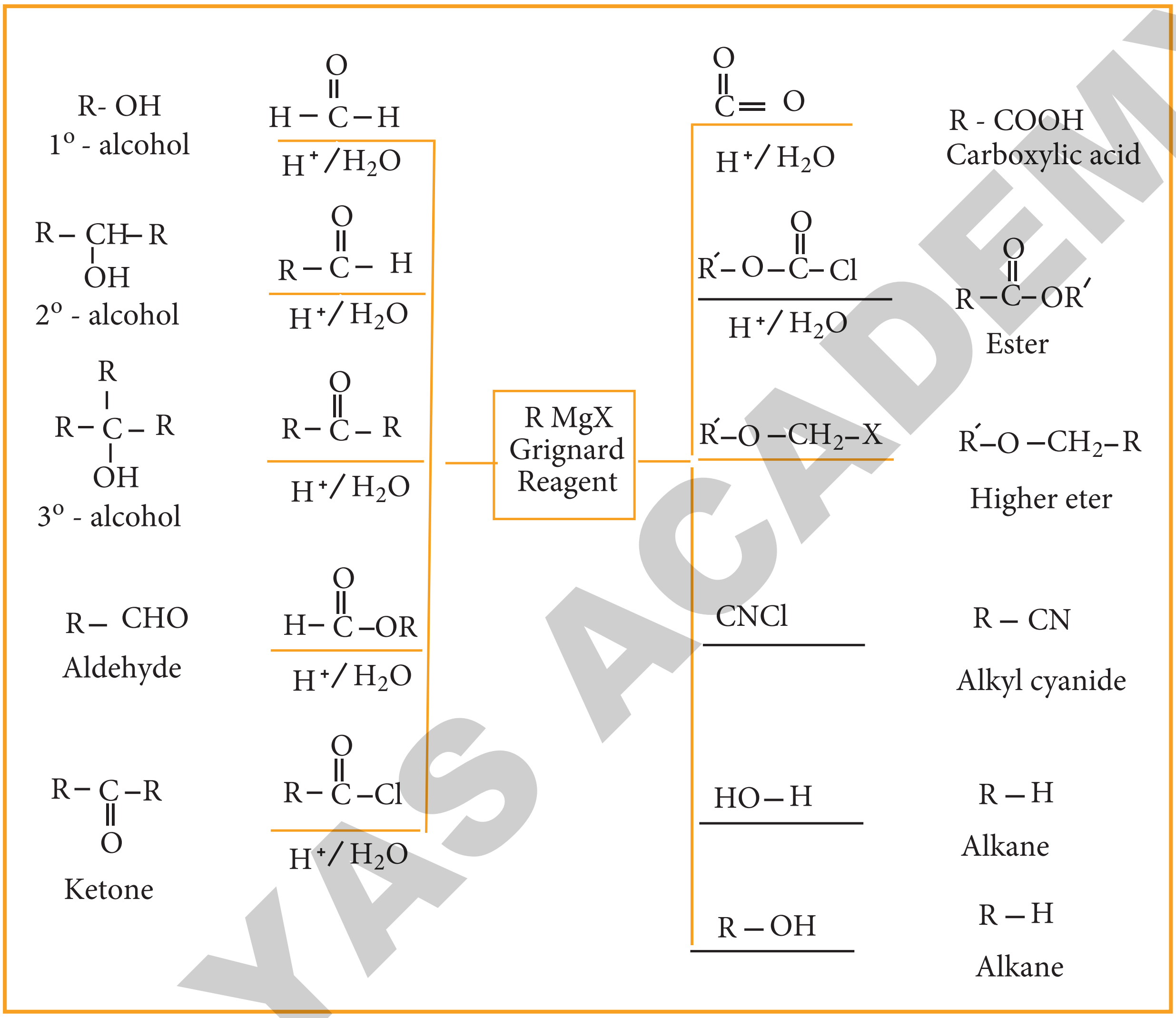
FLOW CHART

Haloalkane

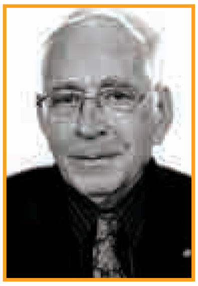


FLOW CHART

Synethetic uses of Grignard reagent



Unit 15 Environmental Chemistry



The Nobel Prize in chemistry 2005 was awarded jointly to **Yves Chauvin, Robert H. Grubbs** and **Richard R. Schrock** for the development of new chemicals based on Green chemistry.

In 1971 Yves Chauvin explainedthe types of metal compound that act as catalysts in the reactions. Richard Schrock was the first to produce efficient metal compound catalysts for metathesis in 1990. Two years later Robert Grubbs developed better catalysts, stable in air thatwas highlighted in many applications.

Learning Objectives

After studying this unit, students will be able to

- Know the various concepts of environmental chemistry
- classify the various types of environmental pollutions.
- recognize the particulate pollutants and their effects.
- explain the cause and hazardous effects of acid rain, greenhouse effect, ozone depletion and global warming.
- know the reason for water pollution and recognize the prescribed standard for drinking water.
- highlight the strategies to control various types of pollution
- appreciate the meaning of green chemistry and comprehend the importance of green chemistry in day today life.

15. INTRODUCTION

We are very familiar with the word environment. It includes the air we breathe, the water that covers most of the earth's surface, the plants and animals around us and much more. These days, when we hear people talk about "the environment", they are often referring to the overall condition of our planet, or how healthy it is.

Environmental chemistry is a branch of chemistry which deals with the study of chemicals and chemical processes. occuring in the enviroment by direct human activities. It also deals with sources, causes and methods of controlling air, water and soil pollution.

15.1 Environmental Pollution

Any undesirable change in our environment that has harmful effects on plants, animals and human beings is called environmental pollution.

Environmental pollution is usually caused by the addition of waste products of human activity to the environment. The substances which cause pollution of environment are called pollutants. The pollutants may be solids, liquids or gaseous substances present in significant concentration in the environment.Our environment becomes polluted day by day, by the increased addition of industrial and domestic wastes to it. The air we breathe, the water we drink and the place where we live in, are highly contaminated.

The pollutants are classified as bio-degradable and non-biodegradable pollutants.

i. Bio-degradable pollutants :

The pollutants which can be easily decomposed by the natural biological processes are called bio-degradable pollutants. Examples:plant wastes, animal wastes etc.

ii. Non bio-degradable pollutants :

The pollutants which cannot be decomposed by the natural biological processes are called Non bio-degradable pollutants. Examples: metal wastes (mainly Hg and Pb), D.D.T, plastics, nuclear wastes etc., These pollutants are harmful to living organisms even in low concentration. As they are not degraded naturally,it is difficult to eliminate them from our environment.

15.2.Atmospheric Pollution

Earth's atmosphere is a layer of gases retained by the earth's gravity. It contains roughly 78% nitrogen, 21% oxygen, 0.93% argon, 0.04% carbon dioxide, trace amounts of other gases and little amount of water vapour. This mixture is commonly known as air.

Earth's atmosphere can be divided into different layers with characteristic altitude and temperature. The various regions of atmosphere are given in table 15.1.

Table 15.1 Regions of atmosphere

Region	Altitude from earth's surface	Temperature range	Gases/ species present
Troposphere	0-10 km	15° C to -56°C	N_2O_2 CO_2 H_2O (vap)

Region	Altitude from earth's surface	Temperature range	Gases/ species present
Stratosphere (ozonosphere)	10-50 km	-56°C to -2°C	N_2 O_2 O_3 O atoms
Mesosphere	50-85 km	-2°C to- 92°C	N_2 O_2^+ N_O^+
Thermosphere	85-500 km	-92°C to 1200°C	O_2^+ O^+ NO^+ e^-

Troposphere :

The lowest layer of the atmosphere is called the troposphere and it extends from 0 – 10 km from the earth surface. About 80% of the mass of the atmosphere is in this layer. This troposphere in further divided as follows.

i) Hydrosphere:

Hydrosphere includes all types of water sources like oceans, seas, rivers, lakes, streams, underground water, polar icecaps, clouds etc. It covers about 75% of the earth's surface. Hence the earth is called as a blue planet.

ii) Lithosphere:

Lithosphere the includes soil, rocks and mountains which are solid components of earth.

iii) Biosphere:

It includes the lithosphere hydrosphere and atmosphere intergrating the living organism present in the lithosphere, hydrosphere and atmosphere.

DO YOU KNOW?

The Bhopal Tragedy

The world's worst chemical disaster happened in the Indian city of Bhopal in the early morning hours of December 3, 1984. An explosion at the Union Carbide pesticide plant released a cloud of toxic gas (methyl isocyanate) CH_3NCO into the air. Since the gas was twice as heavy as air, it did not drift away but formed a 'blanket' over the surrounding area. It attacked people's lungs and affected their breathing. Thousands of people died and the lives of many were ruined. The lungs, brain, eyes, muscles as well as gastrointestinal, neurological and immune systems of those who survived were severely affected.

15.3. Types of environmental pollution

Atmospheric pollution is generally studied as tropospheric pollution. Different types of atmospheric pollutions are

(1) Air pollution (2) Water pollution

(3) Soil pollution.

15.3.1 Air pollution

Any undesirable change in air which adversely affects living organisms is called air pollution. Air pollution is limited to troposphere and stratosphere. Air pollution is mainly due to the excessive discharge of undesirable foreign matter in to the atmospheric air.

Fig 15.1 Air Pollution

types of air pollutants

Air pollutants may exist in two major forms namely, gases and particulates.

15.3.1.1 Gaseous air pollutants

Oxides of sulphur, oxides of nitrogen, oxides of carbon, and hydrocarbons are the gaseous air pollutants.

a. Oxides of Sulphur

Sulphur dioxide and sulphur trioxide are produced by burning sulphur containing fossil fuels and roasting sulphide ores. Sulphur dioxide is a poisonous gas to both animals and plants. Sulphur dioxide causes eye irritation, coughing and respiratory diseases like asthma, bronchitis,etc.

Sulphur dioxide is oxidised into more harmful sulphur trioxide in the presence of particulate matter present in polluted air .

$$2SO_2 + O_2 \xrightarrow{\text{Particulate matter}} 2SO_3$$

SO_3 combines with atmospheric water vapour to form H_2SO_4 , which comes down in the form of acid rain.

$$SO_3 + H_2O \rightarrow H_2SO_4$$

Some harmful effects of acid rain will be discussed in section 15.3

b. Oxides of nitrogen

Oxides of nitrogen are produced during high temperature combustion processes, oxidation of nitrogen in air and from the combustion of fuels (coal, diesel, petrol etc.).

$$N_2 + O_2 \xrightarrow{>1210^\circ C} 2NO$$

$$2NO + O_2 \xrightarrow{1100^\circ C} 2NO_2$$

$$NO + O_3 \longrightarrow NO_2 + O_2$$

The oxides of nitrogen are converted into nitric acid which comes down in the form of acid rain. They also form reddish brown haze in heavy traffic. Nitrogen dioxide potentially damages plant leaves and retards photosynthesis. NO_2 is a respiratory irritant and it can cause asthma and lung injury. Nitrogen dioxide is also harmful to various textile fibres and metals.

c. Oxides of carbon

The major pollutants of oxides of carbon are carbon monoxide and carbon dioxide.

(i) Carbon Monoxide

Carbon monoxide is a poisonous gas produced as a result of incomplete combustion of coal are firewood. It is released into the air mainly by automobile exhaust. It binds with haemoglobin and form carboxy haemoglobin which impairs normal oxygen transport by blood and hence the oxygen carrying capacity of blood is reduced. This oxygen deficiency results in headache, dizziness, tension, Loss of consciousness, blurring of eye sight and cardiac arrest.

(ii) Carbon dioxide

Carbon dioxide is released into the atmosphere mainly by the process of respiration, burning of fossil fuels, forest fire, decomposition of limestone in cement industry etc.

Green plants can convert CO_2 gas in the atmosphere into carbohydrate and oxygen through a process called photosynthesis. The increased CO_2 level in the atmosphere is responsible for global warming. It causes headache and nausea.

(d) Hydrocarbon

The compounds composed of carbon and hydrogen only are called hydrocarbons. They are mainly produced naturally (marsh gas) and also by incomplete combustion of automobile fuel.

They are potential cancer causing (carcinogenic) agents. For example, polynuclear aromatic hydrocarbons (PAH) are carcinogenic, they cause irritation in eyes and mucous membranes.

15.3.1.2Greenhouse effect and Global warming:

In 1987, Jean Baptiste Fourier a French mathematician and scientist coined the term“Greenhouse Effect” for trapping of heat in the atmosphere by certain gases.

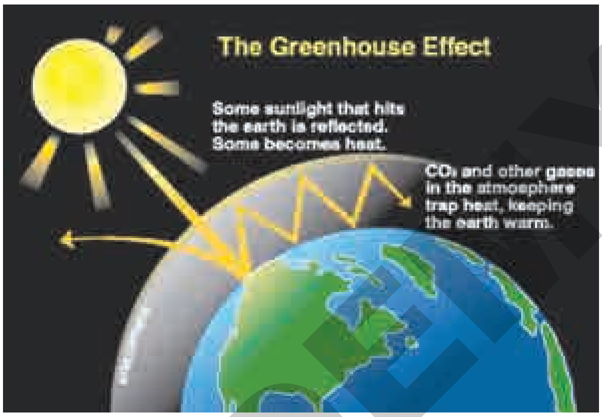


Fig 15.2 Greenhouse effect

The earth’s atmosphere allows most of the visible light from the Sun to pass through and reach Earth’s surface. As Earth’s surface is heated by sunlight, it radiates part of this energy back toward space as longer wavelengths (IR).

Some of the heat is trapped by CH_4, CO_2, CFCs and water vapour present in the atmosphere. They absorb IR radiation and effectively block a large portion of earth’s emitted radiation. The radiation thus absorbed is partly reemitted to earth’s surface. Therefore, the earth’s surface gets heated up by a phenomenon called greenhouse effect.

Thus Greenhouse effect may be defined as the heating up of the earth surface due to trapping of infrared radiations reflected by earth’s surface by CO_2 layer in the atmosphere”. The heating up of earth through the greenhouse effect is called global warming.

Without the heating caused by the

greenhouse effect, Earth's average surface temperature would be only about −18 °C (0 °F). Although the greenhouse effect is a naturally occurring phenomenon, it is intensified by the continuous emission of greenhouse gases into the atmosphere.

During the past 100 years, the amount of carbon dioxide in the atmosphere increased by roughly 30 percent and the amount of methane more than doubled.If these trends continue, the average global temperature will increase which can lead to melting of polar ice caps and flooding of low lying areas. This will increase incidence of infectious diseases like dengue, malaria etc.

15.3.1.3 Acid Rain

Rain water normally has a pH of 5.6 due to dissolution of atmospheric CO_2 into it. Oxides of sulphur and nitrogen in the atmosphere may be absorbed by droplets of water that make up clouds and get chemically converted into sulphuric acid and nitric acid respectively as a results of pH of rain water drops to the level 5.6, hence it is called acid rain.

Acid rain is a by-product of a variety of sulphur and nitrogen oxides in the atmosphere. Burning of fossil fuels (coal and oil) in power stations, furnaces and petrol, diesel in motor engines produce sulphur dioxide and nitrogen oxides. The main contributors of acid rain are SO_2 and NO_2.They are converted into sulphuric acid and nitric acid respectively by the reaction with oxygen and water.

$$2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4$$

$$4NO_2 + O_2 + 2H_2O \rightarrow 4HNO_3$$

Harmful effects of acid rain:

Some harmful effects are discussed below.

(i) Acid rain causes extensive damage to buildings and structural materials of marbles. This attack on marble is termed as Stone leprosy.

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2\uparrow$$

(ii) Acid rain affects plants and animal life in aquatic ecosystem.

(iii) It is harmful for agriculture, trees and plants as it dissolves and removes the nutrients needed for their growth.

(iv) It corrodes water pipes resulting in the leaching of heavy metals such as iron, lead and copper into the drinking water which have toxic effects.

(v) It causes respiratory ailment in humans and animals.

FIG 15. 3. Effect Of Acid Rain On Tajmahal

15.3.2 Particulate matter (Particulate pollutants)

Particulate pollutants are small solid particles and liquid droplets suspended in air. Many of particulate pollutants are hazardous. Examples: dust, pollen, smoke, soot and liquid droplets (aerosols) etc,.

They are blown into the atmosphere by volcanic eruption, blowing of dust, incomplete combustion of fossil fuels induces soot. Combustion of high ash fossil fuels creates fly ash and finishing of metals throws metallic particles into the atmosphere.

15.3.2.1. Types of Particulates:

Particulate in the atmosphere may be of two types, viable or non-viable.

a. Viable particulates

The viable particulates are the small size living organisms such as bacteria, fungi, moulds, algae, etc. which are dispersed in air. Some of the fungi cause allergy in human beings and diseases in plants.

b. Non-viable particulates

The non- viable particulates are small solid particles and liquid droplets suspended in air. They help in the transportation of viable particles. There are four types of non-viable particulates in the atmosphere. They are classified according to their nature and size as follows

(i) Smoke

Smoke particulate consists of solid particles (or) mixture of solid and liquid particles formed by combustion of organic matter.

For example, cigarette smoke, oil smoke, smokes from burning of fossil fuel, garbage and dry leaves.

(ii) Dust:

Dust composed of fine solid particles produced during crushing and grinding of solid materials.

For example, sand from sand blasting, saw dust from wood works, cement dust from cement factories and fly ash from power generating units.

(iii) Mists

They are formed by particles of spray liquids and condensation of vapours in air.

For example, sulphuric acid mist, herbicides and insecticides sprays can form mists.

(iv) Fumes

Fumes are obtained by condensation of vapours released during sublimation, distillation, boiling and calcination and by several other chemical reactions.

For example, organic solvents, metals and metallic oxides form fume particles.

15.3.2.2. Health effects of particulate pollutants:

i. Dust, mist, fumes,etc., are air borne particles which are dangerous for human health. Particulate pollutants bigger than 5 microns are likely to settle in the nasal passage whereas particles of about 10 micron enters the lungs easily and causes scaring or fibrosis of lung lining. They irritate the lungs and causes cancer and asthma. This disease is also called pneumoconiosis. Coal miners may suffer from black lung disease. Textile workers may suffer from white lung disease.

ii. Lead particulates affect children's brain, interferes maturation of RBCs and even cause cancer.

iii. Particulates in the atmosphere reduce visibility by scattering and absorption of sunlight. It is dangerous for aircraft and motor vehicles

iv. Particulates provide nuclei for cloud formation and increase fog and rain.

v. Particulates deposit on plant leaves and hinder the intake of CO_2 from the air and affect photosynthesis.

15.3.2.3. Techniques to reduce particulate pollutants

The particulates from air can be removed by using electrostatic precipitators, gravity settling chambers, and wet scrubbers or by cyclone collectors. These techniques are based on washing away or settling of the particulates.

15.3.3 Smog

Smog is a combination of smoke and fog which forms droplets that remain suspended in the air.

Fig 15.4 classical smog

Smog is a chemical mixture of gases that forms a brownish yellow haze over urban cities.Smog mainly consists of ground level ozone, oxides of nitrogen, volatile organic compounds, SO_2, acidic aerosols and gases, and particulate matter.

There are two types of smog. One is Classical smog caused by coal smoke and fog , second one is photo chemical smog caused by photo chemical oxidants.They are discussed below in detail.

(i) Classical smog or London smog

Classical smog was first observed in London in December 1952 and hence it is also known as London smog. It consists of coal smoke and fog.

It occurs in cool humid climate. This atmospheric smog found in many large cities. The chemical composition is the mixture of SO_2, SO_3 and humidity. It generally occurs in the morning and becomes worse when the sun rises.

This is mainly due to the induced oxidation of SO_2 to SO_3, which reacts with water yielding sulphuric acid aerosol.

Chemically it is reducing in nature because of high concentration of SO_2 and so it is also called as reducing smog.

Effects of classical smog:

a. Smog is primarily responsible for acid rain.

b. Smog results in poor visibility and it affects air and road transport.

c. It also causes bronchial irritation.

DO YOU KNOW?

Great London Smog

The great smog of London, or great smog of 1952, was a severe air-pollution event that affected the British capital of London in early December 1952. It lasted from Friday, 5 December to Tuesday, 9 December 1952 and then dispersed quickly when the weather changed. It caused major disruption by reducing visibility and even penetrating indoor areas. Government medical reports in the following weeks, however, estimated that until 8 December, 4,000 people had died as a direct result of the smog and 100,000 more were made ill by the smog's effects on the human respiratory tract.

ii)Photo chemical smog or Los Angel Smog

Photo Chemical smog was first observed in Los Angels in 1950. It occurs in warm, dry and sunny climate.This type of smog is formed by the combination of smoke, dust and fog with air pollutants like oxides of nitrogen and hydrocarbons in the presence of sunlight.

It forms when the sun shines and becomes worse in the afternoon. Chemically it is oxidizing in nature because of high concentration of oxidizing agents NO_2 and O_3, so it is also called as oxidizing smog.

Photo chemical smog is formed through sequence of following reactions.

$$N_2 + O_2 \rightarrow 2NO$$

$$2NO + O_2 \rightarrow 2NO_2$$

$$NO_2 \xrightarrow{\text{sun light}} NO + (O)$$

$$(O) + O_2 \rightarrow O_3$$

$$O_3 + NO \rightarrow NO_2 + O_2$$

$$NO_2 \xrightarrow{\text{sun light}} NO + (O)$$

NO and O_3 are strong oxidizing agent and can react with unburnt hydrocarbons in polluted air to form formaldehyde,acrolein and peroxy acetyl nitrate(PAN).

Effects of photo chemical smog

The three main components of photo chemical smog are nitrogen oxide, ozone and oxidised hydro carbon like formaldehyde(HCHO), Acrolein (CH_2=CH-CHO),peroxy acetyl nitrate (PAN).

Photochemical smog causes irritation to eyes, skin and lungs, increase in chances of asthma.

High concentrations of ozone and NO can cause nose and throat irritation, chest pain, uncomfortable in breathing, etc.

PAN is toxic to plants, attacks younger leaves and cause bronzing and glazing of their surfaces

It causes corrosion of metals stones, building materials and painted surfaces.

Control of Photo chemical smog

The formation of photochemical smog can be suppressed by preventing the release of nitrogen oxides and hydrocarbons into the atmosphere from the motor vehicles by using catalytic convertors in engines. Plantation of certain trees like Pinus, Pyrus, Querus Vitus and juniparus can metabolise nitrogen oxide.

15.4. Stratospheric pollution

At high altitudes to the atmosphere consists of a layer of ozone (O_3) which acts as an umbrella or shield for harmful UV radiations. It protects us from harmful effect such as skin cancer. UV radiation can convert molecular oxygen into ozone as shown in the following reaction.

$$O_2(g) \xrightarrow{uv} O(g) + O(g)$$

$$O(g) + O_2(g) \xrightarrow{uv} O_3(g)$$

Ozone gas is thermodynamically unstable and readily decomposes to molecular oxygen.

15.4.1 Depletion of Ozone Layer (Ozone hole)

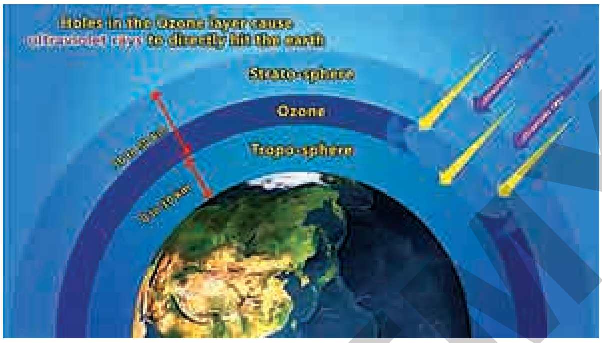


Fig 15.5 Ozone Depletion

In recent years, a gradual depletion of this protective ozone layer has been reported. Nitric oxide and CFC are found to be most responsible for depletion of ozone layer.

Generally substances that cause depletion of ozone or make it thinner are called Ozone Depletion Substances abbreviated as ODS. The loss of ozone molecules in the upper atmosphere is termed as depletion of stratospheric ozone.

Oxides of Nitrogen:

Nitrogen oxides introduced directly into the stratosphere by the supersonic jet aircraft engines in the form of exhaust gases.

These oxides are also released by combustion of fossil fuels and nitrogen fertilizers. Inert nitrous oxide in the stratosphere is photo chemically converted into more reactive nitric oxide. Oxides of nitrogen catalyse the decomposition of ozone and are themselves regenerated. Ozone gets depleted as shown below.

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$O_2 \xrightarrow{h\upsilon} O + O$$

$$NO_2 + O \rightarrow NO + O_2$$

Thus NO is regenerated in the chain reaction.

Chloro Fluoro Carbons (CFC) Freons

The chloro fluoro derivatives of methane and ethane are referred by trade name Freons. These Chloro Fluoro Carbon compounds are stable, non-toxic, noncorrosive and non-inflammable, easily liquefiable and are used in refrigerators, air- conditioners and in the production of plastic foams. CFC's are the exhaust of supersonic air craft's and jumbo jets flying in the upper atmosphere. They slowly pass from troposphere to stratosphere. They stay for very longer period of 50 - 100 years. In the presence of uv radiation, CFC's break up into chlorine free radical

$$CF_2Cl_2 \xrightarrow{h\upsilon} CF_2Cl + Cl^{\cdot}$$

$$CFCl_3 \xrightarrow{h\upsilon} CFCl_2 + Cl^{\cdot}$$

$$Cl^{\cdot} + O_3 \rightarrow ClO + O_2$$

$$ClO^{\cdot} + O \rightarrow Cl + O_2$$

Chlorine radical is regenerated in the course of reaction. Due to this continuous attack of Cl° thinning of ozone layer takes place which leads to formation of ozone hole.

It is estimated that for every reactive chlorine atom generated in the stratosphere 1,00,000 molecules of ozone are depleted.

15.4.2 Environmental Impact of Ozone Depletion

The formation and destruction of ozone is a regular natural process, which never disturbs the equilibrium level of ozone in the stratosphere. Any change in the equilibrium level of the ozone in the atmosphere will adversely affect life in the biosphere in the following ways.

Depletion of ozone layer will allow more UV rays to reach the earth surface and layer would cause skin cancer and also decrease the immunity level in human beings.

UV radiation affects plant proteins which leads to harmful mutation of cells.

UV radiation affects the growth of phytoplankton, as a result ocean food chain is disturbed and even damages the fish productivity.

15.5 Water Pollution

Water is essential for life. Without water life would have been impossible. The slogan, 'Save Water, Water will save you' tell us the importance of water. Such slogans tell us to save water. Apart from saving water, maintaining its quality is also equally important.

Fig 15.6 water pollution

Now a days water is getting polluted due to human activities and the availability of potable water in nature is becoming rare day by day.Water pollution is defined as"The addition of foreign substances or factors like heat which degrades the quality of water, so that it becomes health hazard or unfit to use."

The water pollutants originate from both natural and human activities. The source of water pollution is classified as Point and Non-point source.

Easily identified source of place of pollution is called as point source. Example: municipal and industrial discharge pipes.

Non-point source cannot be identified easily, example: agricultural runoff, mining wastes, acid rain, and storm-water drainage and construction sediments.

Table 15.2: List of major water pollutants and their sources.

No	Pollutant	Sources
1	Microorganisms	Domestic sewage, domestic waste water, dung heap
2	Organic wastes	Domestic sewage, animal excreta, food processing factory waste, detergents and decayed animals and plants,
3	Plant nutrients	Chemical fertilisers
4	Heavy metals	Heavy metal producing factories
5	Sediments	Soil erosion by agriculture and strip-mining
6	Pesticides	Chemicals used for killing insects, fungi and weeds
7	Radioactive substances	Mining of uranium containing minerals
8	Heat	Water used for cooling in industries

15.6 Causes of water pollution

(i) Microbiological (Pathogens)

Disease causing microorganisms like bacteria, viruses and protozoa are most serious water pollutants.

They come from domestic sewage and animal excreta. Fish and shellfish can become contaminated and people who eat them can become ill. Some serious diseases like polio and cholera are water borne diseases.Human excreta contain bacteria such as Escherichia coli and Streptococcus faecalis which cause gastrointestinal diseases

(ii) Organic wastes:

Organic matter such as leaves, grass, trash etc can also pollute water. Water pollution is caused by excessive phytoplankton growth within water.

Microorganisms present in water decompose these organic matter and consume dissolved oxygen in water.

Eutrophication:

Eutrophication is a process by which water bodies receive excess nutrients that stimulates excessive plant growth (algae, other plant weeds).This enhanced plant growth in water bodies is called as algae bloom.

The growth of algae in extreme abundance covers the water surface and reduces the oxygen concentration in water. Thus, bloom-infested water inhibits thegrowth of other living organisms in the water body. This process in which the nutrient rich water bodies support a dense plant population, kills animal life by depriving it of oxygen and results in loss of biodiversity is known as eutrophication.

Biochemical oxygen demand(BOD)

The total amount of oxygen in milligrams consumed by microorganisms in decomposing the waste in one litre of water at 20°C for a period of 5 days is called biochemical oxygen demand (BOD) and its value is expressed in ppm.

BOD is used as a measure of degree of water pollution. Clean water would have BOD value less than 5 ppm whereas highly polluted water has BOD value of 17 ppm or more.

Chemical Oxygen Demand (COD)

BOD measurement takes 5 days so another parameter called the Chemical Oxygen Demand (COD) is measured.

Chemical oxygen demand (COD) is defined asthe amount of oxygen required by the organic matter in a sample of water for its oxidation by a strong oxidising agent like K2Cr2O7 in acid medium for a period of 2 hrs.

(iii) Chemical wastes:

A whole variety of chemicals from industries, such as metals and solvents are poisonous to fish and other aquatic life.

Some toxic pesticides can accumulate in fish and shell fish and poison the people who eat them. Detergents and oils float and spoil the water bodies. Acids from mine drainage and salts from various sources can also contaminate water sources.

Harmful effects of chemical water pollutants:

1. Cadmium and mercury can cause kidney damage.
2. Lead poisoning can leads to the severe damage of kidneys, liver, brain etc. it also affects central nervous system
3. Polychlorinated biphenyls (PCBs) causes skin diseases and are carcinogenic in nature.

15.7 Quality of drinking water:

Now a days most of us hesitate to use natural water directly for drinking, because biological, physical or chemical impurities from different sources mix with surface water or ground water.

Institutions like WHO (World Health Organisation) at world level and BIS (Bureau of Indian Standards) and ICMR (ICMR: Indian Council of Medical Research) at national level have prescribed standards for quality of drinking water. Standard characteristics prescribed for deciding the quality of drinking water by BIS, in 1991 are shown in Table.15.3

Table 15.3 Standard characteristics of drinking water

S.No	Characteristics	Desirable limit
I	**Physico-chemical Characteristics**	
i)	pH	6.5 to 8.5
ii)	Total Dissolved Solids (TDS)	500 ppm
iii)	Total Hardness (as $CaCO_3$)	300 ppm
iv)	Nitrate	45 ppm
v)	Chloride	250 ppm
vi)	Sulphate	200 ppm
vii)	Fluoride	1 ppm
II	**Biological Characteristics**	
i)	Escherichia Coli (E.Coli)	Not at all
ii)	Coliforms	Not to exceed 10 (In 100 ml water sample)

Fluoride:

Fluoride ion deficiency in drinking water causes tooth decay. Water soluble fluorides are added to increase the fluoride ion concentration upto 1 ppm.

The Fluoride ions make the enamel on teeth much harder by converting hydroxyapatite, $[3(Ca_3(PO_4)_2.Ca(OH)_2]$, the enamel on the surface of the teeth, into much harder fluorapatite, $[3(Ca_3(PO_4)_2.CaF_2]$.

However, Fluoride ion concentration above 2 ppm causes brown mottling of teeth. Excess fluoride causes damage to bone and teeth.

Lead :

Drinking water containing lead contamination above 50ppb can cause damage to liver, kidney and reproductive systems.

Sulphate:

Moderate level of sulphate is harmless. Excessive concentration (>500ppm) of sulphates in drinking water causes laxative effect.

Nitrate:

Use of drinking water having concentration of nitrate higher than 45 ppm may causes methemoglobinemia (blue baby syndrome) disease in children.

Total dissolved solids (TDS):

Most of the salts are soluble in water. It includes cations like calcium, magnesium, sodium, potassium, iron and anions like carbonate, bicarbonate, chloride, sulphate, phosphate and nitrate. Use of drinking water having total dissolved solids concentration higher than 500 ppm causes possibilities of irritation in stomach and intestine.

15.8 Soil Pollution

Fig 15.7 soil pollution

Soil is a thin layer of organic and inorganic material that covers the earth's rocky surface. Soil constitutes the upper crust of the earth, which supports land, plants and animals.

Soil pollution is defined as the buildup of persistent toxic compounds , radioactive materials, chemical salts and disease causing agents in soils which have harmful effects on plant growth and animal health.

Soil pollution affects the structure and fertility of soil, groundwater quality and food chain in biological ecosystem.

15.8.1 Sources of soil pollution

The major sources of which pollute the soil are discussed below

1) Artificial fertilizers:

Soil nutrients are useful for growth of plants. Plants obtains carbon, hydrogen and oxygen from air or water, whereas other essential nutrients like nitrogen, phosphorous, potassium, calcium, magnesium, sulphur are being absorbed from soil. To remove the deficiency of nutrients in soil, farmers add artificial fertilizers. Increased use of phosphate fertilizers or excess use of artificial fertilizers like NPK in soil, results in reduced yield in that soil.

2) Pesticides:

Pesticides are the chemicals that are used to kill or stop the growth of unwanted organisms. But these pesticides can affect the health of human beings.

These are further classified as

a. Insecticides:

Insecticides like DDT ,BHC ,aldrin etc. can stay in soil for long period of time and are absorbed by soil . They contaminate root crops like carrot, raddish, etc.

b. Fungicide:

Organo mercury compounds are used as most common fungicide. They dissociate in soil to produce mercury which is highly toxic.

c. Herbicides:

Herbicides are the chemical compounds used to control unwanted plants. They are otherwise known as weed killers. Example sodium chlorate ($NaClO_3$) and sodium arsenite (Na_3 as O_3). Most of the herbicides are toxic to mammals.

3) Industrial wastes

Industrial activities have been the biggest contributor to the soil pollution especially the mining and manufacturing activities.

Large number of toxic wastes are released from industries. Industrial wastes include cyanides, chromates, acids, alkalis, and metals like mercury, copper, zinc, cadmium and lead etc. These industrial wastes in the soil surface lie for a long time and make it unsuitable for use.

15.9 Strategies to control environmental pollution

After studying air, water and soil pollution, as responsible individuals we must take responsibility to protect our environment. Think of steps which you would like to undertake for controlling environmental pollution not only in your locality but also in national and international level. We must realize about our environmental threat, focus strongly on this issues and be an eye opener to save our environment. We can think about following strategies to control environmental pollution.

1. Waste management: Environmental pollution can be controlled by proper disposal of wastes.
2. Recycling: a large amount of disposed waste material can be reused by recycling the waste, thus it reduces the land fill and converts waste into useful forms.
3. Substitution of less toxic solvents for highly toxic ones used in certain industrial processes.
4. Use of fuels with lower sulphur content (e.g., washed coal)
5. Growing more trees.
6. Control measures in vehicle emissions are adequate.

Efforts to control environmental pollution have resulted in development of science for synthesis of chemical favorable to environment and it is called green chemistry.

15.10 Green Chemistry

Green chemistry is a chemical philosophy encouraging the design of products and processes that reduce or eliminate the use and generation of hazardous substances.

For this, scientist are trying to develop methods to produce eco-friendly compounds. This can be best understood by considering the following example in which styrene is produced both by traditional and greener routes.

Traditional route

This method involves two steps. Carcinogenic benzene reacts with ethylene to form ethyl benzene. Then ethyl benzene on dehydrogenation using Fe_2O_3/ Al_2O_3 gives styrene.

Greener route

To avoid carcinogenic benzene, greener route is to start with cheaper and environmentally safer xylenes.

15.10.1. Green chemistry in day-to-day life

A few contribution of green chemistry in our day to day life is given below

(1) Dry cleaning of clothes

Solvents like tetrachloroethylene used in dry cleaning of clothes, pollute the ground water and are carcinogenic. In the place of tetrachloroethylene, liquefied CO_2 with suitable detergent, is an alternate solvent used. Liquified CO_2 is not harmful to the ground water. Now a days H_2O_2 used for bleaching clothes in laundry, gives better results and utilizese less water.

(2) Bleaching of paper

Conventional method of bleaching was done with chlorine. Now a days H_2O_2can be used for bleaching paper in presence of catalyst.

(3) Synthesis of chemicals

Acetaldehyde is now commercially prepared by one step oxidation of ethene in the presence of ionic catalyst in aqueous medium with 90% yield.

$$\underset{\text{Ethylene}}{CH_2 = CH_2} + O \xrightarrow[\text{Pd(II) /CU (II)}]{\text{Catalyst}} \underset{\text{Acetaldehyde}}{CH_3CHO}$$

(4) Instead of petrol, methanol is used as a fuel in automobiles.

(5) Neem based pesticides have been synthesised, which are more safer than the chlorinated hydrocarbons.

Every individual has an important role for preventing pollution and improving our environment. We are responsible for environmental protection. Let us begin to save our environment and provide a clean earth for our future generations.

SUMMARY

Environmental chemistry plays a vital role in environment. Environmental chemistry means scientific study of chemical and bio chemical process occurring in environment. World

Environmental Day is celebrated on fifth of June of every year.

Environmental Pollution:

Environmental pollution is the effect of undesirable changes in the surrounding that haveharmful effects on living things.

Pollutants are generally classified as rapidly degradable (e.g. discarded vegetables),slowly degradable(e.g. Agriculture waste) and non-bio degradable pollutants (e.g. DDT, plastic materials).

Atmospheric pollution

Atmospheric pollutions include tropospheric and stratospheric pollution. Troposphere and stratosphere greatly affect the biosphere of the earth due to which the study of pollutions in these regions is most important.

Tropospheric pollution:

Troposphere is the lowest region of atmosphere in which man, animal and plants exist. Gaseous pollutants like SOx,NOx,CO,CO_2,O_3 hydrocarbons and particulate pollutants like dust, mist, fumes, smog cause pollutions in troposphere

Acid rain:

When the PH of rain water becomes lower than 5.6 it is called acid rain. Acid rain is a byproduct of various human activities that emit sulphuroxides and nitrogen oxides in atmosphere. It damages buildings, statues and other monuments..

The acid rain in water reservoir like rivers, ponds adversely affects microbes ,aquatic plants and fishes.

Greenhouse effect:

The process of warming up of earth is known as greenhouse effect or global warming. CO_2, CH_4, O_3, CFC, N_2 and water vapour present in atmosphere act as a greenhouse gases. Heat retaining capacity of greenhouse gases are called Global Warming Potential (GWP).The GWP based sequence of greenhouse gases is as CFC>N_2O>CH_4>CO_2.

Stratospheric pollution:

Stratosphere extends above troposphere up to 50Km above.

Depletion of ozone layer:

Ozone layer present in stratosphere protect the living species against harmful UV rays from space but Ozone Depletion Substance (ODS) used by humans deplete ozone layer. To create awareness in the Whole world, United Nations decided to celebrate 16th September of every year as “Ozone Layer Protection Day”.

Water pollution

Water is the elixir of life, but it is polluted by point and nonpoint sources.Institutions like World Health Organization (WHO) and Bureau of Indian standards (BIS) and Indian Council of Medical Research (ICMR) have prescribed standards for quality of drinking water.

Soil pollution

Lithosphere with humus cover is known as soil. The topsoil provides water and all nutrients required by plants for their growth. Industrial waste, artificial fertilisers and pesticides result in soil pollution.

Waste management

The strategies for controlling environmental pollution are called can be waste management.Waste management involves reduction and proper disposal of waste. Wastes are produced in three forms, solid, liquid and gase. Solid waste can be disposed by segregation, dumping, incineration and composting.

Green chemistry

Efforts to control environmental pollution resulted in development of science for synthesis of chemicals favorable to environment which is called green chemistry.Green chemistry means science of environmentally favorable chemical synthesis.

Evaluation

1. The gaseous envelope around the earth is known as atmosphere. The region lying between an altitudes of 11-50 km is __________

   a) Troposphere   b) Mesosphere

   c) Thermosphere   d) stratosphere

2. Which of the following is natural and human disturbance in ecology?

   a) Forest fire   b) Floods

   c) Acid rain   d) Green house effect

3. Bhopal Gas Tragedy is a case of ______________

   a) thermal pollution

   b)air pollution

   c) nuclear pollution

   d) land pollution

4. Haemoglobin of the blood forms carboxy haemoglobin with

   a) Carbon dioxide

   b) Carbon tetra chloride

   c) Carbon monoxide

   d) Carbonic acid

5. Which sequence for green house gases is based on GWP?

   a) CFC > N_2O > CO_2> CH_4

   b) CFC > CO_2> N_2O > CH_4

   c) CFC > N_2O > CH_4> CO_2

   d) CFC > CH_4> N_2O > CO_2

6. Photo chemical smog formed in congested metropolitan cities mainly consists of

   a) Ozone, SO_2 and hydrocarbons

   b) Ozone, PAN and NO_2

   c) PAN, smoke and SO_2

   d) Hydrocarbons, SO_2 and CO_2

7. The pH of normal rain water is

   a) 6.5   b) 7.5

   c) 5.6   d) 4.6

8. Ozone depletion will cause

a) forest fires

b) eutrophication

c) bio magnification

d) global warming

9. Identify the wrong statement in the following

a) The clean water would have a BOD value of more than 5 ppm

b) Greenhouse effect is also called as Global warming

c) Minute solid particles in air is known as particulate pollutants

d) Biosphere is the protective blanket of gases surrounding the earth

10. Living in the atmosphere of CO is dangerous because it

a) Combines with O_2 present inside to form CO_2

b) Reduces organic matter of tissues

c) Combines with haemoglobin and makes it incapable to absorb oxygen

d) Dries up the blood

11. Release of oxides of nitrogen and hydrocarbons into the atmosphere by motor vehicles is prevented by using __________

a) grit chamber

b) scrubbers

c) trickling filters

d) catalytic convertors

12. Biochemical oxygen Demand value less than 5 ppm indicates a water sample to be

a) highly polluted

b) poor in dissolved oxygen

c) rich in dissolved oxygen

d) low COD

13. Match the List I with List II and select the correct answer using the code given below the lists

List I		List II	
A	Depletion of ozone layer	1	CO_2
B	Acid rain	2	NO
C	Photochemical smog	3	SO_2
D	Green house effect	4	CFC

Code:

	A	**B**	**C**	**D**
a	3	4	1	2
b	2	1	4	3
c	4	3	2	1
d	2	4	1	3

14.

List I		List II	
A	Stone leprosy	1	CO
B	Biological magnification	2	Green house gases
C	Global warming	3	Acid rain
D	Combination with haemoglobin	4	DDT

Code:

	A	B	C	D
a	1	2	3	4
b	3	4	2	1
c	2	3	4	1
d	4	2	1	3

The questions gives below consists of an assertion the reason. Choose the correct option out of the choices given below each question

i) Both (A) and R are correct and (R) is the correct explanation of (A)

ii) Both (A) and R are correct and (R) is not the correct explanation of (A)

iii) Both (A) and R are not correct

iv) (A) is correct but(R) is not correct

15. Assertion (A): If BOD level of water in a reservoir is more than 5 ppm it is highly polluted

    Reason(R) : High biological oxygen demand means high activity of bacteria in water

    a) i b) ii

    c) iii d) iv

16. **Assertion (A):** Excessive use of chlorinated pesticide causes soil and water pollution.

    Reason (R) : Such pesticides are non-biodegradable.

    a) i b) ii

    c) iii d) iv

17. **Assertion (A):** Oxygen plays a key role in the troposphere

    Reason (R): Troposphere is not responsible for all biological activities

    a) i b) ii

    c) iii d) iv

18. Dissolved oxygen in water is responsible for aquatic life. What processes are responsible for the reduction in dissolved oxygen in water?

19. What would happen, if the greenhouse gases were totally missing in the earth's atmosphere?

20. Define smog.

21. Which is considered to be earth's protective umbrella? Why?

22. What are degradable and non-degradable pollutants?

23. From where does ozone come in the photo chemical smog?

24. A person was using water supplied by corporation. Due to shortage of water he started using underground water. He felt laxative effect. What could be the cause?

25. What is green chemistry?

26. Explain how does greenhouse effect cause global warming

27. Mention the standards prescribed by BIS for quality of drinking water

28. How does classical smog differ from photochemical smog?

29. What are particulate pollutants? Explain any three.

30. Even though the use of pesticides increases the crop production, they adversely affect the living organisms. Explain the function and the adverse effects of the pesticides.

31. Ethane burns completely in air to give CO2, while in a limited supply of air gives CO. The same gases are found in automobile exhaust. Both CO and CO2 are atmospheric pollutants

    i) What is the danger associated with these gases

    ii) How do the pollutants affect the human body?

32. On the basis of chemical reactions involved, explain how do CFC's cause depletion of ozone layer in stratosphere?

33. How is acid rain formed? Explain its effect

34. Differentiate the following

    (i) BOD and COD

    (ii) Viable and non-viable particulate pollutants

35. Explain how oxygen deficiency is caused by carbon monoxide in our blood? Give its effect

36. What are the various methods you suggest to protect our environment from pollution?

CONCEPT MAP