

# Brilliant Preparatory Section, Sitamarhi

## XI Chemistry Advanced Study Material

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# INORGANIC CHEMISTRY

## 1. CHEMICAL CALCULATION

### OBJECTIVES

- \* *Know the method of finding formula weight of different compounds.*
- \* *Recognise the value of Avogadro number and its significance.*
- \* *Learn about the mole concept and the conversions of grams to moles.*
- \* *Know about the empirical and molecular formula and understand the method of arriving molecular formula from empirical formula.*
- \* *Understand the stoichiometric equation.*
- \* *Know about balancing the equation in its molecular form.*
- \* *Understand the concept of reduction and oxidation.*
- \* *Know about the method of balancing redox equation using oxidation number.*

### 1.1 Formula Weight (FW) or Formula Mass

The formula weight of a substance is the sum of the atomic weights of all atoms in a formula unit of the compound, whether molecular or not.

Sodium chloride, NaCl, has a formula weight of 58.44 amu (22.99 amu from Na plus 35.45 amu from Cl). NaCl is ionic, so strictly speaking the expression "molecular weight of NaCl" has no meaning. On the other hand, the molecular weight and the formula weight calculated from the molecular formula of a substance are identical.

### Solved Problem

Calculate the formula weight of each of the following to three significant figures, using a table of atomic weight (AW): (a) chloroform  $\text{CHCl}_3$  (b) Iron (III) sulfate  $\text{Fe}_2(\text{SO}_4)_3$ .

### Solution

- a.
- |                                   |   |                  |
|-----------------------------------|---|------------------|
| 1 x AW of C                       | = | 12.0 amu         |
| 1 x AW of H                       | = | 1.0 amu          |
| 3 x AW of Cl = 3 x 35.45          | = | <u>106.4 amu</u> |
| Formula weight of $\text{CHCl}_3$ | = | <u>119.4 amu</u> |

The answer rounded to three significant figures is 119 amu.

**b. Iron(III)Sulfate**

2 x Atomic weight of Fe = 2 x 55.8 = 111.6 amu

3 x Atomic weight of S = 3 x 32.1 = 96.3 amu

3 x 4 Atomic weight of O = 12 x 16 = 192.0 amu

Formula weight of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> = 399.9 amu

The answer rounded to three significant figures is 4.00 x 10<sup>2</sup> amu.

**Problems for Practice**

Calculate the formula weights of the following compounds

a. NO<sub>2</sub>    b. glucose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>)    c. NaOH    d. Mg(OH)<sub>2</sub>

e. methanol (CH<sub>3</sub> OH)    f. PCl<sub>3</sub>    g. K<sub>2</sub> CO<sub>3</sub>

**1.2 Avogadro's Number (N<sub>A</sub>)**

The number of atoms in a 12-g sample of carbon - 12 is called Avogadro's number (to which we give the symbol N<sub>A</sub>).

Recent measurements of this number give the value 6.0221367 x 10<sup>23</sup>, which is 6.023 x 10<sup>23</sup>.

A mole of a substance contains Avogadro's number of molecules. A dozen eggs equals 12 eggs, a gross of pencils equals 144 pencils and a mole of ethanol equals 6.023 x 10<sup>23</sup> ethanol molecules.

**Significance**

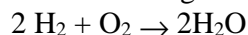
The molecular mass of SO<sub>2</sub> is 64 g mol<sup>-1</sup>. 64 g of SO<sub>2</sub> contains 6.023 x 10<sup>23</sup> molecules of SO<sub>2</sub>. 2.24 x 10<sup>-2</sup> m<sup>3</sup> of SO<sub>2</sub> at S.T.P. contains 6.023 x 10<sup>23</sup> molecules of SO<sub>2</sub>.

Similarly the molecular mass of CO<sub>2</sub> is 44 g mol<sup>-1</sup>. 44g of CO<sub>2</sub> contains 6.023 x 10<sup>23</sup> molecules of CO<sub>2</sub>. 2.24 x 10<sup>-2</sup> m<sup>3</sup> of CO<sub>2</sub> at S.T.P contains 6.023 x 10<sup>23</sup> molecules of CO<sub>2</sub>.

**1.3 Mole concept**

While carrying out reaction we are often interested in knowing the number of atoms and molecules. Some times, we have to take the atoms or molecules of different reactants in a definite ratio.

Eg. Consider the following reaction



In this reaction one molecule of oxygen reacts with two molecules of hydrogen. So it would be desirable to take the molecules of  $\text{H}_2$  and oxygen in the ratio 2:1, so that the reactants are completely consumed during the reaction. But atoms and molecules are so small in size that it is not possible to count them individually.

In order to overcome these difficulties, the concept of mole was introduced. According to this concept number of particles of the substance is related to the mass of the substance.

### Definition

The mole may be defined as the amount of the substance that contains as many specified elementary particles as the number of atoms in 12g of carbon - 12 isotope.

(i.e) one mole of an atom consists of Avogadro number of particles.

One mole	=	$6.023 \times 10^{23}$ particles
One mole of oxygen molecule	=	$6.023 \times 10^{23}$ oxygen molecules
One mole of oxygen atom	=	$6.023 \times 10^{23}$ oxygen atoms
One mole of ethanol	=	$6.023 \times 10^{23}$ ethanol molecules

In using the term mole for ionic substances, we mean the number of formula units of the substance. For example, a mole of sodium carbonate,  $\text{Na}_2\text{CO}_3$  is a quantity containing  $6.023 \times 10^{23}$   $\text{Na}_2\text{CO}_3$  units. But each formula unit of  $\text{Na}_2\text{CO}_3$  contains  $2 \times 6.023 \times 10^{23}$   $\text{Na}^+$  ions and one  $\text{CO}_3^{2-}$  ions and  $1 \times 6.023 \times 10^{23}$   $\text{CO}_3^{2-}$  ions.

When using the term mole, it is important to specify the formula of the unit to avoid any misunderstanding.

Eg. A mole of oxygen atom (with the formula O) contains  $6.023 \times 10^{23}$  Oxygen atoms. A mole of oxygen molecule (formula  $\text{O}_2$ ) contains  $6.023 \times 10^{23}$   $\text{O}_2$  molecules (i.e)  $2 \times 6.023 \times 10^{23}$  oxygen.

### Molar mass

The molar mass of a substance is the mass of one mole of the substance. The mass and moles can be related by means of the formula.

$$\text{Molar mass} = \frac{\text{Mass}}{\text{mole}}$$

Eg. Carbon has a molar mass of exactly 12g/mol.

### Problems

#### Solved Problems

1. What is the mass in grams of a chlorine atom, Cl?
2. What is the mass in grams of a hydrogen chloride, HCl?

#### Solution

1. The atomic weight of Cl is 35.5 amu, so the molar mass of Cl is 35.5 g/mol. Dividing 35.5 g (per mole) by  $6.023 \times 10^{23}$  gives the mass of one atom.

$$\begin{aligned}\text{Mass of a Cl atom} &= \frac{35.5 \text{ g}}{6.023 \times 10^{23}} \\ &= 5.90 \times 10^{-23} \text{ g}\end{aligned}$$

2. The molecular weight of HCl equal to the atomic weight of H, plus the atomic weight of Cl, (ie)  $(1.01 + 35.5) \text{ amu} = 36.5 \text{ amu}$ . Therefore 1 mol of HCl contains 36.5 g HCl

$$\begin{aligned}\text{Mass of an HCl molecule} &= \frac{36.5 \text{ g}}{6.02 \times 10^{23}} \\ &= 6.06 \times 10^{-23} \text{ g}\end{aligned}$$

#### Problems For Practice

1. What is the mass in grams of a calcium atom, Ca?
2. What is mass in grams of an ethanol molecule,  $\text{C}_2\text{H}_5\text{OH}$ ?
3. Calculate the mass (in grams) of each of the following species.
  - a. Na atom
  - b. S atom
  - c.  $\text{CH}_3\text{Cl}$  molecule
  - d.  $\text{Na}_2\text{SO}_3$  formula unit

#### 1.3.1 Mole Calculations

To find the mass of one mole of substance, there are two important things to know.

- i. How much does a given number of moles of a substance weigh?
- ii. How many moles of a given formula unit does a given mass of substance contain.

Both of them can be known by using dimensional analysis.

To illustrate, consider the conversion of grams of ethanol,  $\text{C}_2\text{H}_5\text{OH}$ , to moles of ethanol. The molar mass of ethanol is 46.1 g/mol, So, we write

$$1 \text{ mol C}_2\text{H}_5\text{OH} = 46.1 \text{ g of C}_2\text{H}_5\text{OH}$$

Thus, the factor converting grams of ethanol to moles of ethanol is  $1 \text{ mol C}_2\text{H}_5\text{OH}/46.1 \text{ g C}_2\text{H}_5\text{OH}$ . To convert moles of ethanol to grams of ethanol, we simply convert the conversion factor ( $46.1 \text{ g C}_2\text{H}_5\text{OH}/1 \text{ mol C}_2\text{H}_5\text{OH}$ ).

Again, suppose you are going to prepare acetic acid from 10.0g of ethanol,  $\text{C}_2\text{H}_5\text{OH}$ . How many moles of  $\text{C}_2\text{H}_5\text{OH}$  is this? you convert 10.0g  $\text{C}_2\text{H}_5\text{OH}$  to moles  $\text{C}_2\text{H}_5\text{OH}$  by multiplying by the appropriate conversion factor.

$$\begin{aligned} 10.0 \text{g C}_2\text{H}_5\text{OH} & \times \frac{1 \text{ mol C}_2\text{H}_5\text{OH}}{46.1 \text{ g C}_2\text{H}_5\text{OH}} \\ & = 0.217 \text{ mol C}_2\text{H}_5\text{OH} \end{aligned}$$

### 1.3.2 Converting Moles of Substances to Grams

#### Solved Problems

1.  $\text{ZnI}_2$ , can be prepared by the direct combination of elements. A chemist determines from the amounts of elements that 0.0654 mol  $\text{ZnI}_2$  can be formed.

#### Solution

The molar mass of  $\text{ZnI}_2$  is 319 g/mol. (The formula weight is 319 amu, which is obtained by summing the atomic weight in the formula) Thus

$$\begin{aligned} 0.0654 \text{ mol ZnI}_2 & \times \frac{319 \text{ g ZnI}_2}{1 \text{ mol ZnI}_2} \\ & = 20.9 \text{ gm ZnI}_2 \end{aligned}$$

### Problems for Practice

1.  $\text{H}_2\text{O}_2$  is a colourless liquid. A concentrated solution of it is used as a source of oxygen for Rocket propellant fuels. Dilute aqueous solutions are used as a bleach. Analysis of a solution shows that it contains 0.909 mol  $\text{H}_2\text{O}_2$  in 1.00 L of solution. What is the mass of  $\text{H}_2\text{O}_2$  in this volume of solution?.

2. Boric acid,  $\text{H}_3\text{BO}_3$  is a mild antiseptic and is often used as an eye wash. A sample contains 0.543 mol  $\text{H}_3\text{BO}_3$ . What is the mass of boric acid in the sample?.

3.  $\text{CS}_2$  is a colourless, highly inflammable liquid used in the manufacture of rayon and cellophane. A sample contains 0.0205 mol  $\text{CS}_2$ . Calculate the mass of  $\text{CS}_2$  in the sample.

### Converting Grams of Substances to Moles

In the preparation of lead(II)chromate  $\text{PbCrO}_4$ , 45.6 g of lead(II)chromate is obtained as a precipitate. How many moles of  $\text{PbCrO}_4$  is this?

The molar mass of  $\text{PbCrO}_4$  is 323 g/mol (i.e) 1 mol  $\text{PbCrO}_4$  = 323 g  $\text{PbCrO}_4$

Therefore,

$$45.6 \text{ g PbCrO}_4 \times 1 \text{ mol.PbCrO}_4$$

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$$323 \text{ g PbCrO}_4$$

$$= 0.141 \text{ mol PbCrO}_4$$

### Problems for Practice

1. Nitric acid,  $\text{HNO}_3$  is a colourless, corrosive liquid used in the manufacture of Nitrogen fertilizers and explosives. In an experiment to develop new explosives for mining operations, a 28.5 g sample of  $\text{HNO}_3$  was poured into a beaker. How many moles of  $\text{HNO}_3$  are there in this sample of  $\text{HNO}_3$ ?

2. Obtain the moles of substances in the following.

- |                                   |  |
|-----------------------------------|--|
| a. 3.43 g of C                    | b. 7.05 g $\text{Br}_2$                |
| c. 76g $\text{C}_4 \text{H}_{10}$ | d. 35.4 g $\text{Li}_2 \text{CO}_3$    |
| e. 2.57 g As                      | f. 7.83 g $\text{P}_4$                 |
| g. 41.4 g $\text{N}_2\text{H}_4$  | h. 153 g $\text{Al}_2 (\text{SO}_4)_3$ |

## Calculation of the Number of Molecules in a Given Mass

### Solved Problem

How many molecules are there in a 3.46 g sample of hydrogen chloride, HCl?

Note: The number of molecules in a sample is related to moles of compound (1 mol HCl =  $6.023 \times 10^{23}$  HCl molecules). Therefore if you first convert grams HCl to moles, then you can convert moles to number of molecules).

### Solution

$$\begin{aligned} 3.46\text{g HCl} \times \frac{1\text{ mol HCl}}{36.5\text{g HCl}} \times \frac{6.023 \times 10^{23} \text{ HCl molecules}}{1\text{ mol HCl}} \\ = 5.71 \times 10^{22} \text{ HCl molecules} \end{aligned}$$

### Problems for Practice

1. How many molecules are there in 56mg HCN?
2. Calculate the following
  - a. Number of molecules in 43g NH<sub>3</sub>
  - b. Number of atoms in 32.0 g Br<sub>2</sub>
  - c. Number of atoms in 7.46 g Li

## 1.4 Calculation of Empirical Formula from Quantitative Analysis and Percentage composition

### Empirical Formula

"An empirical formula (or) simplest formula for a compound is the formula of a substance written with the smallest integer subscripts".

For most ionic substances, the empirical formula is the formula of the compound. This is often not the case for molecular substances. For example, the formula of sodium peroxide, an ionic compound of Na<sup>+</sup> and O<sub>2</sub><sup>2-</sup>, is Na<sub>2</sub>O<sub>2</sub>. Its empirical formula is NaO. Thus empirical formula tells you the ratio of numbers of atoms in the compound.

### Steps for writing the Empirical formula

The percentage of the elements in the compound is determined by



suitable methods and from the data collected, the empirical formula is determined by the following steps.

- Divide the percentage of each element by its atomic mass. This will give the relative number of moles of various elements present in the compound.
- Divide the quotients obtained in the above step by the smallest of them so as to get a simple ratio of moles of various elements.
- Multiply the figures, so obtained by a suitable integer of necessary in order to obtain whole number ratio.
- Finally write down the symbols of the various elements side by side and put the above numbers as the subscripts to the lower right hand of each symbol. This will represent the empirical formula of the compound.

#### Solved Problem

A compound has the following composition Mg = 9.76%, S = 13.01%, O = 26.01, H<sub>2</sub>O = 51.22, what is its empirical formula?

[Mg = 24, S = 32, O = 16, H = 1]

#### Solution

Element	%	Relative No. of moles	Simple ratio moles	Simplest whole No. ratio
Magnesium	9.76	$\frac{9.76}{24} = 0.406$	$\frac{0.406}{0.406} = 1$	1
Sulphur	13.01	$\frac{13.01}{32} = 0.406$	$\frac{0.406}{0.406} = 1$	1
Oxygen	26.01	$\frac{26.01}{16} = 1.625$	$\frac{1.625}{0.406} = 4$	4
Water	51.22	$\frac{51.22}{18} = 2.846$	$\frac{2.846}{0.406} = 7$	7

Hence the empirical formula is Mg SO<sub>4</sub>.7H<sub>2</sub>O.

#### Problems for Practice

1. A substance on analysis, gave the following percentage composition, Na = 43.4%, C = 11.3%, O = 43.3% calculate its empirical formula [Na = 23, C = 12, O = 16].

Ans:-  $\text{Na}_2\text{CO}_3$

2. What is the simplest formula of the compound which has the following percentage composition: Carbon 80%, hydrogen 20%.

Ans:-  $\text{CH}_3$

3. A compound on analysis gave the following percentage composition: C - 54.54%, H = 9.09%, O = 36.36%

Ans:-  $\text{C}_2\text{H}_4\text{O}$

#### 1.4.1 Molecular Formula from Empirical Formula

The molecular formula of a compound is a multiple of its empirical formula.

##### *Example*

The molecular formula of acetylene,  $\text{C}_2\text{H}_2$  is equivalent to  $(\text{CH})_2$ , and the molecular formula of benzene,  $\text{C}_6\text{H}_6$  is equivalent to  $(\text{CH})_6$ . Therefore, the molecular weight is some multiple of the empirical formula weight, which is obtained by summing the atomic Weights from the empirical formula. For any molecular compound.

Molecular Weight =  $n \times$  empirical formula weight.

Where 'n' is the whole number of empirical formula units in the molecule. The molecular formula can be obtained by multiplying the subscripts of the empirical formula by 'n' which can be calculated by the following equation

$$n = \frac{\text{Molecular Weight}}{\text{Empirical formula Weight}}$$

#### Steps for writing the molecular formula

- Calculate the empirical formula
- Find out the empirical formula mass by adding the atomic mass of all the atoms present in the empirical formula of the compound.
- Divide the molecular mass (determined experimentally by some

suitable method) by the empirical formula mass and find out the value of n which is a whole number.

- iv. Multiply the empirical formula of the compound with n, so as to find out the molecular formula of the compound.

### Solved Problem

1. A compound on analysis gave the following percentage composition C = 54.54%, H, 9.09% O = 36.36. The vapour density of the compound was found to be 44. Find out the molecular formula of the compound.

### Solution

Calculation of empirical formula

Element	%	Relative No. of moles	Simple ratio moles	Simplest whole No. ratio
C	54.54	$\frac{54.54}{12} = 4.53$	$\frac{4.53}{2.27} = 2$	2
H	9.09	$\frac{9.09}{1} = 9.09$	$\frac{9.09}{2.27} = 4$	4
O	36.36	$\frac{36.36}{16} = 2.27$	$\frac{2.27}{2.27} = 1$	1

Empirical formula is C<sub>2</sub> H<sub>4</sub> O.

### Calculation of Molecular formula

$$\text{Empirical formula mass} = 12 \times 2 + 1 \times 4 + 16 \times 1 = 44$$

$$\begin{aligned} \text{Molecular mass} &= 2 \times \text{Vapour density} \\ &= 2 \times 44 = 88 \end{aligned}$$

$$\frac{\text{Molecular mass}}{88}$$

$$n = \frac{\text{Molecular mass}}{\text{Empirical Formula mass}} = \frac{88}{44} = 2$$

$$\text{Molecular formula} = \text{Empirical formula} \times n$$

$$= \text{C}_2 \text{H}_4 \text{O} \times 2$$

$$= \text{C}_4 \text{H}_8 \text{O}_2$$

2. A compound on analysis gave the following percentage composition: Na=14.31% S = 9.97%, H = 6.22%, O = 69.5%, calculate the molecular formula of the compound on the assumption that all the hydrogen in the compound is present in combination with oxygen as water of crystallisation. Molecular mass of the compound is 322 [Na = 23, S = 32, H = 1, O = 16].

**Solution :- Calculation of empirical formula**

Element	%	Relative No. of moles	Simple ratio moles	Simplest whole No. ratio
Na	14.31	$\frac{14.31}{23} = 0.62$	$\frac{0.62}{0.31} = 2$	2
S	9.97	$\frac{9.97}{32} = 0.31$	$\frac{0.31}{0.31} = 1$	1
H	6.22	$\frac{6.22}{1} = 6.22$	$\frac{6.22}{0.31} = 20$	20
O	69.5	$\frac{69.5}{16} = 4.34$	$\frac{4.34}{0.31} = 14$	14

The empirical formula is  $\text{Na}_2 \text{SH}_{20}\text{O}_{14}$

**Calculation of Molecular formula**

$$\begin{aligned} \text{Empirical formula mass} &= (23 \times 2) + 32 + (20 \times 1) + (16 \times 14) \\ &= 322 \end{aligned}$$

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{322}{322} = 1$$

Hence molecular formula =  $\text{Na}_2 \text{SH}_{20}\text{O}_{14}$

Since all hydrogens are present as  $\text{H}_2\text{O}$  in the compound, it means 20 hydrogen atoms must have combined. It means 20 hydrogen atoms must have combined with 10 atoms of oxygen to form 10 molecules of water of crystallisation. The remaining  $(14 - 10 = 4)$  atoms of oxygen should be present with the rest of the compound.

Hence, molecular formula =  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ .

### Problems for Practice

1. An organic compound was found to have contained carbon = 40.65%, hydrogen = 8.55% and Nitrogen = 23.7%. Its vapour - density was found to be 29.5. What is the molecular formula of the compound?

Ans:-  $\text{C}_2\text{H}_5\text{NO}$

2. A compound contains 32% carbon, 4% hydrogen and rest oxygen. Its vapour density is 75. Calculate the empirical and molecular formula.

Ans:-  $\text{C}_2\text{H}_3\text{O}_3$ ,  $\text{C}_4\text{H}_6\text{O}_6$

3. An acid of molecular mass 104 contains 34.6% carbon, 3.85% hydrogen and the rest is oxygen. Calculate the molecular formula of the acid.

4. What is the simplest formula of the compound which has the following percentage composition: carbon 80%, Hydrogen 20%, If the molecular mass is 30, calculate its molecular formula.

## 1.5 Stoichiometry Equations

### Stoichiometry

Stoichiometry is the calculation of the quantities of reactants and products involved in the chemical reaction. It is the study of the relationship between the number of mole of the reactants and products of a chemical reaction. A stoichiometric equation is a short scientific representation of a chemical reaction.

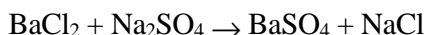
### Rules for writing stoichiometric equations

i. In order to write the stoichiometric equation correctly, we must know the reacting substances, all the products formed and their chemical formula.

ii. The formulae of the reactant must be written on the left side of

arrow with a positive sign between them.

iii. The formulae of the products formed are written on the right side of the arrow mark. If there is more than one product, a positive sign is placed between them. The equation thus obtained is called skeleton equation. For example, the Chemical reaction between Barium chloride and sodium sulphate producing BaSO<sub>4</sub> and NaCl is represented by the equation as



This skeleton equation itself is a balanced one. But in many cases the skeleton equation is not a balanced one.

For example, the decomposition of Lead Nitrate giving Lead oxide, NO<sub>2</sub> and oxygen. The skeletal equation for this reaction is



iv. In the skeleton equation, the numbers and kinds of particles present on both sides of the arrow are not equal.

v. During balancing the equation, the formulae of substances should not be altered, but the number of molecules with it only be suitably changed.

vi. Important conditions such as temperature, pressure, catalyst etc., may be noted above (or) below the arrow of the equation.

vii. An upward arrow (↑) is placed on the right side of the formula of a gaseous product and a downward arrow (↓) on the right side of the formulae of a precipitated product.

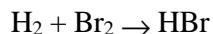
viii. All the reactants and products should be written as molecules including the elements like hydrogen, oxygen, nitrogen, fluorine chlorine, bromine and iodine as H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub> and I<sub>2</sub>.

### 1.5.1 Balancing chemical equation in its molecular form

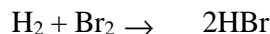
A chemical equation is called balanced equation only when the numbers and kinds of molecules present on both sides are equal. The several steps involved in balancing chemical equation are discussed below.

#### *Example 1*

Hydrogen combines with bromine giving HBr



This is the skeletal equation. The number of atoms of hydrogen on the left side is two but on the right side it is one. So the number of molecules of HBr is to be multiplied by two. Then the equation becomes



This is the balanced (or) stoichiometric equation.

### **Example 2**

Potassium permanganate reacts with HCl to give KCl and other products. The skeletal equation is



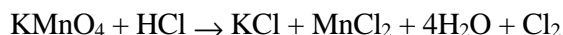
If an element is present only one substance in the left hand side of the equation and if the same element is present only one of the substances in the right side, it may be taken up first while balancing the equation.

According to the above rule, the balancing of the equation may be started with respect to K, Mn, O (or) H but not with Cl.

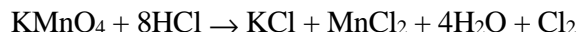
There are

<b>L.H.S.</b>	<b>R.H.S</b>
K = 1	1
Mn = 1	1
O = 4	1

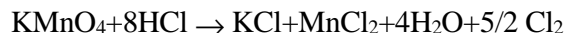
So the equation becomes



Now there are eight hydrogen atoms on the right side of the equation, we must write 8 HCl.



Of the eight chlorine atoms on the left, one is disposed of in KCl and two in MnCl<sub>2</sub> leaving five free chlorine atoms. Therefore, the above equation becomes



Equations are written with whole number coefficient and so the

equation is multiplied through out by 2 to become



### 1.5.2 Redox reactions [Reduction - oxidation]

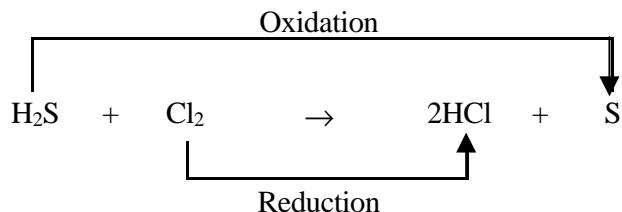
In our daily life we come across process like fading of the colour of the clothes, burning of the combustible substances such as cooking gas, wood, coal, rusting of iron articles, etc. All such processes fall in the category of specific type of chemical reactions called reduction - oxidation (or) redox reactions. A large number of industrial processes like, electroplating, extraction of metals like aluminium and sodium, manufactures of caustic soda, etc., are also based upon the redox reactions. Redox reactions also form the basis of electrochemical and electrolytic cells. According to the classical concept, oxidation and reduction may be defined as,

Oxidation is a process of addition of oxygen (or) removal of hydrogen

Reduction is a process of removal of oxygen (or) addition of hydrogen.

#### *Example*

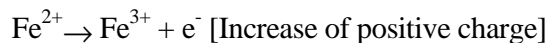
Reaction of  $\text{Cl}_2$  and  $\text{H}_2\text{S}$



In the above reaction, hydrogen is being removed from hydrogen sulphide ( $\text{H}_2\text{S}$ ) and is being added to chlorine ( $\text{Cl}_2$ ). Thus,  $\text{H}_2\text{S}$  is oxidised and  $\text{Cl}_2$  is reduced.

#### **Electronic concept of oxidation and Reduction**

According to electronic concept, oxidation is a process in which an atom taking part in chemical reaction loses one or more electrons. The loss of electrons results in the increase of positive charge (or) decrease of negative of the species. For example.

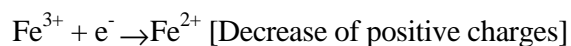




The species which undergo the loss of electrons during the reactions are called reducing agents or reductants.  $\text{Fe}^{2+}$  and Cu are reducing agents in the above example.

### **Reduction**

Reduction is a process in which an atom (or) a group of atoms taking part in chemical reaction gains one (or) more electrons. The gain of electrons result in the decrease of positive charge (or) increase of negative charge of the species. For example,



The species which undergo gain of electrons during the reactions are called oxidising agents (or) oxidants. In the above reaction,  $\text{Fe}^{3+}$  and  $\text{Zn}^{2+}$  are oxidising agents.

### **Oxidation Number (or) Oxidation State**

Oxidation number of the element is defined as the residual charge which its atom has (or) appears to have when all other atoms from the molecule are removed as ions.

Atoms can have positive, zero or negative values of oxidation numbers depending upon their state of combination.

### **General Rules for assigning Oxidation Number to an atom**

The following rules are employed for determining oxidation number of the atoms.

1. The oxidation number of the element in the free (or) elementary state is always Zero.

Oxidation number of Helium in He = 0

Oxidation number of chlorine in  $\text{Cl}_2$  = 0

2. The oxidation number of the element in monoatomic ion is equal to the charge on the ion.

3. The oxidation number of fluorine is always - 1 in all its compounds.

4. Hydrogen is assigned oxidation number +1 in all its compounds except in metal hydrides. In metal hydrides like NaH,  $\text{MgH}_2$ ,  $\text{CaH}_2$ , LiH,

etc., the oxidation number of hydrogen is -1.

5. Oxygen is assigned oxidation number -2 in most of its compounds, however in peroxides like  $\text{H}_2\text{O}_2$ ,  $\text{BaO}_2$ ,  $\text{Na}_2\text{O}_2$ , etc its oxidation number is -1. Similarly the exception also occurs in compounds of Fluorine and oxygen like  $\text{OF}_2$  and  $\text{O}_2\text{F}_2$  in which the oxidation number of oxygen is +2 and +1 respectively.

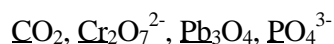
6. The oxidation numbers of all the atoms in neutral molecule is Zero. In case of polyatomic ion the sum of oxidation numbers of all its atoms is equal to the charge on the ion.

7. In binary compounds of metal and non-metal the metal atom has positive oxidation number while the non-metal atom has negative oxidation number. Example. Oxidation number of K in KI is +1 but oxidation number of I is -1.

8. In binary compounds of non-metals, the more electronegative atom has negative oxidation number, but less electronegative atom has positive oxidation number. Example : Oxidation number of Cl in  $\text{ClF}_3$  is positive (+3) while that in  $\text{ICl}$  is negative (-1).

### Problem

Calculate the oxidation number of underlined elements in the following species.



### Solution

1. C in  $\text{CO}_2$ . Let oxidation number of C be x. Oxidation number of each O atom = -2. Sum of oxidation number of all atoms =  $x + 2(-2) \Rightarrow x - 4$ .

As it is neutral molecule, the sum must be equal to zero.

$$\therefore x - 4 = 0 \text{ (or) } x = +4$$

2. Cr in  $\text{Cr}_2\text{O}_7^{2-}$ . Let oxidation number of Cr = x. Oxidation number of each oxygen atom = -2. Sum of oxidation number of all atoms

$$2x + 7(-2) = 2x - 14$$

Sum of oxidation number must be equal to the charge on the ion.

$$\text{Thus, } 2x - 14 = -2$$

$$2x = +12$$

$$x = 12/2$$

$$x = 6$$

### Problems for Practice

Calculate the oxidation number of underlined elements in the following species.

- a.  $\text{MnSO}_4$    b.  $\text{S}_2\text{O}_3$    c.  $\text{HNO}_3$    d.  $\text{K}_2\text{MnO}_4$    e.  $\text{NH}_4^+$

### Oxidation and Reduction in Terms of Oxidation Number

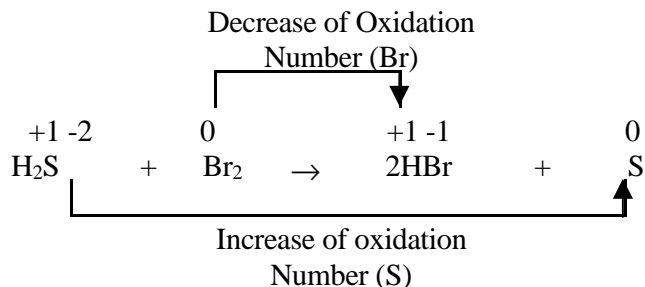
#### Oxidation

"A chemical process in which oxidation number of the element increases".

#### Reduction

"A chemical process in which oxidation number of the element decreases".

Eg. Reaction between  $\text{H}_2\text{S}$  and  $\text{Br}_2$  to give  $\text{HBr}$  and Sulphur.



In the above reaction, the oxidation number of bromine decreases from 0 to -1, thus it is reduced. The oxidation number of S increases from -2 to 0. Hence  $\text{H}_2\text{S}$  is oxidised.

Under the concept of oxidation number, oxidising and reducing agent can be defined as follows.

- Oxidising agent is a substance which undergoes decrease in the oxidation number of one of its elements.

ii. Reducing agent is a substance which undergoes increase in the oxidation number of one of its elements.

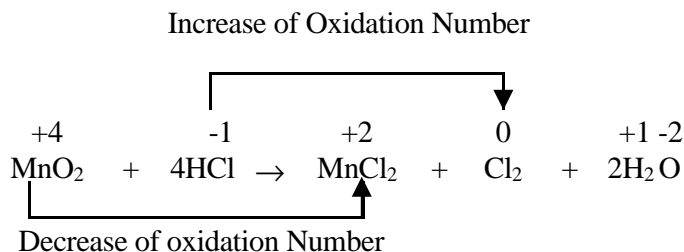
In the above reaction  $\text{H}_2\text{S}$  is reducing agent while  $\text{Br}_2$  is oxidising agent.

### Solved Problem

Identify the oxidising agent, reducing agent, substance oxidised and substance reduced in the following reactions.



### Solution



As it is clear, manganese decrease its oxidation number from +4 to +2. Hence,  $\text{MnO}_2$  gets reduced and it is an oxidising agent. Chlorine atom in  $\text{HCl}$  increases its oxidation number from -1 to 0. Thus,  $\text{HCl}$  gets oxidised and it is reducing agent.

### Balancing Redox reaction by Oxidation Number Method

The various steps involved in the balancing of redox equations according to this method are :

1. Write skeleton equation and indicate oxidation number of each element and thus identify the elements undergoing change in oxidation number.
2. Determine the increase and decrease of oxidation number per atom. Multiply the increase (or) decrease of oxidation number of atoms undergoing the change.
3. Equalise the increase in oxidation number and decrease in oxidation number on the reactant side by multiplying the respective formulae with

4. Balance the equation with respect to all atoms other than O and H atoms.
5. Balance oxygen by adding equal number of water molecules to the side falling short of oxygen atoms.
6. H atoms are balanced depending upon the medium in same way as followed in ion electron method.

$$\text{MnO}_2 + \text{Cl}^- \rightarrow \text{Mn}^{2+} + \text{Cl}_2 + \text{H}_2\text{O}$$

in acidic medium

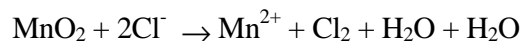
$$\text{MnO}_2 + \text{Cl}^- \rightarrow \text{Mn}^{2+} + \text{Cl}_2 + \text{H}_2\text{O}$$
$$\begin{array}{c}
 \text{O.N. Decreases by 2 per Mn} \\
 \downarrow \\
 \begin{array}{ccccccc}
 4+ & & -1 & & +2 & & \\
 \text{MnO}_2 & + & \text{Cl} & \rightarrow & \text{Mn} & + & \text{Cl}_2 + \text{H}_2\text{O} \\
 & & & & & & \uparrow \\
 & & & & & & \text{O.N. increases by 1 per Cl}
 \end{array}
 \end{array}$$

Equalise the increase / decrease in O.N by multiply  $\text{MnO}_2$  by 1 and  $\text{Cl}^-$  by 2.



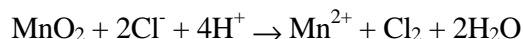
Balance other atoms except H and O. Here they are all balanced.

Balance O atoms by adding H<sub>2</sub>O molecules to the side falling short of oxygen atoms.



## Step 6

Balance H atoms by adding  $\text{H}^+$  ions to the side falling short of H atoms



## Problems for practice

Balance the following equations

1.  $\text{Mg} + \text{NO}_3^- \rightarrow \text{Mg}^{2+} + \text{N}_2\text{O} + \text{H}_2\text{O}$   
(in acidic medium)
2.  $\text{Cr}^{3+} + \text{Na}_2\text{O}_2 \rightarrow \text{CrO}_4^- + \text{Na}^+$
3.  $\text{S}^{2-} + \text{NO}_3^- \rightarrow \text{NO} + \text{S}$
4.  $\text{FeS} + \text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + \text{SO}_2$  (molecular form)
5.  $\text{Cl}_2 + \text{OH}^- \rightarrow \text{Cl}^- + \text{ClO}_3^- + \text{H}_2\text{O}$

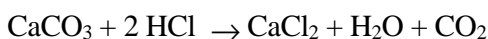
## 1.6 Calculations based on chemical equations

Stoichiometric problems are solved readily with reference to the equation describing the chemical change. From a stoichiometric chemical equation, we know how many molecules of reactant react and how many molecules of products are formed. When the molecular mass of the substances are inserted, the equation indicates how many parts by mass of reactants react to produce how many parts by mass of products. The parts by mass are usually in kg. So it is possible to calculate desired mass of the product for a known mass of the reactant or vice versa.

### 1.6.1 Mass / Mass Relationship

#### *Example 1*

Calculate the mass of  $\text{CO}_2$  that would be obtained by completely dissolving 10kg of pure  $\text{CaCO}_3$  in  $\text{HCl}$ .



$$100 \text{ kg} \times 10^{-3} \qquad \qquad \qquad 44 \text{ kg} \times 10^{-3}$$

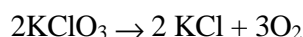
100 kg of  $\text{CaCO}_3$  produces  $44 \times 10^{-3}$  kg of  $\text{CO}_2$

$$44 \times 10^{-3}$$

$$\begin{aligned}
 10 \text{ kg of CaCO}_3 \text{ produces} &= \frac{\quad}{100 \times 10^{-3}} \times 10 \\
 &= 4.4 \text{ kg of CO}_2
 \end{aligned}$$

### Example 2

Calculate the mass of oxygen obtained by complete decomposition of 10kg of pure potassium chlorate (Atomic mass K=39, O=16 and Cl = 35.5)



Molecular mass of  $\text{KClO}_3 = 39 + 35.5 + 48 = 122.5$

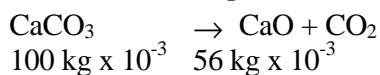
Molecular Mass of  $\text{O}_2 = 16 + 16 = 32$ .

According to the Stoichiometric equation written above  $(2 \times 122.5) \times 10^{-3}$  kg of  $\text{KClO}_3$  on heating gives  $(3 \times 32) \times 10^{-3}$  kg of oxygen.

$$\begin{aligned}
 10\text{kg of KClO}_3 \text{ gives} &= \frac{3 \times 32 \times 10^{-3}}{2 \times 122.5 \times 10^{-3}} \times 10 \\
 &= 3.92 \text{ kg of O}_2
 \end{aligned}$$

### Example 3

Calculate the mass of lime that can be prepared by heating 200 kg of limestone that is 90% pure  $\text{CaCO}_3$



$$\begin{aligned}
 200 \text{ kg of 90\% pure CaCO}_3 &= 200 \times \frac{90}{100} \\
 &= 180 \text{ kg pure CaCO}_3 \\
 100 \times 10^{-3} \text{ kg of pure CaCO}_3 \text{ on heating gives } &56 \times 10^{-3} \text{ kg of CaO} \\
 180 \text{ kg of CaCO}_3 &= \frac{56 \times 10^{-3} \times 180}{100 \times 10^{-3}} \\
 \text{gives on heating} &= 100.8 \text{ kg CaO}
 \end{aligned}$$

## 1.7 Methods of Expressing the concentration of solution

The concentration of a solution refers to the amount of solute present in the given quantity of solution or solvent. The concentration of a solution may be expressed quantitatively in any of the following ways.

### 1. Strength

The Strength of a solution is defined as the amount of the solute in grams, present in one litre of the solution. It is expressed in  $\text{g L}^{-1}$ .

$$\text{Strength} = \frac{\text{Mass of solute in grams}}{\text{Volume of solution in litres}}$$

If X gram of solute is present in  $V \text{ cm}^3$  of a given solution then

$$\text{Strength} = \frac{X \times 1000}{V}$$

### 2. Molarity (M)

Molarity of a solution is defined as the number of gram-moles of solute dissolved in 1 litre of a solution

$$\text{Molarity} = \frac{\text{No. of moles of solute}}{\text{Volume of Solution in litres}}$$

If 'X' grams of the solute is present in  $V \text{ cm}^3$  of a given solution, then,

$$\text{Molarity} = \frac{X}{\text{Mol. mass}} \times \frac{1000}{V}$$

Molarity is represented by the symbol M. Molarity can also be calculated from the strength as follows

$$\text{Molarity} = \frac{\text{Strength in grams per litre}}{\text{Molecular mass of the solute}}$$



**Example**

A 0.1M solution of Sugar,  $C_{12}H_{22}O_{11}$  (mol.mass = 342), means that 34.2 g of sugar is present in one litre ( $1000\text{ cm}^3$ ) of the solution.

**3. Normality**

Normality of a solution is defined as the number of gram equivalents of the solute dissolved per litre of the given solution.

$$\text{Normality} = \frac{\text{Number of gram-equivalents of solute}}{\text{Volume of Solution in litre}}$$

If X grams of the solute is present in  $V\text{ cm}^3$  of a given solution, then,

$$\text{Normality} = \frac{X}{\text{Eq.mass}} \times \frac{1000\text{ mL}}{V}$$

Normality is represented by the symbol N. Normality can also be calculated from strength as follows

$$\text{Normality} = \frac{\text{Strength in grams per litre}}{\text{Eq.mass of the solute}}$$

**Example**

A 0.1N (or decinormal) solution of  $H_2SO_4$  (Eq.mass = 49), means that 4.9 g of  $H_2SO_4$  is present in one litre ( $1000\text{ cm}^3$ ) of the solution.

**4. Molality (m)**

Molality of a solution is defined as the number of gram-moles of solute dissolved in 1000 grams (or 1 kg) of a Solvent. Mathematically,

$$\text{Molality} = \frac{\text{Number of moles of solute}}{\text{Mass of solvent in kilograms}}$$

"If X grams of the solute is dissolved in b grams of the solvent", then

$$\text{Molality} = \frac{X}{\text{Mol. mass}} \times \frac{1000\text{g}}{\text{bg}}$$

Molality is represented by the symbol 'm'.

### **Example**

A 0.1m Solution of glucose  $\text{C}_6\text{H}_{12}\text{O}_6$  (Mol.mass = 180), means that 18g of glucose is present in 1000g (or one kilogram) of water.

### **5. Mole Fraction**

Mole fraction is the ratio of number of moles of one component (Solute or Solvent) to the total number of moles of all the components (Solute and Solvent) present in the Solution. It is denoted by X. Let us suppose that a solution contains 2 components A&B and suppose that  $n_A$  moles of A and  $n_B$  moles of B are present in the solution. Then,

$$\text{Mole fraction of A, } X_A = \frac{n_A}{n_A + n_B} \quad \dots\dots(1)$$

$$\text{Mole fraction of B, } X_B = \frac{n_B}{n_A + n_B} \quad \dots\dots(2)$$

Adding 1 & 2 we get,

$$X_A + X_B = \frac{n_A}{n_A + n_B} + \frac{n_B}{n_A + n_B} = \frac{n_A + n_B}{n_A + n_B}$$

Thus, sum of the two mole fractions is one. Therefore, if mole fraction of one component in a binary solution is known, that of the other can be calculated.

### **Solved Problems**

1. 4.5g of urea (molar mass =  $60\text{g mol}^{-1}$ ) are dissolved in water and solution is made to 100 ml in a volumetric flask. Calculate the molarity of solution.

**Solution**

$$\text{Mass of Urea} = 4.5\text{g}$$

$$\begin{aligned} \text{Moles of Urea} &= \frac{\text{Mass}}{\text{Molar Mass}} = \frac{4.5\text{g}}{60\text{g mol}^{-1}} \\ &= 0.075\text{mol} \end{aligned}$$

$$\begin{aligned} \text{Volume of Solution} &= 1000\text{ ml} = \frac{1000}{1000} \text{ L} \\ &= 1\text{L} \end{aligned}$$

$$\begin{aligned} \text{Molarity of Solution} &= \frac{\text{Moles of Solute}}{\text{Volume of Solution in litres}} \\ &= \frac{0.075}{1} \text{ mol/L} = 0.075\text{M} \end{aligned}$$

2. Calculate the normality of solution containing 3.15g of hydrated oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ) in 250ml of solution (Mol.mass = 126).

**Solution**

$$\begin{aligned} \text{Mass of oxalic acid} &= 3.15\text{g} \\ \text{Mol.mass} &= 126 \end{aligned}$$

$$\begin{aligned} \text{Equivalent mass of oxalic acid} &= \frac{\text{Mol.mass}}{\text{Basicity}} \\ &= \frac{126}{2} = 63 \text{ g equiv}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Equivalents of oxalic acid} &= \frac{\text{Mass of solute}}{\text{Eq.Mass}} \end{aligned}$$

$$\frac{3.15\text{g}}{63 \text{ g equiv}^{-1}} = 0.05 \text{ equiv}^{-1}$$

$$\text{Volume of solution} = 250\text{ml} = \frac{250}{1000} \text{ L} = 0.25\text{L}$$

$$\begin{aligned} \text{Normality} &= \frac{\text{Equivalent of Solute}}{\text{Volume of solution in L}} \\ &= \frac{0.05 \text{ equiv}}{0.25 \text{ L}} = 0.2\text{N} \end{aligned}$$

3. Calculate the molality of an aqueous solution containing 3.0g of urea (mol.mass=60) in 250g of water.

**Solution**

$$\text{Mass of solute} = \frac{3.0\text{g}}{\text{Mass of solute}}$$

$$\text{Moles of solute} = \frac{\text{Molar Mass}}$$

$$\begin{aligned} &= \frac{3.0 \text{ g}}{60 \text{ g mol}^{-1}} = 0.05 \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{Mass of Solvent} &= \frac{250\text{g}}{1000} = 0.25 \text{ kg} \end{aligned}$$

$$\begin{aligned} \text{Molality of Solution} &= \frac{\text{Moles of Solute}}{\text{Mass of Solvent in kg.}} \\ &= \frac{0.05 \text{ Mol}}{0.25 \text{ kg}} = 0.2\text{m} \end{aligned}$$

### Problems for practice

1. Calculate the volume of 14.3m NH<sub>3</sub>, solution needed to prepare 1L of 0.1M solution.

Ans:-6.77 mL

2. How would you make up 425 mL of 0.150M HNO<sub>3</sub> from 68.0% HNO<sub>3</sub>? The density of 68.0% HNO<sub>3</sub> is 1.41g/mL.

Ans: 4.25 mL

3. Calculate the molarity of a solution obtained by mixing 100 mL of 0.3 M H<sub>2</sub>SO<sub>4</sub> and 200 mL of 1.5M H<sub>2</sub>SO<sub>4</sub>

Ans:1.1M

4. Calculate the molality of a solution by dissolving 0.850g of ammonia (NH<sub>3</sub>) in 100g of water.

Ans:0.5m

### 1.8 Calculations based on Principle of Volumetric Analysis

#### 1.8.1 Volumetric Analysis

An important method for determining the amount of a particular substance is based on measuring the volume of reactant solution. Suppose substance A in solution reacts with substance B. If you know the volume and concentration of a solution of B that just reacts with substance A in a sample, you can determine the amount of A.

Titration is a procedure for determining the amount of substance A by adding a carefully measured volume of a solution of A with known concentration of B until the reaction of A and B is just completed. Volumetric analysis is a method of analysis based on titrations.

#### Law

"Equal volume of equinormal solutions exactly neutralise the other solution having same concentration and volume".

$$V_1 N_1 = V_2 N_2$$

V<sub>1</sub>, V<sub>2</sub> - Volume of solutions.

N<sub>1</sub>, N<sub>2</sub> - Strength of solutions.

### Solved problem

#### Calculating the volume of reactant solution needed

1. What volume of 6M HCl and 2M HCl should be mixed to get one litre of 3M HCl?

#### Solution

Suppose the volume of 6M HCl required to obtain 1L of 3M HCl = XL

Volume of 2M HCl required = (1-x)L

Applying the molarity equation

$$M_1V_1 + M_2V_2 = M_3V_3$$



$$6x + 2(1-x) = 3 \times 1$$

$$6x + 2 - 2x = 3$$

$$4x = 1$$

$$x = 0.25\text{L}$$

hence, volume of 6M HCl required = 0.25L

Volume of 2M HCl required = 0.75L

2. How much volume of 10M HCl should be diluted with water to prepare 2.00L of 5M HCl.

#### Solution

$$N_1V_1 = N_2V_2$$

$$10\text{N HCl} = 5\text{N HCl}$$

$$10xV_1 = 5 \times 2.00$$

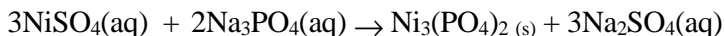
$$5 \times 2.00$$

$$\therefore V_1 = \frac{\quad}{10}$$

$$= 1.00\text{L}$$

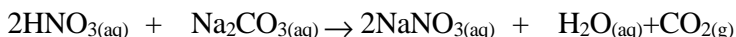
#### Problems for Practice

1.  $\text{NiSO}_4$  reacts with  $\text{Na}_3\text{PO}_4$  to give a yellow green precipitate of  $\text{Ni}_3(\text{PO}_4)_2$  and a solution of  $\text{Na}_2\text{SO}_4$ .

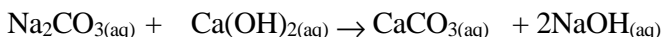


How many mL of 0.375M NiSO<sub>4</sub> will react with 45.7 mL of 0.265M Na<sub>3</sub>PO<sub>4</sub>?

2. What volume of 0.250M HNO<sub>3</sub> reacts with 42.4 mL of 0.150M Na<sub>2</sub>CO<sub>3</sub> in the following reaction?



3. A flask contains 53.1 mL of 0.150M Ca(OH)<sub>2</sub> solution. How many mL of 0.350M Na<sub>2</sub>CO<sub>3</sub> are required to react completely with Ca(OH)<sub>2</sub> in the following reaction.



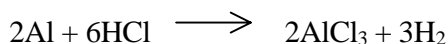
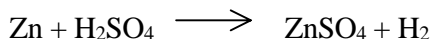
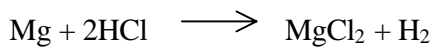
### 1.8.2 Determination of equivalent masses of elements

Equivalent masses can be determined by the following methods:

1. Hydrogen displacement method
2. Oxide method
3. Chloride method
4. Metal displacement method

#### Hydrogen displacement method

This method is used to determine the equivalent mass of those metals such as magnesium, zinc and aluminium which react with dilute acids and readily displace hydrogen.



From the mass of the metal and the volume of hydrogen displaced, the equivalent mass of the metal can be calculated.

#### Problem 1

0.548 g of the metal reacts with dilute acid and liberates 0.0198 g of hydrogen at S.T.P. Calculate the equivalent mass of the metal.

0.548 g of the metal displaces 0.0198 g of hydrogen

The mass of the metal which will displace

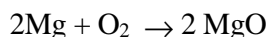
$$1.008 \text{ g of hydrogen} = \frac{1.008 \times 0.548}{0.0198} \text{ g of metal}$$

The equivalent mass of the metal =  $27.90 \text{ g equiv}^{-1}$

### Oxide Method

This method is employed to determine the equivalent mass of those elements which readily form their oxides eg. magnesium, copper etc. Oxide of an element can be formed by direct method or by indirect method.

Magnesium forms its oxide directly on heating



In the case of copper, its oxide is obtained in an indirect manner i.e. copper is dissolved in concentrated nitric acid and the copper(II) nitrate formed after evaporation is strongly heated to give copper (II) oxide.



### Calculations

Mass of the element taken =  $w_1 \text{ g}$

Mass of the oxide of the element =  $w_2 \text{ g}$

Mass of oxygen =  $(w_2 - w_1) \text{ g}$

$(w_2 - w_1) \text{ g}$  of oxygen has combined with  $w_1 \text{ g}$  of the metal.

$$\therefore 8 \text{ g of oxygen will combine with } \frac{w_1}{w_2 - w_1} \times 8$$

This value represents the equivalent mass of the metal.

### Problem 2

0.635 g of a metal gives on oxidation 0.795g g of its oxide. Calculate the equivalent mass of the metal.



Mass of the metal oxide = 0.795g  
 Mass of the metal = 0.635g  
 Mass of oxygen = 0.795 - 0.635 = 0.16g  
 0.16 g of oxygen has combined with 0.635 g of a metal

∴ 8 g of oxygen will combine with  

$$\frac{8 \times 0.635}{0.16} = 31.75 \text{ of the metal}$$

Equivalent mass of the metal = 31.75g equiv<sup>-1</sup>

### Chloride Method

The equivalent mass of those elements which readily form their chlorides can be determined by chloride method. For example, a known mass of pure silver is dissolved completely in dilute nitric acid. The resulting silver nitrate solution is treated with pure hydrochloric acid when silver chloride is precipitated. It is then filtered, dried and weighed. Thus from the masses of the metal and its chloride, the equivalent mass of the metal can be determined as follows :

### Calculations

Mass of the metal =  $w_1$  g  
 Mass of the metal chloride =  $w_2$  g  
 Mass of chlorine =  $(w_2 - w_1)$  g

$(w_2 - w_1)$  g of chlorine has combined with  $w_1$  of the metal

35.46 g of chlorine will combine with

$$\frac{35.46 \times w_1}{(w_2 - w_1)} \text{ g of the metal}$$

This value gives the equivalent mass of the metal.

### Uses of volumetric laws

If the volume of the acid is represented as  $V_1$ , the normality of the acid as  $N_1$ , volume of base as  $V_2$  the normality of the base as  $N_2$ , then from the law of volumetric analysis it follows that

$$V_1 \times N_1 = V_2 \times N_2$$

All volumetric estimations are based on the above relationship. If any three quantities are known, the fourth one can readily be calculated using the above expression.

### 1.8.3 Equivalent mass of acid, base, salt, oxidising agent and reducing agent

Acids contain one or more replaceable hydrogen atoms. The number of replaceable hydrogen atoms present in a molecule of the acid is referred to its basicity.

Equivalent mass of an acid is the number of parts by mass of the acid which contains 1.008 part by mass of replaceable hydrogen atom.

$$\begin{aligned} \text{Equivalent mass of an acid} &= \frac{\text{molar mass of the acid}}{\text{No. of replaceable hydrogen atom}} \\ & \quad \text{(or)} \\ &= \frac{\text{molar mass of the acid}}{\text{basicity of the acid}} \end{aligned}$$

For example, the basicity of sulphuric acid is 2.

$$\begin{aligned} \text{Equivalent mass of H}_2\text{SO}_4 &= \frac{\text{Molar mass of H}_2\text{SO}_4}{2} \\ &= \frac{98}{2} = 49 \end{aligned}$$

## 2. Equivalent mass of the base

Equivalent mass of a base is the number of parts by mass of the base which contains one replaceable hydroxyl ion or which completely neutralises one gram equivalent of an acid. The number of hydroxyl ions present in one mole of a base is known as the acidity of the base. Sodium hydroxide, potassium hydroxide, ammonium hydroxide are examples of monoacidic bases.

Calcium hydroxide is a diacidic base

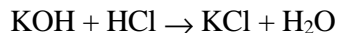
In general, 
$$\text{equivalent mass of a base} = \frac{\text{molar mass of the base}}{\text{acidity of the base}}$$

$$\text{Equivalent mass of KOH} = 56 / 1 = 56$$

### 3. Equivalent mass of a salt

Equivalent mass of a salt is a number of parts by mass of the salt that is produced by the neutralisation of one equivalent of an acid by a base.

In the case of salt like potassium chloride, the salt formed by the neutralisation of one equivalent of an acid by a base.

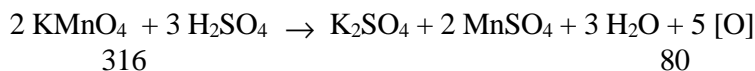


Therefore, the equivalent mass of the salt is equal to its molar mass.

### 4. Equivalent mass of an oxidising agent

The equivalent mass of an oxidising agent is the number of parts by mass which can furnish 8 parts by mass of oxygen for oxidation either directly or indirectly.

For example, potassium permanganate is an oxidising agent. In acid medium potassium permanganate reacts as follows



80 parts by mass of oxygen are made available from 316 parts by mass of  $\text{KMnO}_4$

8 parts by mass of oxygen will be furnished by

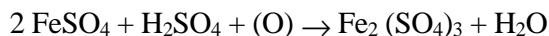
$$\frac{316 \times 8}{80} = 3.16$$

$$\text{Equivalent mass of KMnO}_4 = 31.6 \text{g equiv}^{-1}$$

### 5. Equivalent mass of a reducing agent

The equivalent mass of a reducing agent is the number of parts by mass of the reducing agent which is completely oxidised by 8 parts by mass of oxygen or with one equivalent of any oxidising agent.

(i) Ferrous sulphate reacts with an oxidising agent in acid medium according to the equation



2 x 152g                      16g

16 parts by mass of oxygen oxidised 304 parts by mass of ferrous sulphate

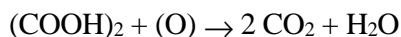
8 parts by mass of oxygen will oxidise  $304/16 \times 8$  parts by mass of ferrous sulphate.

The equivalent mass of ferrous sulphate (anhydrous) is 152.

The equivalent mass of crystalline ferrous sulphate,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  is  $152 + 126 = 278$

126 is the mass corresponding to 7 moles of water.

(ii) In acid medium, oxalic acid is oxidised according to the equation



16 Parts by mass of oxygen oxidised 90 parts by mass of anhydrous oxalic acid.

8 parts by mass of oxygen will oxidise  $90/16 \times 8 = 45$  parts by mass of anhydrous oxalic acid.

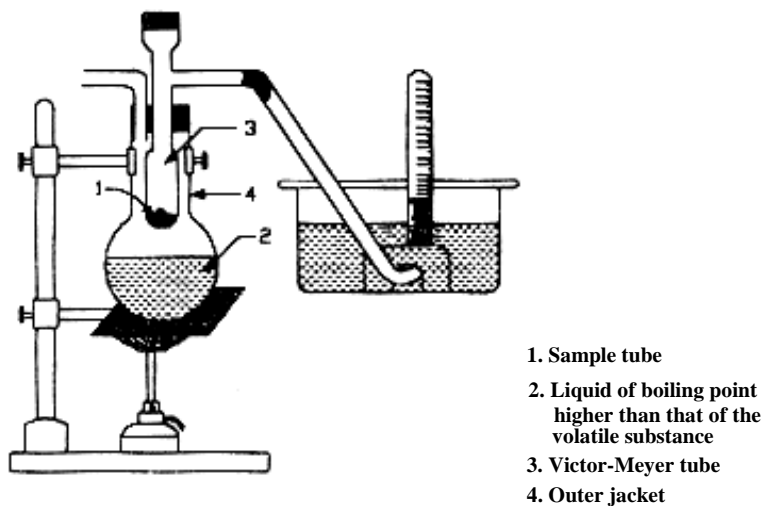
$\therefore$  Equivalent mass of anhydrous oxalic acid =  $45 \text{ g equiv}^{-1}$

But equivalent mass of crystalline oxalic acid,  $(\text{COOH})_2 \cdot 2\text{H}_2\text{O} = 126/2$   
 $= 63 \text{ g equiv}^{-1}$ .

#### 1.8.4 Determination of Molecular Mass Victor-Meyer's Method

##### Principle

In this method a known mass of a volatile liquid or solid is converted into its vapour by heating in a Victor-Meyer's tube. The vapour displaces its own volume of air. The volume of air displaced by the vapour is measured at the experimental temperature and pressure. The volume of the vapour at s.t.p is then calculated. From this the mass of  $2.24 \times 10^{-2} \text{m}^3$  of the vapour at S.T.P. is calculated. This value represents the molecular mass of the substance.



**Figure 1.1 Determination of molecular mass by victor-Meyers method**

The apparatus consists of an inner Victor-Meyer tube, the lower end of which is in the form of a bulb. The upper end of the tube has a side tube which leads to a trough of water. The Victor-Meyer tube is surrounded by an outer jacket. In the outer jacket is placed a liquid which boils at a temperature at least 30 K higher than the boiling point of the volatile substance under study. A small quantity of glass wool or asbestos fiber covers the bottom of the Victor-Meyer tube to prevent breakage when the bottle containing the substance is dropped in.

### **Procedure**

The liquid in the outer jacket is allowed to boil and when no more air escapes from the side tube, a graduated tube filled with water is inverted over the side tube dipping in a trough full of water. A small quantity of the substance is exactly weighed in a small stoppered bottle and quickly dropped in the heated Victor-Meyer tube and corked immediately.

The bottle falls on the asbestos pad and its content suddenly changes into vapour, blow out the stopper and displace an equal volume of air which collects in the graduated tube. The volume of air in the graduated tube is measured by taking it out by closing its mouth with the thumb and dipping

it in a jar full of water. When the water levels outside and inside the tube are the same, the volume of air displaced is noted. The atmospheric pressure and laboratory temperature are noted.

### Calculations

Mass of the volatile substance =  $w$  g

Volume of air displaced = Volume of vapour =  $V_1$  m<sup>3</sup>

Laboratory temperature =  $T_1$  K

Let the atmospheric pressure be  $P$

Pressure of dry vapour = Atmospheric pressure - aqueous tension at  $T_1$  K

Let the aqueous tension be  $p$  Nm<sup>-2</sup> at that temperature.

Pressure of dry vapour =  $P_1$  =  $[P-p]$

Standard temperature =  $T_0$  = 273 K

Standard pressure =  $P_0$  =  $1.013 \times 10^5$  Nm<sup>-2</sup>

Let the volume of the vapour at standard temperature and pressure be  $V_0$  m<sup>3</sup>

From the gas equation, it follows

$$\frac{P_0 V_0}{T_0} = \frac{P_1 V_1}{T_1}$$

$$V_0 = \frac{P_1 V_1}{T_1} \times \frac{T_0}{P_0}$$

The mass of  $V_0$  m<sup>3</sup> of vapour at s.t.p is  $w$  g.

The mass of  $2.24 \times 10^{-2}$  m<sup>3</sup> of the vapour at s.t.p. is

$$\frac{2.24 \times 10^{-2} \times W}{V_0}$$

The value thus calculated gives the molecular mass

$$\text{Molecular mass} = 2 \times \text{vapour density}$$

$$\text{Vapour density} = \frac{\text{Molecular mass}}{2}$$

### Problem

In the determination of molecular mass by Victor-Meyer's Method 0.790 g of a volatile liquid displaced  $1.696 \times 10^{-4} \text{ m}^3$  of moist air at 303 K and at  $1 \times 10^5 \text{ Nm}^{-2}$  pressure. Aqueous tension at 303 K is  $4.242 \times 10^3 \text{ Nm}^{-2}$ . Calculate the molecular mass and vapour density of the compound.

$$\text{Mass of the organic compound} = 0.79 \text{ g}$$

$$\text{Volume of Vapour} = V_1 = 1.696 \times 10^{-4} \text{ m}^3$$

$$\text{Volume of air displaced} = \text{Volume of vapour.}$$

$$P_1 = (\text{atmospheric pressure} - \text{aqueous tension})$$

$$= (1.0 \times 10^5) - (4.242 \times 10^3) = 0.958 \times 10^5 \text{ Nm}^{-2}$$

$$T_1 = 303 \text{ K}$$

#### Lab Values

$$V_1 = 1.696 \times 10^{-4} \text{ Nm}^{-2}$$

$$P_1 = 0.958 \times 10^5 \times 10^5 \text{ Nm}^{-2}$$

$$T_1 = 303 \text{ K}$$

#### Values at S.T.P

$$V_0 = ?$$

$$P_0 = 1.013 \times 10^5 \text{ Nm}^{-2}$$

$$T_0 = 273 \text{ K}$$

$$\frac{P_1 V_1}{T_1} = \frac{P_0 V_0}{T_0}$$

$$V_0 = \frac{P_1 V_1 T_0}{P_0 T_1}$$

$$V_0 = \frac{0.958 \times 10^5 \times 1.696 \times 10^{-4}}{1.013 \times 10^5} \times \frac{273}{303}$$

$$V_0 = 1.445 \times 10^{-4} \text{ m}^3$$

The mass of  $1.445 \times 10^{-4} \text{ m}^3$  of vapour at S.T.P = 0.79 g.

The mass of  $2.24 \times 10^{-2} \text{ m}^3$  of vapour at S.T.P is  
 $2.24 \times 10^{-2} \times 0.79$

$$= \frac{\quad}{1.445 \times 10^{-4}}$$

The molecular mass of the substance = 122.46  
 molecular mass

$$\text{Vapour density of the compound} = \frac{\quad}{2}$$

$$122.46$$

$$= \frac{\quad}{2} = 61.23$$

### Questions

#### A. Choose the best answer :

- The volume occupied by 16g of oxygen at S.T.P.  
 a) 22.4 L    b) 44.8 L    c) 11.2 L    d) 5.6 L
- Avogadro's number represents the number of atoms in  
 a) 12g of  $\text{C}^{12}$     b) 320g of S  
 c) 32g of Oxygen    d) 12.7g of iodine.
- The value of gram molecular volume of ozone at S.T.P is  
 a) 22.4 L    b) 2.24 L    c) 11.2 L    d) 67.2 L
- The number of atoms present in 0.5 gram- atoms of Nitrogen is same as the atoms in  
 a) 12g of C    b) 32g of S  
 c) 8g of the oxygen    d) 24g of magnesium.
- The number of gram-atoms of oxygen in 128g of oxygen is  
 a) 4    b) 8    c) 128    d)  $8 \times 6.02 \times 10^{23}$
- The total number of moles present in 111 g of  $\text{CaCl}_2$  is  
 a) One mole    b) Two moles    c) Three moles    d) Four moles
- Which of the following weighs the most?  
 a) One gram-atom of nitrogen    b) One mole of water  
 c) One mole of Sodium    d) One molecule of  $\text{H}_2\text{SO}_4$



8. Which of the following contains same number of carbon atoms as are in 6.0g of carbon (C-12)?  
a) 6.0g ethane b) 8.0g methane c) 21.0g Propane d) 28.0g CO
9. Which of the following contains maximum number of atoms?  
a) 2.0g hydrogen b) 2.0g oxygen c) 2.0g nitrogen d) 2.0g methane
10. Which one among the following is the standard for atomic mass?  
a) H b)  $^{12}_6\text{C}$  c)  $^{14}_6\text{C}$  d)  $^{16}_8\text{O}$
11. Which of the following pair of species have same number of atoms under similar conditions ?  
a) 1L each of  $\text{SO}_2$  and  $\text{CO}_2$  b) 2L each of  $\text{O}_3$  and  $\text{O}_2$   
c) 1L each of  $\text{NH}_3$  and  $\text{Cl}_2$  d) 1L each of  $\text{NH}_3$  and 2L of  $\text{SO}_2$
12. 2.0 g of oxygen contains number of atoms same as in  
a) 4 g of S b) 7 g of nitrogen  
c) 0.5 g of  $\text{H}_2$  d) 12.3 g of Na
13. The number of gm-molecules of oxygen in  $6.02 \times 10^{24}$  CO molecules is  
a) 1 gm-molecule b) 0.5 gm-molecule  
c) 5 gm-molecule d) 10 gm-molecule
14. Hydrogen phosphate of certain metal has a formula  $\text{MHPO}_4$ , the formula of metal chloride is  
a)  $\text{MCl}$  b)  $\text{MCl}_3$  c)  $\text{MCl}_2$  d)  $\text{MCl}_4$
15. A compound contains 50% of X (atomic mass 10) and 50% Y (at. mass 20). Which formulae pertain to above data ?  
a)  $\text{XY}$  b)  $\text{X}_2\text{Y}$  c)  $\text{X}_4\text{Y}_3$  d)  $(\text{X}_2)_3\text{Y}_3$
16. Which of the following compound has / have percentage of carbon same as that in ethylene ( $\text{C}_2\text{H}_4$ ) ?  
a) propene b) Cyclohexane c) Ethyne d) Benzene
17. 5L of 0.1 M solution of sodium Carbonate contains  
a) 53 g of  $\text{Na}_2\text{CO}_3$  b) 106 g of  $\text{Na}_2\text{CO}_3$   
c) 10.6 of  $\text{Na}_2\text{CO}_3$  d)  $5 \times 10^2$  millimoles of  $\text{Na}_2\text{CO}_3$

**B. Fill in the blanks**

1. One mole of a triatomic gas contains \_\_\_\_\_ atoms.
2. One mole of Sulphuric acid contains \_\_\_\_\_ Oxygen atoms.
3. 11.2 L of carbon dioxide at S.T.P contains \_\_\_\_\_ oxygen atoms.
4. Equal volumes of different gases under similar conditions of temperature and pressure contain equal number of \_\_\_\_\_

5. A decimolar solution of NaOH contains \_\_\_\_ of NaOH per litre of the solution.
6. 7 g of CO contains \_\_\_\_\_ O atoms.
7. The mass of  $1 \times 10^{22}$  formula units of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is \_\_\_\_\_

**C. Match the following**

Column A	Column B
1. $\text{CaC}_2$	a. 106 g
2. Law of multiple proportions	b. $6.02 \times 10^{23}$ Ne atoms
3. Hydrargyrum	c. Molarity of solution
4. 2 gm-equivalents of $\text{Na}_2\text{CO}_3$	d. 0.01 moles of solute in one L of solution
5. 22.4 L at S.T.P	e. Liquid element
6. Number of gm-molecules per litre of solution	f. Calcium carbide
7. 1 gm-atom of rhombic sulphur	g. $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}(\text{SO}_4) \cdot 6\text{H}_2\text{O}$
8. Centimolar solution	h. 1/8 gm-molecules
9. Mohr's Salt	i. John Dalton

**D. Answer the following**

1. Can two different compounds have same molecular formula ? Illustrate your answer with two examples.
2. What are the essentials of a chemical equation ?
3. What are the informations conveyed by a chemical equation ?
4. Balance the following equations
  - i.  $\text{Fe} + \text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + \text{H}_2$
  - ii.  $\text{Fe}_2(\text{SO}_4)_3 + \text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_3 + (\text{NH}_4)_2\text{SO}_4$
  - iii.  $\text{KMnO}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + \text{MnSO}_4 + \text{H}_2\text{O} + \text{O}_2$
  - iv.  $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + \text{H}_2\text{O} + \text{O}_2$

**SUMMARY**

SI units and different scientific notation. Molecular mass, Mole

concept, Avogadro number and its significance are dealt. The application of the various concepts are explained by solving problems. By knowing the percentage composition of elements in a compound, empirical formula and molecular formula can be calculated.

It is important to write the stoichiometric equation. So, the method of balancing the any equation explained and given or practice. And also the method of balancing redox equation using oxidation number is dealt.

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## 2. GENERAL INTRODUCTION TO METALLURGY

### OBJECTIVES

- *Know the ores and minerals of elements*
- *Learn the purification methods of ores*
- *Understand the different metallurgical processes*
- *Know the importance of purification of metals*
- *Understand clearly the extraction of Cu, Au, Ag, Pb, Zn and Al*
- *Gain knowledge about the mineral wealth of India and Tamilnadu*

### 2.1 Ores and minerals

Metals occur in nature sometimes in **free or native state**, but most of these occur in nature in the form of **chemical combination**, i.e., in the form of their stable compounds which are associated with **gangue or matrix**. The earthy impurities such as sand, clay, rocks etc. associated with ore are collectively known as **gangue or matrix**. Thus a large number of metals in nature occur in the combined form along with other elements, but some metals, such as Ag, Au, Pt etc. occur in the **native form (metallic state)** in some regions. Ag occurs in **native (or free)** as well as in the form of **compounds**. The natural material in which the metal or their compounds occur in the earth is known as **mineral**. Thus a mineral is a naturally occurring material present in earth's crust which contains metal in the native (or free state) or in combined state.

A mineral may be a single compound or a complex mixture of various compounds. When a mineral contains sufficient amount of a metal in combined state, from which it can be readily and profitably separated on commercial scale, then the mineral is said to be an ore of the metal. **Thus all ores are minerals, but all minerals are not ores.** A mineral from which a metal can be profitably extracted is called an **ore**. For example, clay ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ) and bauxite ( $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ ) are two minerals of aluminium, but aluminium, can be profitably extracted only from bauxite and not from the clay. **Hence bauxite is an ore of aluminium, while clay is a mineral.** The biggest source of metal is the

earth's crust and the process of taking out the ores from the earth crust is called **mining**.

In the combined state ores are generally found in the form of oxides, sulphides, carbonates, sulphates, chlorides and silicates. The important ores are given in Table 2.1.

**Table 2.1 Classification of ores**

Ore	Ore or Mineral	Composition	Metal Present
Oxide ores	Bauxite	$\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$	Al
	Cuprite	$\text{Cu}_2\text{O}$	Cu
	Haematite	$\text{Fe}_2\text{O}_3$	Fe
	Zincite	$\text{ZnO}$	Zn
	Tinstone or Cassiterite	$\text{SnO}_2$	Sn
	Pyrolusite	$\text{MnO}_2$	Mn
	Pitch Blende	$\text{U}_3\text{O}_8$	U
Sulphide ores	Copper Pyrites	$\text{Cu}_2\text{S}$ , $\text{Fe}_2\text{S}_3$ or $\text{Cu}_2\text{S} \cdot \text{FeS}_2$	Cu
	Copper Glance	$\text{Cu}_2\text{S}$	Cu
	Zinc Blende	$\text{ZnS}$	Zn
	Cinnabar	$\text{HgS}$	Hg
	Galena	$\text{PbS}$	Pb
	Argentite or Silver Glance	$\text{Ag}_2\text{S}$	Ag
Carbonate ores	Magnesite	$\text{MgCO}_3$	Mg
	Dolomite	$\text{CaCO}_3 \cdot \text{MgCO}_3$	Mg
	Calamine	$\text{ZnCO}_3$	Zn
	Malachite	$\text{CuCO}_3 \cdot \text{Cu(OH)}_2$	Cu
	Limestone	$\text{CaCO}_3$	Ca

Halide ores	Rock Salt	NaCl	Na
	Carnallite	KCl.MgCl <sub>2</sub> .6H <sub>2</sub> O	Mg
	Horn Silver	AgCl	Ag
	Sylvine	KCl	K
	Cryolite	3 NaF.AlF <sub>3</sub> or Na <sub>3</sub> AlF <sub>6</sub>	Al
Sulphate ores	Epsom Salt	MgSO <sub>4</sub> .7H <sub>2</sub> O	Mg
	Gypsum	CaSO <sub>4</sub> .2H <sub>2</sub> O	Ca
	Barytes	BaSO <sub>4</sub>	Ba
	Anglesite	PbSO <sub>4</sub>	Pb
Silicate ores	Asbestos	CaSiO <sub>3</sub> .3MgSiO <sub>3</sub>	Mg
	Felspar	K <sub>2</sub> O.Al <sub>2</sub> O <sub>3</sub> .6SiO <sub>2</sub> or KAlSi <sub>3</sub> O <sub>8</sub>	Al
	Mica	K <sub>2</sub> O.3Al <sub>2</sub> O <sub>3</sub> .6SiO <sub>2</sub> .2H <sub>2</sub> O	Al
Phosphate ores	Phosphorite	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	P

## 2.2 Sources from earth, living systems and in sea

### Sources from earth

Nearly 80 elements are obtained from mineral deposits on or beneath the surface of the earth.

- Metals which are sufficiently unreactive to occur uncombined (ie in elementary form) are present in group 10 and 11 of the 2nd and 3rd transition series (e.g Pt, Au, Ag; free Ag is also found in nature).
- Metalloids (e.g Ge, As, Sb) and neighbouring metals, all of which have relatively large ionization energies, generally occur as sulphides.
- The more strongly metallic elements that form positive ions readily are found as oxides (transition metals), carbonates (group 2 metals) or chlorides (group 1 metals).
  - Three noble metals (Cu, Ag, Au), Hg and six platinum metals (Ru, Os, Rh, Ir, Pd and Pt) occur in nature in free state. All other metals are found in combined state in the nature.

- (ii) The composition of earth's crust is : O (49.1%), Si (26%), Al(7.5%), Fe(4.2%), Ca (3.2%), Na (2.4%), Mg (2.3%) and H (1.0%) by weight.
- (iii) In combined state metals are found as (a) Oxides- Mg, Cu, Zn, Al, Mn, Fe, etc. (b) Carbonates- Na, Cu, Mg, Ca, Ba, Zn, Fe etc. (c) Phosphates- Ca, Pb, Fe etc (d) Silicates- Li, Cu, Zn, Al, Mn, Ni, etc and (e) Sulphates- Fe, Cu, Pb, Hg etc.

#### Source from sea

Four elements such as Na, Mg,  $\text{Cl}_2$  and  $\text{Br}_2$  can be extracted from the oceans or salt brines, where they are present as monoatomic ions ( $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ).

#### Source from living system

Table 3.2 represents the descending mass abundance of elements. About 30 percent of enzymes have a metal atom at the active site. A large number of biomolecules contain metal ions ; many of these molecules are proteins. In addition metal ions in the form of crystalline minerals or amorphous solids are important as structural materials in many organisms.

**Table 2.2 Descending mass abundance of the elements**

Earth Crust	Oceans	Human s
O	O	H
Si	H	O
Al	Cl	C
Fe	Na	N
Ca	Mg	Na
Mg	S	K
Na	Ca	Ca
K	K	Mg
Ti	C	P
H	Br	S
P	B	Cl

### 2.3 Purification of ores

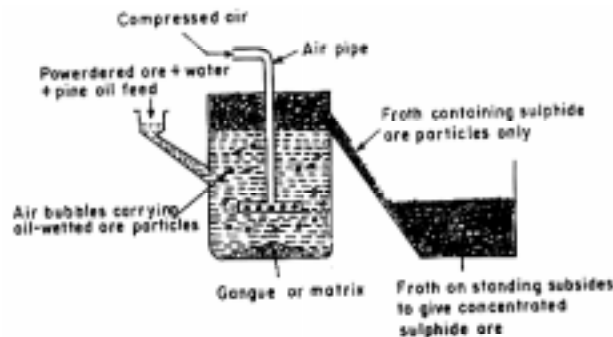
The ore is generally associated with rock impurities like clay, sand etc. called '**gangue or matrix**'. The purification of ore means removal of gangue from the powdered ore. This process is otherwise called concentration of the ore or ore dressing. Thus, the percentage of the ore in the concentrated ore is higher than that in the original ore. The purification or concentration of ore can be brought about in the following ways, depending upon the type of ore.

#### (i) **Gravity separation process or hydraulic washing**

This method is especially suitable for heavy 'oxide' ores like haematite, tinstone, etc. In this, the powdered ore is placed on a sloping floor (or platform) and washed by directing on it a strong current of water. The lighter sandy, and earthy impurities are washed away; while the heavier ore particles are left behind.

#### (ii) **Froth flotation process**

This method is especially suitable for sulphide ores like zinc blende ( $\text{ZnS}$ ), and copper pyrites ( $\text{CuFeS}_2$ ). This process is based on the fact that the sulphide ore particles are only moistened by **oil**; while those of oxide, and gangue particles are moistened only by **water**. In this process, the powdered ore is mixed with water and a little pine oil (a foaming agent) and the whole mixture is then stirred vigorously by blowing compressed air. The oil forms a foam (or froth) with air. The ore particles stick to the froth, which rises to the surface; while the rocky, and earthy impurities (gangue) are left in water Fig. 2.1. The froth is skimmed off, collected, and allowed to subside to get concentrated ore.

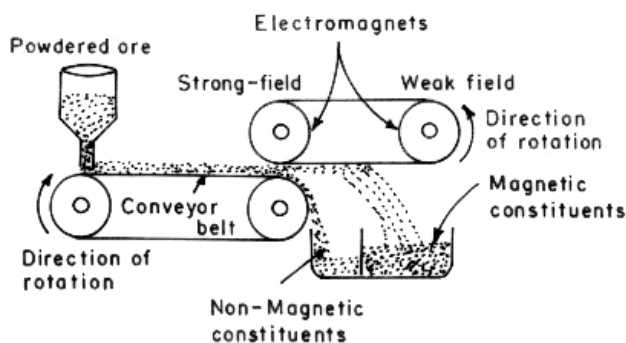


**Fig. 2.1 Froth flotation process**



### (iii) Electromagnetic separation process

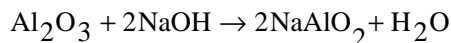
This method is meant for separating **magnetic impurities from non-magnetic ore particles**, e.g., tinstone (a tin ore) in which tinstone is non-magnetic; while impurities iron, manganese and tungstates are magnetic. The powdered ore (containing the associated magnetic impurities) is made to fall (from a hopper) on a belt moving over electromagnetic roller. The magnetic impurities fall from the belt in a heap near the magnet, due to attraction; while the non-magnetic concentrated ore falls in separate heap, away from the magnet, due to the influence of centrifugal force Fig. 2.2.



**Fig. 2.2 Electromagnetic separation method**

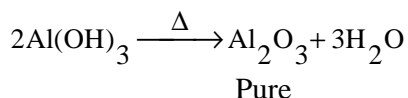
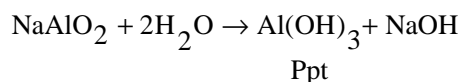
### (iv) Chemical method

This method is employed in case where the ore is to be in a very pure form, e.g., aluminium extraction. Bauxite ( $\text{Al}_2\text{O}_3$ ), an ore of aluminium, contains  $\text{SiO}_2$  and  $\text{Fe}_2\text{O}_3$  as impurities. When bauxite ore is treated with  $\text{NaOH}$ , the  $\text{Al}_2\text{O}_3$  goes into solution as sodium meta-aluminate leaving behind the undissolved impurities [ $\text{Fe}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{Fe}(\text{OH})_3$ , etc.], which are then filtered off.



Sod. meta. aluminate  
(In solution form)

The filtrate (containing sodium meta-aluminate) on dilution, and stirring gives a precipitate of aluminium hydroxide, which is filtered, and ignited to get pure alumina.



## 2.4 Metallurgical processes

Metallurgy is a branch of chemistry which deals with,

- (i) Extraction of metals from ores
- (ii) Refining of crude metal
- (iii) Producing alloys and the study of their constitution, structure and properties.
- (iv) The relationship of physical and mechanical treatment of metals to alloys.

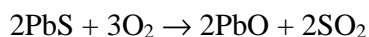
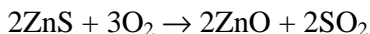
The extraction of metals cannot be carried out by any universal method because extraction of each metal requires different methods of extraction. This depends upon the nature and preparation of metals. In general, noble metals such as Au, Ag, etc are usually extracted by electrolysis of their chlorides, oxides or hydroxides. Heavy metals, e.g. Cu, Zn, Fe, Pb, Sn, etc., are extracted by making use of roasting and smelting methods.

### 2.4.1 Roasting- oxidation

Roasting is one of the oxidation method where ore is converted into metal oxide. In the process of roasting, the ore either alone or with the addition of suitable material, is subjected to the action of heat in excess of air at temperature below its melting point. Roasting is usually carried out in a reverberatory furnace or in a blast furnace. During roasting

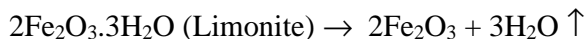
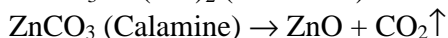
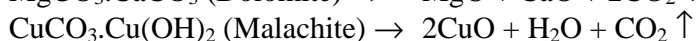
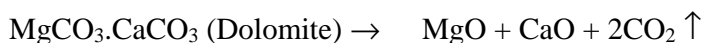
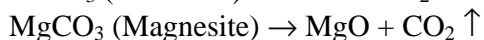
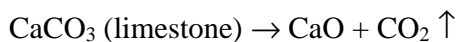
- (a) Volatile impurities like S, As, Sb etc. get oxidized and escape out as volatile gases  $\text{SO}_2$ ,  $\text{As}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_3$
- (b) The sulphide ores decompose to their oxides evolving  $\text{SO}_2$
- (c) The moisture is removed. Mass becomes porous and thus it can easily be reduced. Roasting may be of many types.

**Oxidising Roasting** – In this type of roasting S, As, and Sb impurities are removed in the form of their volatile oxides as  $\text{SO}_2$ ,  $\text{As}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_3$  etc. due to combined action of heat and air. The ore is simultaneously converted into its oxides. This type of roasting is carried out for ores like copper pyrites, zinc blende and lead ores ( $\text{PbS}$ ) etc.



### Calcination

Another method of conversion of ore into metal oxide (oxidation) is called calcination. It is the process in which the ore is subjected to the action of heat at high temperature in the absence of air below its melting point. The process of calcination is carried out in the case of carbonate and hydrated ore. As a result of calcination (a) The moisture is removed. (b) Gases may be expelled. (c) Volatile impurities are removed. (d) The mass becomes porous. (e) Thermal decomposition of the ore takes place. For example,



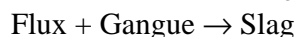
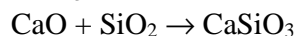
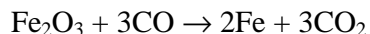
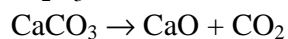
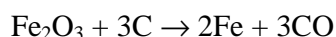
The name calcination originated from the ore calcite which on thermal decomposition gives quick lime. Calcination is usually carried out in reverberatory furnace.

### 2.4.2 Smelting – Reduction

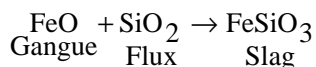
Smelting is one of reduction method where the metal oxide is converted into metal. It is the process used for all operations where the metal is separated by fusion from the ore. The process of smelting is that in which ore is melted with a flux and often with a reducing agent, and it involves, calcination, roasting and reduction. In general, the process of separation of a metal or its sulphide mixture from its ore in fused state is

called smelting. Smelting is generally carried out in a blast furnace and high temperature is produced by burning coal or by using electric energy.

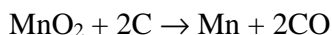
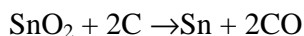
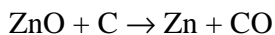
In smelting, the roasted or calcined ore is mixed with coke and then heated in a furnace. As a result, (carbon and CO produced by the incomplete combustion) carbon reduces the oxide to the metal. For example, in the extraction of iron, haematite ore( $\text{Fe}_2\text{O}_3$ ) is smelted with coke and limestone (flux). As a result of reduction, iron is obtained in fused or molten state.



Similarly, in the extraction of copper from **copper pyrites**, the ore is mixed with coke and heated in blast furnace (smelted). Infusible impurity FeO is converted to  $\text{FeSiO}_3$ (slag) and is removed. A mixture containing sulphide of copper and iron, called **matte** is formed in the molten state.



### Other Examples



### 2.4.3 Bessemerisation

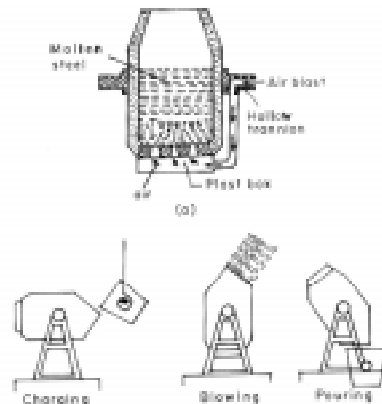
It is the process used for the manufacture of steel from pig iron. Steel is an alloy of carbon and iron and contains 0.15-1.5% of carbon with traces of sulphur, phosphorus, manganese and silicon as impurities. Depending upon the carbon content, steel are classified into three classes namely mild carbon steel (0.15-0.3%), medium carbon steel (0.3-0.8%) and high carbon steel (0.8-1.50).

The process was discovered by Henry Bessemer in England (1856). The principle involved in this process is that cold air blown through refractory lined vessel known as converter containing molten pig iron at about 2 atmospheric pressure, oxidizing the impurities and simultaneously converting pig iron to steel.

This process mainly differs in the use of acidic and basic refractory linings of the converters. In this process low phosphorus pig iron (below 0.09%) is treated by acidic Bessemer process and high phosphorus pig iron (more than 1.5%) is treated in basic.

The converter is a pear shaped furnace about 6m high and 3m in diameter. It is made of steel plates and is lined inside with silica or magnesia (MgO), depending upon the nature of impurities present in the pig iron. If the impurities present in the pig iron are basic, e.g., manganese, a lining of silica brick is used and the process is known as **acid Bessemer process**. If impurities are acidic, e.g., sulphur, phosphorus etc., a basic lining of lime (CaO) or magnesia (MgO) is used in the converter and process is then known as **basic Bessemer process**. The capacity of the converter is from 10-25 tonnes of charge at a time. The converter is mounted on shafts or trunnions, one of which is hollow and serves as a wind pipe and upon which the converter can rotate in any position. The converter is also provided with a number of holes at the bottom through which a hot blast of air can be introduced.

The molten pig iron is mixed in mixers and then charged into converter. About 15-16 tonnes of iron can be charged at a time. The converter is first set in the horizontal position and after charging the converter is adjusted in vertical position. After charging a blast of cold air is admitted through the hole provided at the bottom at a pressure of about  $2-3 \text{ kg/cm}^2$ . The blast is continued for about 15 minutes during which the impurities are oxidized. Mn is oxidized to MnO and Si is oxidized to  $\text{SiO}_2$ . Carbon is also oxidized to CO. The resulting oxides of Mn and Si (MnO and  $\text{SiO}_2$ ) combine together to form slag of manganese silicate Fig.3.4.1.



**Fig. 2.3 Bessemer Converter and Bessemer Process**

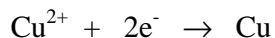
#### 2.4.4 Purification of metals

##### (a) Electrolytic refining

This is one of the most convenient and important method of refining and gives a metal of high purity. This method is applicable to many metals such as **Cu, Ag, Pb, Au, Ni, Sn, Zn etc.** The blocks of impure metal form the anode and thin sheets of pure metal form the cathode. A solution of a salt of the metal is taken as an electrolyte. On passing an electric current through the solution pure metal dissolves from the anode and deposits on cathode. By this process, more metal ions undergo reduction and pure metal is deposited at the cathode. The insoluble impurities either dissolve in the electrolyte or fall at the bottom and collect as **anode mud**. For example, in the refining of copper, impurities like Fe and Zn dissolve in the electrolyte, while Au, Ag and Pt are left behind as anode mud.

(i) **Copper:** During the electrolytic refining of a copper, a thick block of impure copper is made anode, and thin plate of pure copper is made cathode. Copper sulphate solution is used as an electrolyte. On passing electric current, following reactions take place:

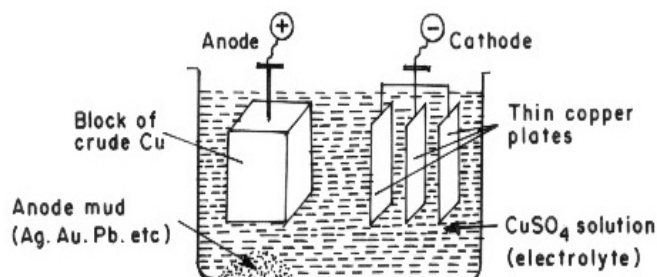
- 1)  $\text{Cu}^{2+}$  ions (from copper sulphate solution) go to the cathode (negative electrode), where they are reduced to copper, which gets deposited on the cathode.



- 2) Copper (of impure anode) forms copper ions, and these go into solution of electrolyte.



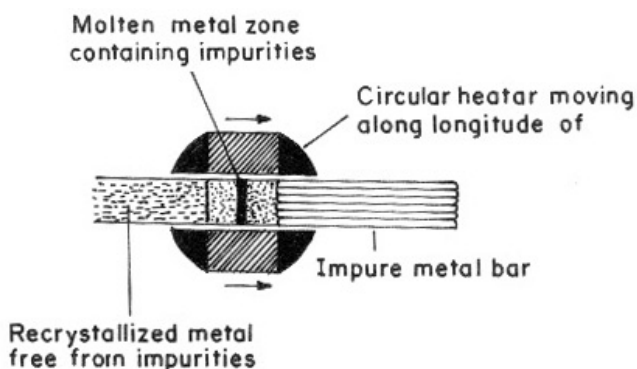
Thus, the net result is transfer of pure copper from anode to the cathode. Impurities like zinc, iron, etc., go into solution; while noble impurities like silver, gold, etc., are left behind as anode mud. Copper is refined to 99.98% pure copper by electrolytic refining (Fig. 2.4).



**Fig. 2.4 Electrolytic refining of copper**

**(b) Zone refining**

This method is employed for preparing highly pure metal (such as silicon, tellurium, germanium), which are used as semiconductors. It is based on the principle that melting point of a substance is lowered by the presence of impurities. Consequently, when an impure molten metal is cooled, crystals of the pure metal are solidified, and the impurities remain behind the remaining metal. (Fig. 2.5).



**Fig. 2.5 Zone refining**

The process consists in casting the impure metal in the form of a bar. A circular heater fitted around this bar is slowly moved longitudinally from one end to the other. At the heated zone, the bar melts, and as the heater moves on, pure metal crystallizes, while the impurities pass into the adjacent molten part. In this way, the impurities are swept from one end of the bar to the other. By repeating the process, ultra pure metal can be obtained.

**(c) Mond's process**

Thermal methods include methods as carbonyl method, decomposition of hydrides etc. The carbonyl method is used for the refining of metals like Ni and Fe. For example, in case of nickel, the impure metal is heated with CO. The nickel carbonyl thus formed is then decomposed (after distilling off the impurities) to get pure nickel metal and CO. The process is known as **Mond's process**.



It is based on the following facts:

- (a) Only nickel (and not Cu, Fe, etc.) forms a volatile carbonyl,  $\text{Ni}(\text{CO})_4$ , when CO is passed over it at  $50^\circ\text{C}$ .
- (b) the nickel carbonyl decomposes at  $180^\circ\text{C}$  to yield pure nickel.

**Questions**

**A. Fillup the blanks**

- 1. The earthy impurities associated with ores are .....
- 2. Froth flotation process is suitable for concentrating ..... ores.
- 3. Highly pure metals are obtained by ..... process.
- 4. Gangue + flux  $\rightarrow$  .....
- 5. A mineral from which metal can be profitably extracted is called .....
- 6. A mixture containing sulphides of copper and iron is called .....
- 7. .... is used as a foaming agent.

**B. Write in one or two sentence**

- 1. Distinguish between ore and mineral with suitable example ?
- 2. What are the elements obtained from sea water source?
- 3. What are the different methods of concentration of ores?
- 4. What is gravity separation ?
- 5. Name the ores which are concentrated by froth floatation process.
- 6. Define Metallurgy.
- 7. What are the major steps involved in the metallurgical process ?
- 8. What is calcination? Give example.



9. What is the principle involved in Bessemer process ?
10. What is meant by electrolytic refining? Give example.
11. What is anode mud?
12. What do you understand by the following terms (i) roasting  
(ii) smelting

**C. Explain briefly on the following**

1. Write short note on source of element in living system.
2. Explain froth flotation process with neat diagram.
3. How electrolytic separation process is useful in the separation of magnetic impurities from nonmagnetic ores? Draw the diagram.
4. How the impurities of ore are removed by chemical method?
5. What is roasting ? Explain different types of roasting with suitable example.
6. What is smelting ? Explain the process with example.
7. What is Zone refining ? Describe the principle involved in the purification of the metal by this method.
8. How nickel is extracted by Mond's process? Write the various reactions involved in the process.
9. Write short note on mineral wealth of India.
10. Give a brief account of the mineral wealth of Tamil Nadu.

**SUMMARY**

- This chapter explains and summarizes the salient features of metallurgy
- Different types of ores and their purification methods
- Chemistry behind roasting, smelting and bessemerisation processes
- Various methods of refining process

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### 3. ATOMIC STRUCTURE - I

#### OBJECTIVES

- *Know about the history of structure of atom.*
- *Recognise the merits and demerits of Niels Bohr's model of an atom.*
- *Learn about Sommerfield's atom model.*
- *Analyse the significance of quantum number.*
- *Learn about the shapes of orbitals.*
- *Understand the quantum designation of electron.*
- *Know the application of Pauli's exclusion principle, Hund's rule and Aufbau principle.*
- *Understand the stability of different orbitals and its application in writing the electronic configuration.*
- *Know about the classification of elements based on electronic configuration.*

#### 3.1 Brief introduction of history of structure of atom

The introduction of the atomic theory by John Dalton in 1808 marks the inception of a modern era in chemical thinking. According to this theory, all matter is composed of very small particles called atoms. The atoms were regarded to be structureless, hard, impenetrable particles which cannot be subdivided. Dalton's ideas of the structure of matter were born out by a considerable amount of subsequent experimental evidences towards the end of the nineteenth century. Early in the twentieth century, it has been proved that an atom consists of smaller particles such as electrons, protons and neutrons. The proton, a positively charged particle, is present in the central part of the atom called nucleus. The electron, a negatively charged particle, is present around the nucleus. The neutron, a neutral particle, is also present in the nucleus of the atom. Since the atom is electrically neutral, the number of positive charges on the nucleus is exactly balanced by an equal number of orbital electrons.

### **Thomson's Model of atom**

In 1904 Sir J. J. Thomson proposed the first definite theory as to the internal structure of the atom. According to this theory the atom was assumed to consist of a sphere of uniform distribution of about  $10^{-10}$  m positive charge with electrons embedded in it such that the number of electrons equal to the number of positive charges and the atom as a whole is electrically neutral.

This model of atom could account the electrical neutrality of atom, but it could not explain the results of gold foil scattering experiment carried out by Rutherford.

### **Rutherford's Scattering Experiment**

Rutherford conducted a scattering experiment in 1911 to find out the arrangement of electrons and protons. He bombarded a thin gold foil with a stream of fast moving positively charged  $\alpha$ -particles emanating from radium.

### **Rutherford's Nuclear model of a atom**

This model resulted from conclusion drawn from experiments on the scattering of alpha particles from a radio active source when the particles were passed through thin sheets of metal foil. According to him

- (i) Most of the space in the atom is empty as most of the  $\alpha$ -particles passed through the foil.
- (ii) A few positively charged  $\alpha$ -particles are deflected. The deflection must be due to enormous repulsive force showing that the positive charge of the atom is not spread throughout the atom as Thomson had thought. The positive charge has to be concentrated in a very small volume that repelled and deflected the positively charged  $\alpha$ -particles. This very small portion of the atom was called **nucleus** by Rutherford.
- (iii) Calculations by Rutherford showed that the volume occupied by the nucleus is negligibly small as compared to the total volume of the atom. The diameter of the atom is about  $10^{-10}$  m while that of nucleus is  $10^{-15}$  m. One can appreciate this difference in size by realizing that

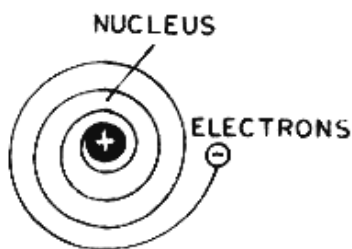
if a cricket ball represents a nucleus, then radius of the atom would be about 5 km.

On the basis of above observations and conclusions, Rutherford proposed the nuclear model of atom. According to this model:

- (a) An atom consists of a tiny positively charged nucleus at its centre.
- (b) The positive charge of the nucleus is due to protons. The mass of the nucleus, on the other hand, is due to protons and some neutral particles each having mass nearly equal to the mass of proton. This neutral particle, called neutron, was discovered later on by Chadwick in 1932. Protons and neutrons present in the nucleus are collectively also known as nucleons. The total number of nucleons is termed as **mass number(A)** of the atom.
- (c) The nucleus is surrounded by electrons that move around the nucleus with very high speed in circular paths called **orbits**. Thus, Rutherford's model of atom resembles the solar system in which the sun plays the role of the nucleus and the planets that of revolving electrons.
- (d) The number of electrons in an atom is equal to the number of protons in it. Thus, the total positive charge of the nucleus exactly balances the total negative charge in the atom making it electrically neutral. The number of protons in an atom is called its atomic number(**Z**).
- (e) Electrons and the nucleus are held together by electrostatic forces of attraction.

### 3.2 Defects of Rutherford's model

According to Rutherford's model, an atom consists of a positive nucleus with the electrons moving around it in circular orbits. However it had been shown by J. C. Maxwell that whenever an electron is subjected to acceleration, it emits radiation and loses energy. As a result of this, its orbit should become smaller and smaller Fig. 3.1. and finally it should drop into the nucleus by following a spiral path. This means that atom would collapse and thus Rutherford's model failed to explain stability of atoms.



**Fig. 3.1 Failure of Rutherford's atom model**

Another drawback of the Rutherford's model is that it says nothing about the electronic structure of the atoms i.e., how the electrons are distributed around the nucleus and what are the energies of these electrons. Therefore, this model failed to explain the existence of certain definite lines in the hydrogen spectrum.

### **Postulates of Bohr's model of an atom**

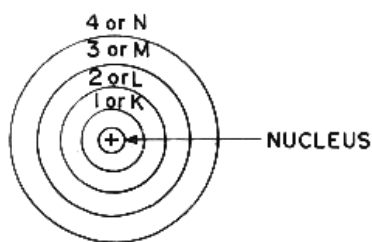
To overcome the above defects of Rutherford's model, Niels Bohr in 1913 gave a modification based on Quantum theory of radiation. The important postulates are:

- (1) The electrons revolve round the nucleus only in certain selected circular paths called orbits. These orbits are associated with definite energies and are called energy shells or energy levels or quantum levels. These are numbered as 1, 2, 3, 4 ..... etc. (starting from the nucleus) are designated as K, L, M, N ....etc. (Fig. 3.2).
- (2) As long as an electron remains in a particular orbit, it does not lose or gain energy. This means that energy of an electron in a particular path remains constant. Therefore, these orbits are also called stationary states.
- (3) Only those orbits are permitted in which angular momentum of the electron is a whole number multiple of  $h/2\pi$ , where 'h' is Planck's constant. An electron moving in a circular orbit has an angular momentum equal to  $mvr$  where  $m$  is the mass of the electron and  $v$ , the angular momentum,  $mvr$  is a whole number multiple of  $h/2\pi$  i.e.,

$$mvr = nh/2\pi \text{ where } n = 1, 2, 3, \dots$$

In other words, angular velocity of electrons in an atom is quantised.

- (4) If an electron jumps from one stationary state to another, it will absorb or emit radiation of a definite frequency giving a spectral line of that frequency which depends upon the initial and final levels. When an electron jumps back to the lower energy level, it radiates same amount of energy in the form of radiation.



**Fig. 3.2 Bohr's orbits**

#### **Limitation of Bohr's Theory**

- (i) According to Bohr, the radiation results when an electron jumps from one energy orbit to another energy orbit, but how this radiation occurs is not explained by Bohr.
- (ii) Bohr Theory had explained the existence of various lines in H-spectrum, but it predicted that only a series of lines exist. At that time this was exactly what had been observed. However, as better instruments and techniques were developed, it was realized that the spectral line that had been thought to be a single line was actually a collection of several lines very close together (known as fine spectrum). Thus for example, the single  $H_{\infty}$ -spectral line of Balmer series consists of many lines very close to each other.
- (iii) Thus the appearance of the several lines implies that there are several energy levels, which are close together for each quantum number  $n$ . This would require the existence of new quantum numbers.
- (iv) Bohr's theory has successfully explained the observed spectra for hydrogen atom and hydrogen like ions (e.g.  $\text{He}^+$ ,  $\text{Li}^{2+}$ ,  $\text{Be}^{3+}$  etc.), it can not explain the spectral series for the atoms having a large number of electrons.

- (v) There was no satisfactory justification for the assumption that the electron can rotate only in those orbits in which the angular momentum of the electron ( $mvr$ ) is a whole number multiple of  $h/2\pi$ , i.e. he could not give any explanation for using the principle of quantisation of angular momentum and it was introduced by him arbitrarily.
- (vi) Bohr assumes that an electron in an atom is located at a definite distance from the nucleus and is revolving round it with definite velocity, i.e. it is associated with a fixed value of momentum. This is against the Heisenberg's Uncertainty Principle according to which it is impossible to determine simultaneously with certainty the position and the momentum of a particle.
- (vii) No explanation for Zeeman effect: If a substance which gives a line emission spectrum, is placed in a magnetic field, the lines of the spectrum get split up into a number of closely spaced lines. This phenomenon is known as Zeeman effect. Bohr's theory has no explanation for this effect.
- (viii) No explanation of the Stark effect: If a substance which gives a line emission spectrum is placed in an external electric field, its lines get split into a number of closely spaced lines. This phenomenon is known as Stark effect. Bohr's theory is not able to explain this observation as well.

### **3.3 Electronic configuration and quantum numbers**

#### **Quantum Numbers**

The quantum numbers are nothing but the details that are required to locate an electron in an atom. In an atom a large number of electron orbitals are permissible. An orbital of smaller size means there is more chance of finding the electron near the nucleus. These orbitals are designated by a set of numbers known as quantum numbers. In order to specify energy, size, shape and orientation of the electron orbital, three quantum numbers are required these are discussed below.

#### **1. The principal quantum number (n)**

The electrons inside an atom are arranged in different energy levels called electron shells or orbits. Each shell is characterized by a quantum

number called principal quantum number. This is represented by the letter 'n' and 'n' can have values, 1,2,3,4 etc. The first level is also known as K level. Second as L level, third as M level, fourth as N level and so on. The first or K level is the orbit nearest to the nucleus and next one is second or L level and so on.

## 2. The subsidiary or azimuthal quantum number ( $l$ )

According to Sommerfield, the electron in any particular energy level could have circular path or a variety of elliptical paths about the nucleus resulting in slight differences in orbital shapes with slightly differing energies due to the differences in the attraction exerted by the nucleus on the electron. This concept gave rise to the idea of the existence of sub-energy levels in each of the principal energy levels of the atom. This is denoted by the letter ' $l$ ' and have values from 0 to  $n-1$ .

Thus, if  $n=1$ ,  $l=0$  only one value (one level only)  $s$  level.

$n=2$ ,  $l=0$  and 1 ( 2 values or 2 sub- levels)  $s$  and  $p$  level.

$n=3$ ,  $l=0$ , 1 and 2 (3 values or 3 sub-levels)  $s$ ,  $p$  and  $d$  level.

$n=4$ ,  $l=0$ , 1, 2 and 3 (4 values or 4 sub-levels)  $s$ ,  $p$ ,  $d$  and  $f$  level.

## 3. Magnetic quantum number ( $m$ )

In a strong magnetic field a sub-shell is resolved into different orientations in space. These orientations called orbitals have slight differences in energy. This explains the appearance of additional lines in atomic spectra produced when atoms emit light in magnetic field. Each orbitals is designated by a magnetic quantum number  $m$  and its values depends on the value of ' $l$ '. The values are ' $-l$ ' through zero to ' $+l$ ' and thus there are  $(2l+1)$  values.

Thus when  $l=0$ ,  $m= 0$  (only one value or one orbital)

$l=1$ ,  $m= -1, 0, +1$  (3 values or 3 orbitals)

$l=2$ ,  $m= -2, -1, 0, +1, +2$  (5 values or 5 orbitals)

$l=3$ ,  $m= -3,-2, -1, 0, +1, +2, +3$  (7 values or 7 orbitals).

The three quantum numbers labeling an atomic orbital can be used equally well to label electron in the orbital. However, a fourth quantum



number, the spin quantum number, ( $s$ ) is necessary to describe an electron completely.

#### 4. Spin quantum number ( $s$ )

The electron in the atom rotates not only around the nucleus but also around its own axis and two opposite directions of rotation are possible (clock wise and anticlock wise). Therefore the spin quantum number can have only two values  $+1/2$  or  $-1/2$ . For each values of  $m$  including zero, there will be two values for  $s$ .

To sum up, the four quantum numbers provide the following informations:

1.  $n$  identifies the shell, determines the size of the orbital and also to a large extent the energy of the orbit.
2. There are  $n$  subshells in the  $n^{\text{th}}$  shell.  $l$  identifies the subshell and determines the shape of the orbital. There are  $(2l+1)$  orbitals of each type in a subshell i.e., one s orbital ( $l=0$ ), three p orbitals ( $l=1$ ), and five d orbitals ( $l=2$ ) per subshell. To some extent  $l$  also determines the energy of the orbital in a multi-electron atom.
3.  $m_l$  designates the orientation of the orbital. For a given value of  $l$ ,  $m_l$  has  $(2l+1)$  values, the same as the number of orbitals per subshell. It means that the number of orbitals is equal to the number of ways in which they are oriented.
4.  $m_s$  refers to orientation of the spin of the electron.

#### *Example 1*

What is the total number of orbitals associated with the principal quantum number  $n=3$  ?

#### *Solution*

For  $n = 3$ , the possible values of  $l$  are 0,1 and 2. Thus, there is one 3s orbital ( $n = 3, l = 0$  and  $m_l = 0$ ); there are three p orbitals ( $n = 3, l = 1$  and  $m_l = -1, 0, 1$ ) there are five 3d orbitals ( $n = 3, l = 2, m_l = -2, -1, 0, 1, 2$ ).

Therefore, the total number of orbitals is  $1+3+5 = 9$ .

### Example 2

Using s, p, d, f notations, describe the orbital with the following quantum numbers (a)  $n=2, l=1$  (b)  $n=4, l=0$  (c)  $n=5, l=3$  (d)  $n=3, l=2$ .

### Solution

	n	$l$	orbital
(a)	2	1	2p
(b)	4	0	4s
(c)	5	3	5f
(d)	3	2	3d

### 3.4 Shapes or boundary surfaces of Orbitals

**s-orbitals:** For s-orbital  $l=0$  and hence,  $m$  can have only one value, i.e.,  $m=0$ . This means that the probability of finding the electron in s-orbital is the same in all directions at a particular distance. In other words s-orbitals are spherically symmetrical.

The electron cloud picture of 1s-orbital is spherical. The s-orbitals of higher energy levels are also spherically symmetrical. However, they are more diffused and have spherical shells within them where probability of finding the electron is zero. These are called nodes. In 2s-orbital there is one spherical node. In the ns orbital, number of nodes are  $(n-1)$ .

**p-orbitals:** For p-orbitals  $l=1$  and hence 'm' can have three possible values +1, 0, -1. This means that there are three possible orientations of electron cloud in a p-sub-shell. The three orbitals of a p-sub-shell are designated as  $p_x$ ,  $p_y$  and  $p_z$  respectively along x-axis, y-axis and z-axis respectively. Each p-orbital has two lobes, which are separated by a point of zero probability called node. Each p-orbital is thus dumb bell shaped.

In the absence of magnetic field these three p-orbitals are equivalent in energy and are, therefore, said to be three-fold degenerate or triply degenerate. In the presence of an external magnetic field, the relative energies of the three p orbitals vary and depend on their orientation or

magnetic quantum number. This probably accounts for the splitting of a single spectral line into a number of closely spaced lines in presence of a magnetic field (fine structure).

**d-orbitals:** For  $d$ -orbitals  $l = 2$ ,  $m = 0, \pm 1, \pm 2$  indicating that  $d$ -orbitals have five orientations, i.e., there are five  $d$ -orbitals which are named as  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$ ,  $d_z^2$  and  $d_{x^2-y^2}$ . All these five orbitals, in the absence of magnetic field, are equivalent in energy and are, therefore, said to be five-fold degenerate

The three orbitals namely  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  have their lobes lying symmetrically between the coordinate axes indicated in the subscript to  $d$ , e.g. the lobes of  $d_{xy}$  orbital are lying between the  $x$ - and  $y$ -axes. This set of three orbitals is known as  $t_{2g}$  set.  $d_{x^2-y^2}$  and  $d_z^2$  orbitals have their lobes along the axes (i.e. along the axial directions), e.g., the lobes of  $d_{x^2-y^2}$  orbital lie along the  $x$  and  $y$ -axes, while those of  $d_z^2$  orbital lie along the  $z$ -axis. This set is known as  $e_g$  set.

### 3.5 Pauli's exclusion principle

The filling of electron into the orbitals of different atoms takes place according to the Aufbau principle, which is based on the Pauli's exclusion principle and the Hund's rule of maximum multiplicity.

The distribution of quantum numbers among the electrons in a given atom is governed by Pauli's Exclusion principle, which states that ***"it is impossible for any two electrons in a given atom to have all the four quantum numbers identical"*** i.e., in an atom, two electrons can have maximum three quantum numbers ( $n$ ,  $l$  and  $m$ ) the same and the fourth ( $s$ ) will definitely be having a different value. Thus if  $s = +1/2$  for one electron,  $s$  should be equal to  $-1/2$  for the other electron. In other words the two electrons in the same orbital should have opposite spins ( $\uparrow\downarrow$ ).

#### Uses of the principle

The greatest use of the principle is that it is helpful in determining the maximum number of electrons that a main energy level can have. Let us illustrate this point by considering K and L shells.

- (a) K-shell: For this shell  $n = 1$ . For  $n = 1$ ,  $l = 0$  and  $m = 0$ . Hence  $s$  can have a value either  $+1/2$  or  $-1/2$ . The different values of  $n$ ,  $l$ ,  $m$  and  $s$

given above give the following two combinations of the four quantum numbers, keeping in view the exclusion principle. Combination (i) is for one electron and combination (ii) is for the other electron.

(i)  $n = 1, l = 0, m = 0$

$s = +1/2$  (1st electron)

(ii)  $n = 1, l = 0, m = 0,$

$s = -1/2$  (2nd electron)

(Two electrons in  $l = 0$  sub-shell i.e.,  $1s$ -orbital)

These two combinations show that in K shell there is only one sub-shell corresponding to  $l = 0$  value ( $s$ -sub-shell) contains only two electrons with opposite spins.

(b) L-shell: For this shell  $n = 2$ . For  $n = 2$  the different values of  $l, m$  and  $s$  give the following eight combinations of four quantum numbers.

(i)  $n = 2, l = 0, m = 0, s = +1/2$

(ii)  $n = 2, l = 0, m = 0, s = -1/2$

(iii)  $n = 2, l = 1, m = 0, s = +1/2$

(iv)  $n = 2, l = 1, m = 0, s = -1/2$

(v)  $n = 2, l = 1, m = +1, s = +1/2$

(vi)  $n = 2, l = 1, m = +1, s = -1/2$

(vii)  $n = 2, l = 1, m = -1, s = +1/2$

(viii)  $n = 2, l = 1, m = -1, s = -1/2$

Eight combinations given above show that L shell is divided into two sub-shells corresponding to  $l = 0$  ( $s$  sub-shell) and  $l = 1$  ( $p$  sub-shell) and this shell cannot contain more than 8 electrons, i.e., its maximum capacity for keeping the electrons is eight.

### 3.6 Hund's rule of maximum multiplicity

Hund's rule of maximum multiplicity states, that in filling p, d or f orbitals, as many unpaired electrons as possible are placed before pairing of electrons with opposite spin is allowed. Pairing of electrons requires energy. Therefore **no pairing occurs until all orbitals of a given sub-level are half filled**. This is known as Hund's rule of maximum multiplicity. It states that when electrons enter sub-levels of fixed (n+1) values, available orbitals are singly occupied (Table 3.1).

**Table 3.1 Representation of arrangements of electrons**

Atomic Number	Element	1s	2s	2p <sub>x</sub>	2p <sub>y</sub>	2p <sub>z</sub>	Number of unpaired electrons
1	H	↑					1
2	He	↑↓					0
3	Li	↑↓	↑				1
4	Be	↑↓	↑↓				0
5	B	↑↓	↑↓	↑	↑		1
6	C	↑↓	↑↓	↑	↑		2
7	N	↑↓	↑↓	↑	↑	↑	3
8	O	↑↓	↑↓	↑↓	↑	↑	2
9	F	↑↓	↑↓	↑↓	↑↓	↑	1
10	Ne	↑↓	↑↓	↑↓	↑↓	↑↓	0

Thus, if three electrons are to be filled in the p- level of any shell, one each will go into each of the three ( $p_x$ ,  $p_y$ ,  $p_z$ ) orbitals. The fourth electron entering the p- level will go to  $p_x$  orbital which now will have two electrons with opposite spins (as shown above) and said to be paired. The unpaired electrons play an important part in the formation of bonds.

### 3.7 Aufbau Principle

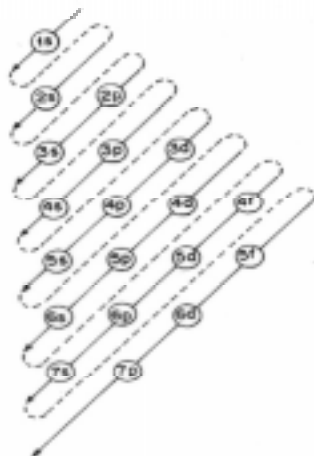
The word 'aufbau' in German means 'building up'. The building up of orbitals means the filling up of orbitals with electrons. The principles states: **In the ground state of the atoms, the orbitals are filled in**

**order of their increasing energies.** In other words, electrons first occupy the lowest-energy orbital available to them and enter into higher energy orbitals only after the lower energy orbitals are filled. The order in which the energies of the orbitals increase and hence the order in which the orbitals are filled is as follows:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s.....

This order may be remembered by using the method given in Fig. 3.3. Starting from the top, the direction of the arrows gives the order of filling of orbitals. Alternatively, the order of increase of energy of orbitals can be calculated from  $(n + 1)$  rule, explained below:

**The lower the value of  $(n+1)$  for an orbital, the lower is its energy. If two orbitals have the same  $(n+1)$  value, the orbital with lower value of  $n$  has the lower energy.**



**Fig. 3.3 Order of filling of orbitals**

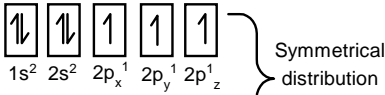
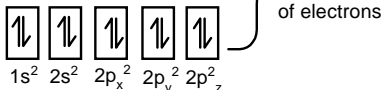
It may be noted that different subshells of a particular shell have different energies in case of many-electron atoms. However in hydrogen atom, they have the same energy.

### **3.8 Stability of orbitals**

According to Hund's rule atoms having half-filled or completely-filled orbitals are comparatively more stable and hence more energy is

needed to remove an electron from such atoms. The ionization potential or ionization enthalpy of such atom is, therefore, relatively higher than expected normally from their position in the periodic table.

The extraordinary stability of half-filled and completely filled electron configuration can be explained in terms of symmetry and exchange energy. The half-filled and completely filled electron configurations have symmetrical distribution of electrons and this symmetry leads to stability. Moreover, in such configuration electron can exchange their positions among themselves to maximum extent. This exchange leads to stabilization for example, half-filled  $2p$  orbital is Nitrogen and completely filled orbitals in Neon are given as follows.

Element	Atomic Number	Electronic configuration in the ground state
N	7	 $1s^2 \quad 2s^2 \quad 2p_x^1 \quad 2p_y^1 \quad 2p_z^1$
Ne	10	 $1s^2 \quad 2s^2 \quad 2p_x^2 \quad 2p_y^2 \quad 2p_z^2$

Thus the  $p^3, p^6, d^5, d^{10}, f^7$  and  $f^{14}$  configuration which are either completely filled or exactly half-filled are more stable.

Further, it may be noted that chromium and copper have five and ten electrons in  $3d$  orbitals rather than four and nine electrons respectively as expected. Therefore, to acquire more stability one of the  $4s$  electron goes into  $3d$  orbitals so that  $3d$  orbitals get half-filled or completely filled in chromium and copper respectively.

### Chromium

Expected configuration :  $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^4, 4s^2$

Actual configuration :  $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^5, 4s^1$   
} Electron exchange

## Copper

Expected configuration :  $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^9, 4s^2$

Actual configuration :  $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, \underbrace{3d^{10}, 4s^1}_{\text{Electron exchange}}$

## Questions

### A. Choose the best answer

1. Atomic mass of an element is not necessarily a whole number because :  
(a) It contains electrons, protons and neutrons  
(b) It contains allotropic forms  
(c) Atoms are no longer considered indivisible  
(d) It contains isotopes (e) None of these.
2. No two electrons in an atom will have all four quantum numbers equal. The statement is known as  
(a) Exclusion principle (b) Uncertainty principle  
(c) Hund's rule (d) Aufbau principle  
(e) Newlands law.
3. When the 3d orbital is complete, the new electron will enter the  
(a) 4p orbital (b) 4f orbital (c) 4s orbital  
(d) 4d orbital (e) 5s orbital.
4. The preference of three unpaired electrons in the nitrogen atom can be explained by : (a) Pauling's exclusion principle (b) Aufbau principle (c) Uncertainty principle (d) Hund's rule (e) None of these.
5. The number of orbitals in a p-sub-shell is  
(a) 1 (b) 2 (c) 3 (d) 6 (e) 5.
6. The nucleus of an atom contains :  
(a) Electrons and protons (b) Neutrons and protons  
(c) Electrons, protons and neutrons (d) Neutrons and electrons  
(e) None of these.



7. Which is the lightest among the following? (a) An atom of hydrogen (b) An electron (c) A neutron (d) A proton (e) An alpha particle.
8. Which of the following has no neutrons in the nucleus? (a) Deuterium (b) Helium (c) Hydrogen (d) Tritium (e) An alpha particle.
9. When the value of the azimuthal quantum number is 3, the magnetic quantum number can have values :  
 (a) +1,-1 (b) +1,0, 1 (c) +2,+1,0, -1,-2  
 (d) +3,+2, +1,0, -1,-2,-3 (e) +3,-3.
10. 2p orbitals have :  
 (a)  $n = 1, l = 2$  (b)  $n = 1, l = 0$  (c)  $n = 2, l = 0$   
 (d)  $n = 2, l = 1$  (e)  $n = 1, l = 1$ .
11. The atomic number of an element is 17 and its mass number is 37. The number of protons, electrons and neutrons present in the neutral atom are :  
 (a) 17, 37, 20 (b) 20, 17, 37 (c) 17, 17, 20 (d) 17, 20, 17 (e) 37, 20, 17.
12. The maximum number of electrons that can be accommodated in the  $n$ th level is : (a)  $n^2$  (b)  $n+1$  (c)  $n-1$  (d)  $2n^2$  (e)  $2 + n$ .
13. The magnetic quantum number decides : (a) The distance of the orbital from the nucleus (b) The shape of the orbital (c) The orientation of the orbital in space (d) The spin of the electron (e) None of these.

**B. Fill up the blanks**

1. The decomposition of an electrolyte by passage of electricity is known as .....
2. When cathode rays are focused on thin metal foil, it gets heated up to .....
3. Cathode rays produce .....on the walls of the discharge tube.
4. The radiations which were not influenced by a magnet were called.....
5. Neutrons are discovered by .....

**C. Write in one or two sentence**

1. What is the charge of an electron, proton and a neutron ?
2. What is atomic number?
3. What is the maximum number of electrons that an orbital can have?
4. How many orbitals are there in the second orbit? How are they designated?
5. Sketch the shape of s and p-orbital indicating the angular distribution of electrons.
6. What are the charge and mass of an electron?
7. What is an orbital?
8. Give the order of filling of electrons in the following orbitals 3p, 3d, 4p, 3d and 6s.
9. What is meant by principal quantum number?
10. How many protons and neutrons are present in  $^{18}_8\text{O}$ ?
11. What are the particles generally present in the nuclei of atoms?
12. The atomic mass of an element is 24 and its atomic number is 12. Show how the atom of the element is constituted?
13. How will you experimentally distinguish between a ray of neutron and ray of proton?
14. What is the principal defect of Bohr atom model?
15. Write the complete symbol for : (a) The nucleus with atomic number 56 and mass number 138 ; (b) The nucleus with atomic number 26 and mass number 55 ; (c) The nucleus with atomic number 4 and mass number 9.
16. An atomic orbital has  $n = 3$ . What are the possible values of  $l$  ?
17. An atomic orbital has  $l = 3$ . What are the possible values of  $m$ ?
18. Give the electronic configuration of chromium. ( $Z=24$ ).
19. Which energy level does not have p-orbital?

20. An atom of an element has 19 electrons. What is the total number of p-orbital?
21. How many electrons can have  $s + \frac{1}{2}$  in a d-sub-shell?
22. Write the values of  $l$  and  $m$  for p-orbitals.
23. Which quantum accounts for the orientation of the electron orbital?
24. What is shape of the orbital with (i)  $n = 2$  and  $l = 0$  ; (ii)  $n = 2$  and  $l = 1$ ?
25. Give the values for all quantum numbers for 2p electrons in nitrogen ( $Z = 7$ ).
26. Give the electronic configuration of  $Mn^{2+}$  and Cu. Atomic number of Cu = 29 and Mn = 25.
27. Explain why the electronic configuration of Cr and Cu are written as  $3d^5, 4s^1$  and  $3d^{10} 4s^1$  instead of  $3d^4 4s^2$  and  $3d^9 4s^2$ ?

**D. Explain briefly on the following**

1. Describe Aufbau principle. Explain its significance in the electronic build up of atoms.
2. Using the s, p, d, notation, describe the orbital with the following quantum numbers? (a)  $n = 1, l=0$ ; (b)  $n = 2, l = 0$ ; (c)  $n = 3, l = 1$ ; (d)  $n = 4, l = 3$ .
3. Using the Aufbau principle, write the electronic configuration in the ground state of the following atoms : Boron ( $Z = 5$  ) Neon ( $Z = 10$ ) and Aluminium ( $Z = 13$ ).
4. What is Rutherford's  $\alpha$ - ray scattering experiment? What are its conclusions?
5. What are the postulates of Bohr theory of atom?
6. Explain the various quantum numbers which completely specify the electron of an atom.

**SUMMARY**

- The model of the nuclear atom developed by Thomson, Rutherford and their defects are explained.

- Niel's Bohr model and sommerfield's extension were mentioned with diagrammatic representation.
- The location of electron in an atom through four quantum numbers are explained including their significance.
- Occupancy of electrons following Hund's rule Aufbau principle, Pauli's exclusion principle are explained with represnetation.

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## 4. PERIODIC CLASSIFICATION- I

### OBJECTIVES

- *Recall the history of periodic classification.*
- *Understand the IUPAC periodic table and the nomenclature of elements with atomic number greater than 100.*
- *Understand the electronic configuration of the elements and the classification based on it.*
- *Analyse the periodicity of properties like atomic radii, ionisation potential, electron affinity electronegativity etc.*
- *Know the anomalous periodic properties of elements and to reason it.*

### 4.1 Brief history of periodic classification

More than one hundred and nine elements are known today,. The periodic table of elements is an important landmark in the history of chemistry. It would be difficult to study individually the chemistry of all the elements and their numerous compounds. The periodic table provides a systematic and extremely useful framework for organizing a lot of information available on the chemical behaviour of the elements into a few simple and logical patterns. This gave rise to the necessity of classifying the elements into various groups or families having similar properties. This classification has resulted in the formulation of periodic table. Periodic table may be defined as the arrangements of various elements according to their properties in a tabular form.

All earlier attempts on the classification of elements were based on atomic mass. Several chemists have for long tried to classify the elements and to find patterns in their properties.

#### Dobereiner's Triads

In 1829, *John Dobereiner* (German Chemist) classified elements having similar properties into groups of three. These groups were called triads. According to this law when elements are arranged in the order of increasing atomic mass in a triad, the atomic mass of the middle element

was found to be approximately equal to the arithmetic mean of the other two elements. For example lithium, sodium and potassium constituted one triad. However, only a limited number of elements could be grouped into triads.

**Table 4.1 Dobereiner's Triads**

Elements	Atomic weight	Element	Atomic weight	Element	Atomic weight
Li	7	Ca	40	Cl	35.5
Na	23	Sr	88	Br	80
K	39	Ba	137	I	127

### **Newlands Law of Octaves**

In 1865, John Newlands (English Chemist) observed that if the elements were arranged in order of their increasing atomic weights, the eighth element starting from a given one, possessed properties similar to the first, like the eighth note in an octave of music. He called it the law of octaves. It worked well for the lighter elements but failed when applied to heavier elements.

### **Lothar-Meyer's Arrangement**

In 1869, **J. Lothar-Meyer** in Germany gave a more detailed and accurate relationship among the elements., Lothar-Meyer plotted atomic volumes versus atomic weights of elements and obtained a curve. He pointed out that elements occupying similar positions in the curve possessed similar properties.

### **Mendeleev's Periodic Table**

In 1869, Dimitriv Mendeleev (Russian Chemist) arranged the 63 chemical elements, then known, according to their increasing order of atomic weights. He gave his famous scheme of the periodic classification of elements known as the periodic law. The law states that “ the properties of the elements are the periodic function of their atomic

weights". It means that when elements are arranged in order of increasing atomic weights, the elements with similar properties recur after regular intervals. On the basis of this periodic law Mendeleev constructed a periodic table in such a way that the elements were arranged horizontally in order of their increasing atomic weights. Mendeleev, while studying his Periodic Table had found that in certain cases the regularity in behaviour between two succeeding elements was not observed. In order to overcome this he had kept gaps between such elements and had predicted that the gaps would be filled by new elements, to be discovered in future. For example, both gallium and germanium were not discovered at the time when Mendeleev proposed the periodic table. Mendeleev named these elements as eka-aluminium and eka-silicon because he believed that they would be similar to aluminium and silicon respectively. These elements were discovered later and Mendeleev's prediction proved remarkably correct. The discoveries / synthesis of new elements have continued even to the present day, raising their number to 120. The elements with atomic numbers up to 92 (i.e. uranium) are found in nature. The rest known as transuranium elements have been synthesized in the laboratories, which are highly unstable. They decay radioactively.

The modified periodic table is essentially similar to that of Mendeleev with a separate column added for noble gases, which were not discovered until the closing years of the nineteenth century. The general plan of the modified Mendeleev's periodic table is improved.

The Mendeleev's modified periodic table consists of:

(1) Nine vertical columns called groups. These are numbered from I to VIII and zero. (The members of zero group were not discovered at the time of Mendeleev). Each group from I to VII is further sub-divided into two sub-groups designated as A and B. Group VIII consists of three sets, each one containing three elements. Group zero consists of inert gases.

(2) Seven horizontal rows, called periods. These are numbered from 1 to 7. First period contains two elements. Second and third periods contain eight elements each. These periods are called short periods. Fourth and fifth contain eighteen elements each. These periods are called long periods. Sixth period contains thirty two elements and is called longest

period. Seventh period is incomplete and contains nineteen elements according to early classification.

#### **4.2 IUPAC periodic table and IUPAC nomenclature of elements with atomic number greater than 100**

##### **Modern Periodic Law**

In 1913, a British Physicist Henry Moseley showed that the atomic number is a more fundamental property of an element than its atomic weight. This observation led to the development of modern periodic law. The modern periodic law states that “ the physical and chemical properties of the elements are periodic function of their atomic numbers.”

This means that when the elements are arranged in order of increasing atomic numbers, the elements with similar properties recur after regular intervals. The periodic repetition is called periodicity. The physical and chemical properties of the elements are related to the arrangement of electrons in the outermost shell. Thus, if the arrangement of electrons in the outermost shell (valence shell) of the atoms is the same, their properties will also be similar. For example, the valence shell configurations of alkali metals show the presence of one electron in the s-orbital of their valence shells.

Similar behaviour of alkali metals is attributed to the similar valence shell configuration of their atoms. Similarly, if we examine the electronic configurations of other elements, we will find that there is repetition of the similar valence shell configuration after certain regular intervals with the gradual increase of atomic number. Thus we find that the periodic repetition of properties is due to the recurrence of similar valence shell configuration after certain intervals. It is observed that similarity in properties is repeated after the intervals of 2, 8, 18, or 32 in their atomic numbers.

**Long form of the Periodic Table:** The periodic table is constructed on the basis of repeating electronic configurations of the atoms when they are arranged in the order of increasing atomic numbers. The long form of the Periodic table is given in a modified form in page number 70. Readers are advised to follow the periodic table closely while studying the structural features of the long form of the Periodic Table.



**Structural Features of the Long form of the periodic Table:** The long form of the periodic table consists of horizontal rows called periods and vertical columns called groups.

**Periods:** In terms of electronic structure of the atom, a period constitutes a series of elements whose atoms have the same number of electron shell i.e., principal quantum number ( $n$ ). There are seven periods and each period starts with a different principal quantum number.

The first period corresponds to the filling of electrons in the first energy shell ( $n = 1$ ). Now this energy level has only one orbital ( $1s$ ) and, therefore, it can accommodate two electrons. This means that there can be only two elements (hydrogen,  $1s^1$  and helium,  $1s^2$ ) in the first period.

The second period starts with the electron beginning to enter the second energy shell ( $n = 2$ ). Since there are only four orbitals (one  $2s$ - and three  $2p$ - orbitals) to be filled, it can accommodate eight electrons. Thus, second period has eight elements in it. It starts with lithium ( $Z = 3$ ) in which one electron enters the  $2s$ -orbital. The period ends with neon ( $Z = 10$ ) in which the second shell is complete ( $2s^2 2p^6$ ).

The third period begins with the electrons entering the third energy shell ( $n = 3$ ). It should be noted that out of nine orbitals of this energy level (one  $s$ , three  $p$  and five  $d$ ) the five  $3d$ -orbitals have higher energy than  $4s$ -orbitals. As such only four orbitals (one  $3s$  and three  $3p$ ) corresponding to  $n = 3$  are filled before fourth energy level begins to be filled. Hence, third period contains only eight elements from sodium ( $Z = 11$ ) to argon ( $Z = 18$ ).

The fourth period corresponding to  $n = 4$  involves the filling of one  $4s$  and three  $4p$ -orbitals ( $4d$  and  $4f$  orbitals have higher energy than  $5s$ -orbital and are filled later). In between  $4s$  and  $4p$ -orbitals, five  $3d$ -orbitals are also filled which have energies in between these orbitals. Thus, altogether nine orbitals (one  $4s$ , five  $3d$  and three  $4p$ ) are to be filled and therefore, there are eighteen elements in fourth period from potassium ( $Z = 19$ ) to krypton ( $Z = 36$ ). The elements from scandium ( $Z = 21$ ) to zinc ( $Z = 30$ ) are called  $3d$ - transition series.

The fifth period beginning with  $5s$ -orbital ( $n=5$ ) is similar to fourth period. There are nine orbitals (one  $5s$ , five  $4d$  and three  $5p$ ) to be filled and, therefore, there are eighteen elements in fifth period from rubidium ( $Z = 37$ ) to xenon ( $Z = 54$ ).

The sixth period starts with the filling of 6s-orbitals ( $n=6$ ). There are sixteen orbitals (one 6s, seven 4f, five 5d, and three 6p) in which filling of electrons takes place before the next energy level starts. As such there are thirty two elements in sixth period starting from cesium ( $Z=55$ ) and ending with radon ( $Z=86$ ). The filling up of 4f orbitals begins with cerium ( $Z=58$ ) and ends at lutetium ( $Z=71$ ). It constitutes the first f-inner transition series which is called lanthanide series.

The seventh period begins with 7s-orbital ( $n=7$ ). It would also have contained 32 elements corresponding to the filling of sixteen orbitals (one 7s, seven 5f, five 6d and three 7p), but it is still incomplete. At present there are 23 elements in it. The filling up of 5f-orbitals begins with thorium ( $Z=90$ ) and ends up at lawrencium ( $Z=103$ ). It constitutes second f-inner transition series which is called actinide series. It mostly includes man made radioactive elements. In order to avoid undue extension of the periodic table the 4f and 5f-inner transition elements are placed separately.

The number of elements and the corresponding orbitals being filled are given below.

**Table 4.2**

<b>Period</b>	<b>Principal Valence shell (=n)</b>	<b>Orbitals being filled up</b>	<b>Electrons to be accommodated</b>	<b>Number of electrons</b>
First	$N=1$	1s	2	2
Second	$N=2$	2s, 2p	2+6	8
Third	$n=3$	3s, 3p	2+6	8
Fourth	$n=4$	4s, 3d, 4p	2+10+6	18
Fifth	$n=5$	5s, 4d, 5p	2+10+6	18
Sixth	$n=6$	6s, 4f, 5d, 6p	2+14+10+6	32
Seventh	$n=7$	7s, 5f, 6d, 7p	2+14+10+6	32

The first three periods containing 2, 8 and 8 elements respectively are called short periods, the next three periods containing 18, 18 and 32 elements respectively are called long periods.

### Groups

A vertical column in the periodic table is known as group. A group consists of a series of elements having similar configuration of the outer energy shell. There are eighteen vertical columns in long form of the periodic table. According to the recommendations of the **International Union of Pure and Applied Chemistry (IUPAC)**, these groups are numbered from 1 to 18. Previously, these were numbered from I to VII as A and B, VIII and zero groups elements. The elements belonging to the same group are said to constitute a family. For example, elements of group 17 (VII A) constitute halogen family.

### IUPAC Nomenclature for Elements with $Z > 100$

The elements beyond uranium ( $Z = 92$ ) are all synthetic elements and are known as transuranium elements. The elements beyond fermium are known as transfermium elements. These elements fermium ( $Z = 100$ ), mendelevium ( $Z = 101$ ), nobelium ( $Z = 102$ ) and lawrencium ( $Z = 103$ ) are named after the names of famous scientists. Although names and symbols to many of these elements have been assigned by these are still not universally accepted. Also some of these elements have been assigned two names/symbols. For example, element with atomic number 104 is called either Kurchatovium (Ku) or Rutherfordium (Rf) while element with atomic number 107 is called Neilsbohrium (Ns) or Borium (Bh). But the following elements have been assigned only one official name. For example element with atomic number 105 is called Dubnium, with atomic number 106 as Seaborgium, with atomic number 108 as Hassnium and with atomic number 109 is named as Meiternium. To overcome all these difficulties, IUPAC nomenclature has been recommended for all the elements with  $Z > 100$ . It was decided by IUPAC that the names of elements beyond atomic number 100 should use Latin words for their numbers. The names of these elements are derived from their numerical roots.

Numerical →  
roots

0	1	2	3	4	5	6	7	8	9
nil	un	bi	tri	quad	pent	hex	sept	oct	en

**Table 4.3**

<b>Atomic number</b>	<b>Name of the element</b>	<b>Symbol</b>
101	Unnilunium	Unu
102	Unnilbium	Unb
103	Unniltrium	Unt
104	Unnilquadium	Unq
105	Unnilpentium	Unp
106	Unnilhexium	Unh
107	Unnilseptium	Uns
108	Unniloctium	Uno
109	Unnilennium	Une
110	Ununnilium	Uun
111	Unununium	Uuu
112	Ununbium	Uub
113	Ununtrium	Uut
114	Ununquadium	Uuq
115	Ununpentium	Uup
116	Ununhexium	Uuh
117	Ununseptium	Uus
118	Ununoctium	Uuo
119	Ununennium	Uue
120	Unbinilium	Ubn

# PERIODIC CHART OF THE ELEMENTS

PERIODIC CHART OF THE ELEMENTS

1s		2s		3s		4s		5s		6s		7s		8s		9s		10s		11s		12s		13s		14s		15s		16s		17s		18s	
1	H	2	He	3	Li	4	Be	5	B	6	C	7	N	8	O	9	F	10	Ne	11	Na	12	Mg	13	Al	14	Si	15	P	16	S	17	Cl	18	Ar
19	K	20	Ca	21	Sc	22	Ti	23	V	24	Cr	25	Mn	26	Fe	27	Co	28	Ni	29	Cu	30	Zn	31	Ga	32	Ge	33	As	34	Se	35	Br	36	Kr
37	Rb	38	Sr	39	Y	40	Zr	41	Nb	42	Mo	43	Tc	44	Ru	45	Rh	46	Pd	47	Ag	48	Cd	49	In	50	Sn	51	Sb	52	Te	53	I	54	Xe
55	Cs	56	Ba	57	La	58	Ce	59	Pr	60	Nd	61	Pm	62	Sm	63	Eu	64	Gd	65	Tb	66	Dy	67	Ho	68	Er	69	Tm	70	Yb	71	Lu	72	Hf
73	Ta	74	W	75	Re	76	Os	77	Ir	78	Pt	79	Au	80	Hg	81	Tl	82	Pb	83	Bi	84	Po	85	At	86	Rn	87	Fr	88	Ra	89	Ac	90	Th
91	Pa	92	U	93	Np	94	Pu	95	Am	96	Cm	97	Bk	98	Cf	99	Es	100	Fm	101	Md	102	No	103	Lr	104	Rf	105	Db	106	Sg	107	Bh	108	Hs
109	Me	110	La	111	Ce	112	Pr	113	Nd	114	Pm	115	Sm	116	Eu	117	Gd	118	Tb	119	Dy	120	Ho	121	Er	122	Tm	123	Yb	124	Lu	125	Hf	126	Ta
127	W	128	Re	129	Os	130	Ir	131	Pt	132	Au	133	Hg	134	Tl	135	Pb	136	Bi	137	Po	138	At	139	Rn	140	Fr	141	Ra	142	Ac	143	Th	144	Pa
145	U	146	Np	147	Pu	148	Am	149	Cm	150	Bk	151	Cf	152	Es	153	Fm	154	Md	155	No	156	Lr	157	Rf	158	Db	159	Sg	160	Bh	161	Hs	162	Me
163	Me	164	La	165	Ce	166	Pr	167	Nd	168	Pm	169	Sm	170	Eu	171	Gd	172	Tb	173	Dy	174	Ho	175	Er	176	Tm	177	Yb	178	Lu	179	Hf	180	Ta
181	W	182	Re	183	Os	184	Ir	185	Pt	186	Au	187	Hg	188	Tl	189	Pb	190	Bi	191	Po	192	At	193	Rn	194	Fr	195	Ra	196	Ac	197	Th	198	Pa
199	U	200	Np	201	Pu	202	Am	203	Cm	204	Bk	205	Cf	206	Es	207	Fm	208	Md	209	No	210	Lr	211	Rf	212	Db	213	Sg	214	Bh	215	Hs	216	Me
217	Me	218	La	219	Ce	220	Pr	221	Nd	222	Pm	223	Sm	224	Eu	225	Gd	226	Tb	227	Dy	228	Ho	229	Er	230	Tm	231	Yb	232	Lu	233	Hf	234	Ta
235	W	236	Re	237	Os	238	Ir	239	Pt	240	Au	241	Hg	242	Tl	243	Pb	244	Bi	245	Po	246	At	247	Rn	248	Fr	249	Ra	250	Ac	251	Th	252	Pa
253	U	254	Np	255	Pu	256	Am	257	Cm	258	Bk	259	Cf	260	Es	261	Fm	262	Md	263	No	264	Lr	265	Rf	266	Db	267	Sg	268	Bh	269	Hs	270	Me
271	Me	272	La	273	Ce	274	Pr	275	Nd	276	Pm	277	Sm	278	Eu	279	Gd	280	Tb	281	Dy	282	Ho	283	Er	284	Tm	285	Yb	286	Lu	287	Hf	288	Ta
289	W	290	Re	291	Os	292	Ir	293	Pt	294	Au	295	Hg	296	Tl	297	Pb	298	Bi	299	Po	300	At	301	Rn	302	Fr	303	Ra	304	Ac	305	Th	306	Pa
307	U	308	Np	309	Pu	310	Am	311	Cm	312	Bk	313	Cf	314	Es	315	Fm	316	Md	317	No	318	Lr	319	Rf	320	Db	321	Sg	322	Bh	323	Hs	324	Me
325	Me	326	La	327	Ce	328	Pr	329	Nd	330	Pm	331	Sm	332	Eu	333	Gd	334	Tb	335	Dy	336	Ho	337	Er	338	Tm	339	Yb	340	Lu	341	Hf	342	Ta
345	W	346	Re	347	Os	348	Ir	349	Pt	350	Au	351	Hg	352	Tl	353	Pb	354	Bi	355	Po	356	At	357	Rn	358	Fr	359	Ra	360	Ac	361	Th	362	Pa
365	U	366	Np	367	Pu	368	Am	369	Cm	370	Bk	371	Cf	372	Es	373	Fm	374	Md	375	No	376	Lr	377	Rf	378	Db	379	Sg	380	Bh	381	Hs	382	Me
385	Me	386	La	387	Ce	388	Pr	389	Nd	390	Pm	391	Sm	392	Eu	393	Gd	394	Tb	395	Dy	396	Ho	397	Er	398	Tm	399	Yb	400	Lu	401	Hf	402	Ta
405	W	406	Re	407	Os	408	Ir	409	Pt	410	Au	411	Hg	412	Tl	413	Pb	414	Bi	415	Po	416	At	417	Rn	418	Fr	419	Ra	420	Ac	421	Th	422	Pa
425	U	426	Np	427	Pu	428	Am	429	Cm	430	Bk	431	Cf	432	Es	433	Fm	434	Md	435	No	436	Lr	437	Rf	438	Db	439	Sg	440	Bh	441	Hs	442	Me
445	Me	446	La	447	Ce	448	Pr	449	Nd	450	Pm	451	Sm	452	Eu	453	Gd	454	Tb	455	Dy	456	Ho	457	Er	458	Tm	459	Yb	460	Lu	461	Hf	462	Ta
465	W	466	Re	467	Os	468	Ir	469	Pt	470	Au	471	Hg	472	Tl	473	Pb	474	Bi	475	Po	476	At	477	Rn	478	Fr	479	Ra	480	Ac	481	Th	482	Pa
485	U	486	Np	487	Pu	488	Am	489	Cm	490	Bk	491	Cf	492	Es	493	Fm	494	Md	495	No	496	Lr	497	Rf	498	Db	499	Sg	500	Bh	501	Hs	502	Me
505	Me	506	La	507	Ce	508	Pr	509	Nd	510	Pm	511	Sm	512	Eu	513	Gd	514	Tb	515	Dy	516	Ho	517	Er	518	Tm	519	Yb	520	Lu	521	Hf	522	Ta
525	W	526	Re	527	Os	528	Ir	529	Pt	530	Au	531	Hg	532	Tl	533	Pb	534	Bi	535	Po	536	At	537	Rn	538	Fr	539	Ra	540	Ac	541	Th	542	Pa
545	U	546	Np	547	Pu	548	Am	549	Cm	550	Bk	551	Cf	552	Es	553	Fm	554	Md	555	No	556	Lr	557	Rf	558	Db	559	Sg	560	Bh	561	Hs	562	Me
565	Me	566	La	567	Ce	568	Pr	569	Nd	570	Pm	571	Sm	572	Eu	573	Gd	574	Tb	575	Dy	576	Ho	577	Er	578	Tm	579	Yb	580	Lu	581	Hf	582	Ta
585	W	586	Re	587	Os	588	Ir	589	Pt	590	Au	591	Hg	592	Tl	593	Pb	594	Bi	595	Po	596	At	597	Rn	598	Fr	599	Ra	600	Ac	601	Th	602	Pa
605	U	606	Np	607	Pu	608	Am	609	Cm	610	Bk	611	Cf	612	Es	613	Fm	614	Md	615	No	616	Lr	617	Rf	618	Db	619	Sg	620	Bh	621	Hs	622	Me
625	Me	626	La	627	Ce	628	Pr	629	Nd	630	Pm	631	Sm	632	Eu	633	Gd	634	Tb	635	Dy	636	Ho	637	Er	638	Tm	639	Yb	640	Lu	641	Hf	642	Ta
645	W	646	Re	647	Os	648	Ir	649	Pt	650	Au	651	Hg	652	Tl	653	Pb	654	Bi	655	Po	656	At	657	Rn	658	Fr	659	Ra	660	Ac	661	Th	662	Pa
665	U	666	Np	667	Pu	668	Am	669	Cm	670	Bk	671	Cf	672	Es	673	Fm	674	Md	675	No	676	Lr	677	Rf	678	Db	679	Sg	680	Bh	681	Hs	682	Me
685	Me	686	La	687	Ce	688	Pr	689	Nd	690	Pm	691	Sm	692	Eu	693	Gd	694	Tb	695	Dy	696	Ho	697	Er	698	Tm	699	Yb	700	Lu	701	Hf	702	Ta
705	W	706	Re	707	Os	708	Ir	709	Pt	710	Au	711	Hg	712	Tl	713	Pb	714	Bi	715	Po	716	At	717	Rn	718	Fr	719	Ra	720	Ac	721	Th	722	Pa
725	U	726	Np	727	Pu	728	Am	729	Cm	730	Bk	731	Cf	732	Es	733	Fm	734	Md	735	No	736	Lr	737	Rf	738	Db	739	Sg	740	Bh	741	Hs	742	Me
745	Me	746	La	747	Ce	748	Pr	749	Nd	750	Pm	751	Sm	752	Eu	753	Gd	754	Tb	755	Dy	756	Ho	757	Er	758	Tm	759	Yb	760	Lu	761	Hf	762	Ta
765	W	766	Re	767	Os	768	Ir	769	Pt	770	Au	771	Hg	772	Tl	773	Pb	774	Bi	775	Po	776	At	777	Rn	778	Fr	779	Ra	780	Ac	781	Th	782	Pa
785	U	786	Np	787	Pu	788	Am	789	Cm	790	Bk	791	Cf	792	Es	793	Fm	794	Md	795	No	796	Lr	797	Rf	798	Db	799	Sg	800	Bh	801	Hs	802	Me
805	Me	806	La	807	Ce	808	Pr	809	Nd	810	Pm	811	Sm	812	Eu	813	Gd	814	Tb	815	Dy	816	Ho	817	Er	818	Tm	819	Yb	820	Lu	821	Hf	822	Ta
825	W	826	Re	827	Os	828	Ir	829	Pt	830	Au	831	Hg	832	Tl	833	Pb	834	Bi	835	Po	836	At	837	Rn	838	Fr	839	Ra	840	Ac	841	Th	842	Pa
845	U	846	Np	847	Pu	848	Am	849	Cm	850	Bk	851	Cf	852	Es	853	Fm	854	Md	855	No	856	Lr	857	Rf										

### 4.3 Electronic configuration and periodic table

There is a close connection between the electronic configuration of the elements and the long form of the Periodic Table. We have already learnt that an electron in an atom is characterized by a set of four quantum numbers and the principal quantum number ( $n$ ) defines the main energy level known as the **Shell**. The electronic configuration of elements can be best studied in terms of variations in periods and groups of the periodic table.

#### (a) Electronic Configuration in periods

Each successive period in the periodic table is associated with the filling up of the next higher principal energy level ( $n=1, n=2$ , etc.). It can be readily seen that the number of elements in each period is twice the number of atomic orbitals available in the energy level that is being filled. The first period starts with the filling of the lowest level ( $1s$ ) and has thus the two elements-hydrogen ( $1s^1$ ) and helium ( $1s^2$ ) when the first shell (K) is completed. The second period starts with lithium and the third electron enters the  $2s$  orbital. The next element, beryllium has four electrons and has the electronic configuration  $1s^2 2s^2$ . Starting from the next element boron, the  $2p$  orbitals are filled with electrons when the L shell is completed at neon ( $2s^2 2p^6$ ). Thus there are 8 elements in the second period. The third period ( $n=3$ ) begins at sodium, and the added electron enters a  $3s$  orbital. Successive filling of  $3s$  and  $3p$  orbitals gives rise to the third period of 8 elements from sodium to argon.

The fourth period ( $n=4$ ) starts at potassium with the filling up of  $4s$  orbital. Now you may note that before the  $4p$  orbital is filled, filling up of  $3d$  orbitals becomes energetically favourable and we come across the so-called  $3d$  Transition Series of elements. The fourth period ends at krypton with the filling up of the  $4p$  orbitals. Altogether we have 18 elements in this fourth period. The fifth period ( $n=5$ ) beginning with rubidium is similar to the fourth period and contains the  $4d$  transition series starting at yttrium ( $Z=39$ ). This period ends at xenon with filling up of the  $5p$  orbitals. The sixth period ( $n=6$ ) contains 32 elements and successive electrons enter  $6s$ ,  $4f$ ,  $5d$  and  $6p$  orbitals, in that order. Filling up of the  $4f$  orbitals begins with cerium ( $Z=58$ ) and ends at lutetium ( $Z=71$ ) to give the  $4f$ -inner transition series, which is called the **Lanthanoid Series**. The seventh period ( $n=7$ ) is similar to the sixth

period with the successive filling up of the 7s, 5f, 6d and 7p orbitals and includes most of the man-made radioactive elements. This period will end at the element with atomic number 118 which would belong to the noble gas family. Filling up of the 5f orbitals after actinium (Z=89) gives the 5f-inner transition series known as the **Actinoid Series**. The 4f- and 5f- transition series of elements are placed separately in the periodic table to maintain its structure and to preserve the principle of classification by keeping elements with similar properties in a single column.

#### (b) Groupwise/electronic configuration

Elements in the same vertical column or group have similar electronic configurations, have the same number of electrons in the outer orbitals, and similar properties. Group 1 (the alkali metals) is an example.

Thus it can be seen that the properties of an element have periodic dependence upon the atomic number and not on relative atomic mass (Table 4.4).

**Table 4.4 Types of elements : Electronic configuration of alkali metals**

Atomic number	Symbol	Electronic configuration
3	Li	$1s^2 2s^1$ or [He] $2s^1$
11	Na	$1s^2 2s^2 2p^6 3s^1$ or [Ne] $3s^1$
19	K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ or [Ar] $4s^1$
37	Rb	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1$ or [Kr] $5s^1$
55	Cs	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^1$ or [Xe] $6s^1$

#### Types of elements: s-, p-, d-, f- Blocks

The aufbau principle and the electronic configuration of atoms provide a theoretical foundation for the periodic classification. The

elements in a vertical column of the periodic table constitute a group or family and exhibit similar chemical behaviour. Strictly, helium belongs to the s-block but its positioning in the p-block along with other group 18 elements is justified because it has a completely filled valence shell ( $1s^2$ ) and as a result, exhibits properties characteristic of other noble gases. The other exception is hydrogen. It has a lone s- electron and hence can be placed in group 1 (alkali metals). It can also gain an electron to achieve a noble gas arrangement and hence it can behave similar to a group 17 (halogen family) elements. Because it is a special case, we shall place hydrogen separately at the top of the Periodic Table. We will briefly discuss the salient features of the four types of elements marked in the periodic table.

### **s-Block Elements**

The elements of group 1 (alkali metals) and group 2 (alkaline earth metals) which have  $ns^1$  and  $ns^2$  outermost electronic configuration belong to the **s-block elements**. They are all reactive metals with low ionization enthalpies. They lose the outermost electron(s) readily to form  $1+$  (in the case of alkali metal) or  $2+$  ions (in the case of alkaline earth metals). The metallic character and the reactivity increase as we go down the group. The compounds of the s-block elements, with the exception of those of beryllium are predominantly ionic.

### **p-Block Elements**

The **p-Block Elements** comprise those belonging to groups 13 to 18 and together with the s-block elements are called the **Representative Elements or Main Group Elements**. The outermost electronic configuration varies from  $ns^2np^1$  to  $ns^2np^6$  in each period. Each period ends in a noble gas with a closed shell  $ns^2np^6$  configuration. All the orbitals in the valence shell of the **noble gases** are completely filled by electrons and it is very difficult to alter this stable arrangement by the addition or removal of electrons. The noble gases thus exhibit very low chemical reactivity. Preceding the noble gas family are two chemically important groups of nonmetals. They are the **halogens** (group 17) and **chalcogens** (group 16). These two groups of elements have higher negative electron gain enthalpies and readily add one or two electrons respectively to attain the stable noble gas configuration. The nonmetallic



character increases as we move from left to right across a period and metallic character increases as we go down the group.

### The *d*-block Elements (Transition Elements)

These are the elements of group 3 to 12 in the center of the periodic table. These elements are characterized by filling of inner d orbitals by electrons and are therefore referred to as ***d*-Block Elements**. These elements have the outer electronic configuration  $(n-1) d^{1-10} ns^{1-2}$ . They are all metals. They mostly form colored ions and exhibit variable valency. However, Zn, Cd and Hg, which have the  $(n-1)d^{10} ns^2$  electronic configuration, do not show most of the properties of transition elements in a way, transition metals form a bridge between the chemically active metals of s-block elements and less active metals of groups 13 and 14 and thus take their familiar name “transition elements”

### The *f*-Block Elements (Inner-Transition elements)

The two rows of elements at the bottom of the periodic table, called the **Lanthanoids**  $_{58}\text{Ce}$ - $_{71}\text{Lu}$  and **Actinoids**.  $_{90}\text{Th}$ - $_{103}\text{Lr}$  are characterized by the outer electronic configuration  $(n-2) f^{1-14} (n-1) d^{0-10} ns^2$ . The last electron added to each element is an f-electron. These two series of elements are hence called the inner transition elements (*f*-Block Elements). They are all metals within each series, the properties of the elements are quite similar. The chemistry of the early actinoids is more complicated than the corresponding lanthanoids, due to the large number of oxidation states possible for these actinoid elements. Actinoid elements are radioactive. Many of the actinoid elements have been made only in nanogram quantities or less by nuclear reactions and their chemistry is not fully studied. The elements coming after uranium are called **transuranium** elements.

#### *Example 1*

The elements  $Z=117$  and  $120$  have not yet been discovered. In which family / group would you place these elements and also give the electronic configuration in each case.

#### *Solution*

We see from the periodic table that element with  $Z=117$ , would belong to the halogen family (group 17) and the electronic configuration

would be.  $[\text{Rn}] 4f^{14} 5d^{10} 7s^2 7p^5$ . the element with  $Z=120$ , will be placed in group 2 (alkaline earth metals), and will have the electronic configuration  $[\text{Uuo}]8s^2$ .

In addition to displaying the classification of elements into s-, p-, d-, and f-blocks, the periodic table shows another broad classification of elements based on their properties. The elements can be divided into **Metals** and **Non-metals**. Metals comprise more than 75% of all known elements and appear on the left side of the Periodic Table. Metals are usually solids at room temperature (Mercury is an exception); they have high melting and boiling points. They are good conductors of heat and electricity. They are malleable (can be flattened into thin sheets by hammering) and ductile (can be drawn into wires). In contrast non-metals are located at the top right hand side of the Periodic Table. Non-metals are usually solids or gases at room temperature with low melting and boiling points. They are poor conductors of heat and electricity. Most non-metallic solids are brittle and are neither malleable nor ductile. The elements become more metallic as we go down a group; the non-metallic character increases as one goes from left to right across the Periodic Table. The change from metallic to non-metallic character is not abrupt as shown by the thick zig-zag line in the periodic table. The elements (e.g. germanium, silicon, arsenic, antimony and tellurium) bordering this line and running diagonally across the Periodic Table show properties that are characteristic of both metals and non-metals. These elements are called **Semi Metals** or **Metalloids**.

### ***Example 2***

Arrange the following elements in the increasing order of metallic character: Si, Be, Mg, Na, P.

### ***Solution***

Metallic character increases down a group and decreases along a period as we move from left to right. Hence the order of increasing metallic character is,  $\text{P} < \text{Si} < \text{Be} < \text{Mg} < \text{Na}$ .

## **4.4 Periodicity of properties**

Repetition of properties of elements at regular intervals is called periodicity in properties. The periodicity is due to similar electronic

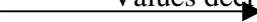
configuration of outer-most shells. Some of the properties are discussed below.

**(i) Atomic and ionic radii**

The size of an atom can be visualized from its atomic radius. The term atomic or ionic radius is generally defined as the distance between the centers of the nucleus and the outermost shell of electrons in an atom or ion. For example, the atomic radius of hydrogen atom is equal to  $74/2 \text{ pm} = 37$  (bond distance in hydrogen molecule ( $\text{H}_2$ ) is  $74 \text{ pm}$ ).

Atomic and ionic radii both decrease from left to right across a period in the periodic table when we consider only normal elements, e.g. in the elements of 2<sup>nd</sup> period the covalent radii decrease as we move from Li to F as shown below:

Elements of 2<sup>nd</sup> period :

	Li	Be	B	C	N	O	F
Covalent radii							Values decreasing

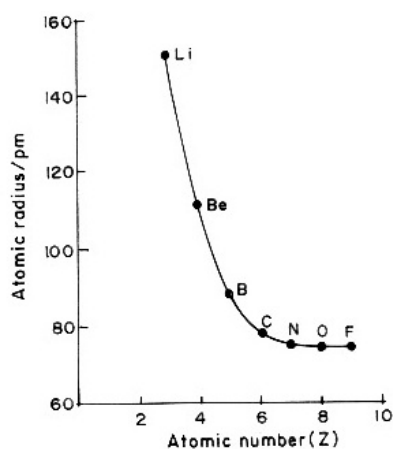
Thus in any period the alkali metals (that are present at the extreme left of the periodic table) have the largest size while the halogens (that are present at the extreme right, excluding the zero group elements) have the smallest size.

**Explanations**

We know that as we proceed from left to right in a period, the electrons are added to the orbitals of the same main energy level. Addition of different electrons to the same main energy level puts the electrons, on the average, no farther from the nucleus and hence the size can not be increased. But with the addition of each electron, the nuclear charge (i.e. atomic number) increases by one. The increased nuclear charge attracts the electrons more strongly close to the nucleus and thus decreases the size of the atoms.

### Table 4.5 Atomic Radii / pm Across the periods


Atom	Atomic radius	Atom	Atomic radius
Li	152	Na	186
Be	111	Mg	160
B	88	Al	143
C	77	Si	117
N	70	P	110
O	74	S	104
F	72	Cl	99



**Fig. 4.1 Variation of atomic radius with atomic number across the second period**

(b) **In a group**

On moving down a group of regular elements both atomic and ionic radii increase with increasing atomic number, e.g. in the elements of IA Group both covalent and ionic radii of  $M^+$  ions increase when we pass from Li to Cs

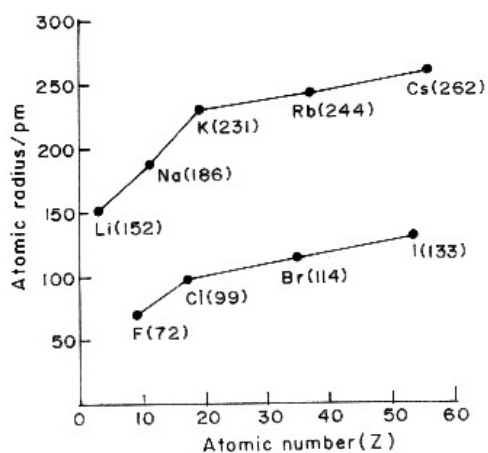
Elements of IA Group : Li Na K Rb Cs  
Covalent radii/Ionic radii Values increasing 

### Explanation

On proceeding downwards in a group the electrons are added to higher main energy levels, which are, on the average, farther from the nucleus. This effect decreases the electrostatic attraction between the nucleus and the valence-shell electrons and this decreased electrostatic attraction increases the atomic and ionic radii.

**Table 4.6 Atomic Radii / pm Down the Group Across a Family**

Atom	Atomic radius	Atom	Atomic radius
Li	152	F	72
Na	186	Cl	99
K	231	Br	114
Rb	244	I	133
Cs	262	At	140



**Fig. 4.2 Variation of atomic radius with atomic number for alkali metals and halogens**

When we find some atoms and ions, which contain the same number of electrons, we call them **isoelectronic**. For example,  $O^{2-}$ ,  $F^-$ ,  $Na^+$  and  $Mg^{2+}$  have the same number of electrons (10). Their radii would be different because of their different nuclear charges. The cation with the greater positive charge will have a smaller radius because of the greater attraction of the electrons to the nucleus. Anions with the greater negative charge will have the larger radius. In this case, the net repulsion of the electrons will outweigh the nuclear charge and the ion will expand in size.

### **Example**

Which of the following species will have the largest and the smallest size  $Mg$ ,  $Mg^{2+}$ ,  $Al$ ,  $Al^{3+}$ ?

### **Solution**

Atomic radii decrease across a period. Cations are smaller than their parent atoms. Among isoelectronic ions, the one with the large positive nuclear charge will have a smaller radius.

Hence the largest species is  $Mg$ ; the smallest one is  $Al^{3+}$ .

The size of an anion is greater while that of the cation is smaller than that of its parent atom, e.g.  $F^- (=1.36 \text{ \AA}) > F (=0.72 \text{ \AA})$ ;  $Cl^- (=1.81 \text{ \AA}) > Cl (=0.99 \text{ \AA})$ ;  $Na^+ (=0.95 \text{ \AA}) < Na (=1.90 \text{ \AA})$ ;  $Ca^{2+} (=0.99 \text{ \AA}) < Ca (=1.97 \text{ \AA})$ .

### **Explanation**

Let us consider the radii of  $Na$ ,  $Na^+$ ,  $Cl$  and  $Cl^-$ . The reason of the fact that  $Na^+$  ion is smaller than  $Na$  atom is that  $Na^+$  ion has 10 electrons ( $Na^+ \rightarrow 1s^2, 2s^2, 2p^6$ ) while  $Na$  atom has 11 electrons ( $Na \rightarrow 1s^2, 2s^2, 2p^6, 3s^1$ ). The nuclear charge (charge on the nucleus) in each case is the same, i.e. equal to +11 (atomic number of  $Na$ ). This nuclear charge of +11 can pull 10 electrons of  $Na^+$  ion inward more effectively than it can pull a greater number of 11 electrons of  $Na$  atom. Thus  $Na^+$  ion is smaller than  $Na$  atom.

The reason why  $Cl^-$  ion is bigger than  $Cl$  atom can also be explained on a similar basis. The  $Cl^-$  ion has 18 electrons ( $Cl^- \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6$ ) while  $Cl$  atom has only 17 electrons ( $Cl \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^5$ ). The nuclear charge in each case is +17, which cannot pull 18 electrons of  $Cl^-$  ion as effectively as it can pull 17 electrons of  $Cl$  atom inward. Thus  $Cl^-$  ion is bigger than  $Cl$  atom.

## (ii) Ionization Energy: (Ionization Potential)

In modern terminology, ionization energy is known as **ionization enthalpy**. The energy required to remove an electron from an atom is known as ionization enthalpy (IE). The first ionization enthalpy may be defined as the amount of energy required to remove the most loosely bound electron from the isolated gaseous atom.

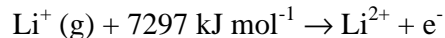


For example,

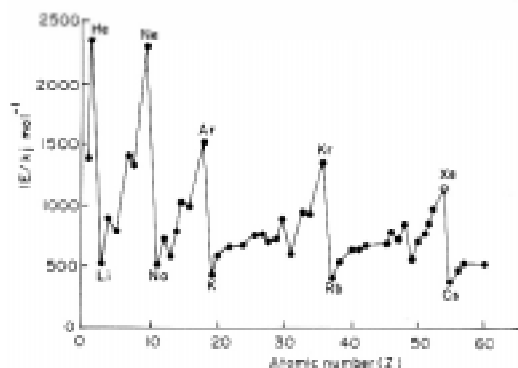


Ionization enthalpy is also called *ionization potential* because it is measured as the amount of potential required to remove the most loosely held electron from the gaseous atom. It is expressed in terms of either kJ/mol or electron Volts/atom.

If a second electron is to be removed from the same element the energy required will be higher than that required for removal of the first electron because it is more difficult to remove an electron from a positively charged species than from a neutral atom.



Similarly the third ionization enthalpy will be higher than the second and so on. Fig. 4.3 shows a plot of first ionization enthalpy of some elements.

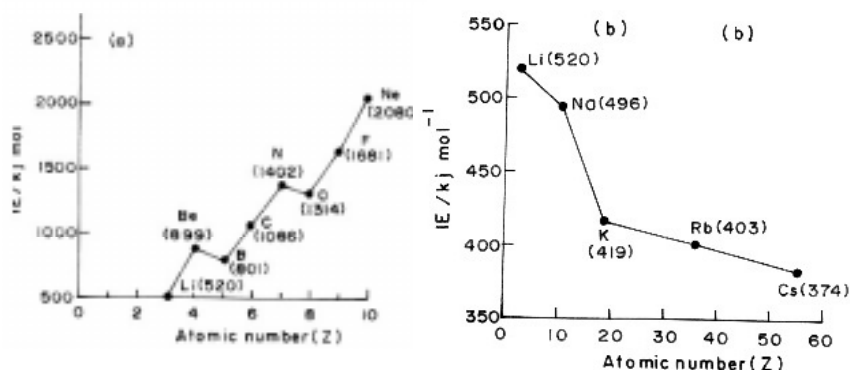


**Fig. 4.3 Variation of first ionization analysis with atomic number for elements with Z = 1 to 60**

### Variation of Ionization Energy in the periodic Table

It is seen from the Fig. 4.4 that the ionization enthalpy of an element depends on its electronic configuration. Ionization potentials of noble gases are found to be maximum and those of alkali metals are found to be minimum. The high values of noble gases are due to completely filled electronic configurations in their outermost shells and the low values of alkali metals are due to their large size and a single electron in the outermost shell.

The ionization potentials increases from left to right in a period. This trend can be explained in terms of increase in nuclear charge and decrease in size from left to right in a period. Generally the first ionization enthalpy decreases down a group in the periodic table. As we move down the group, the outer electrons, which are to be removed, are farther from the nucleus and there is an increasing screening of the nuclear charge by the electrons in the inner shells. Consequently the removal of electrons becomes easier down the group.



**Fig. 4.4 (a) First ionization enthalpies of elements of the second period as a function of atomic number (b) First ionization enthalpies of alkali metals as a function of atomic number**

### Factors Influencing Ionization Enthalpy

The ionization enthalpy of an atom depends on the following factors.

#### (i) Size of the atom

As the distance between the electron and the nucleus increases, i.e., as the size of the atom increases, the outermost electrons are less tightly



held by the nucleus. Thus, it becomes easier to remove an outermost electron. Thus ionization enthalpy decreases with increases in atomic size.

**(ii) Charge on the nucleus**

Ionization enthalpy increases with increase in nuclear charge because of the increase in the attractive force between the nucleus and the electron.

**(iii) Screening effect of inner electrons**

Ionization enthalpy decreases when the shielding effect of inner electrons increases. This is because when the inner electron shells increases, the attraction between the nucleus and the outermost electron decreases.

**(iv) Penetration effect of electrons**

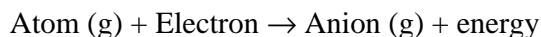
The penetration power of the electrons in various orbitals decreases in a given shell (same value of  $n$ ) in the order:  $s > p > d > f$ . Since the penetration power of s-electron towards the nucleus is more, it will be closer to the nucleus and will be held firmly. Thus, for the same shell, the ionization enthalpy would be more to remove the s-electrons in comparison with the p-electron which in turn would be more than that for d-electron and so on.

**(v) Effect of half-filled and completely filled sub-levels**

If an atom has half-filled or completely filled sub-levels, its ionization enthalpy is higher than that expected normally from its position in the periodic table. This is because such atom, have extra stability and hence it is difficult to remove electrons from these stable configurations.

**(iii) Electron affinity**

*In modern terminology, electron affinity is known as the electron gain enthalpy. Electron gain enthalpy is the amount of energy released when an isolated gaseous atom accepts an electron to form a monovalent gaseous anion.*



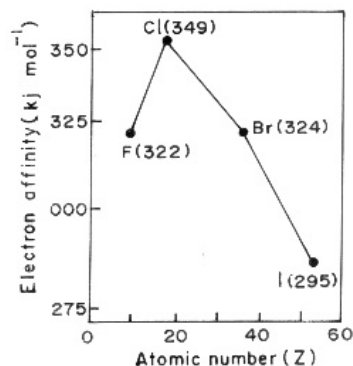
Example,  $\text{Cl (g)} + \text{e}^- \rightarrow \text{Cl}^- \text{(g)} + \text{EA}$

If an atom has high tendency to accept an electron, large energy will be released. Consequently, electron gain enthalpy will be high. On the other hand if an atom has less tendency to accept the electron small amount of energy will be released, leading to small value of electron gain enthalpy. The values of electron gain enthalpy are expressed either in electron volt per atom or kilo joules per mole of atoms. For example, electron gain enthalpy of

$\text{F} = 322 \text{ kJ mol}^{-1}$   
 $\text{Cl} = 349 \text{ kJ mol}^{-1}$   
 $\text{Br} = 324 \text{ kJ mol}^{-1}$  and  
 $\text{I} = 295 \text{ kJ mol}^{-1}$

Halogens (elements of group 17) can take up an electron to acquire the stable noble gas configuration. Their values for electron gain enthalpy are thus very high. Electron gain enthalpy values for the halogens are as in Fig. 4.5.

Electron gain enthalpies generally decrease on moving down the group. This is expected on account of the increase in size of atoms, the effective nuclear attraction for electrons decreases. As a result, there is less tendency to attract additional electrons with an increase in atomic number down the group.



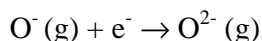
**Fig. 4.5** Electron affinity enthalpies of halogens

From the electron gain enthalpy data of halogens it is clear that, contrary to expectation, the electron gain enthalpy of fluorine is lower than that of chlorine. This is because the fluorine atom has a very compact electronic shell due to its small size. The compactness of the fluorine shell results in electron repulsion whenever an electron is introduced into its 2p-orbital. This is why its electron gain enthalpy is less than the expected value. In Cl atom, 3p-orbitals are not as compact as the 2p-orbitals in fluorine atom. The incoming electron is more readily accepted by the chlorine atom because of weaker electron-electron repulsion. The electron gain enthalpy of chlorine is, therefore, higher than that of fluorine.

In the case of noble gases, the outer s-and p-orbitals are completely filled. No more electrons can be accommodated in these orbitals. *Noble gases, therefore, show no tendency to accept electrons.* Their electron gain enthalpies are zero.

Electron gain enthalpies generally increase as we move across a period from left to right. This is due to the increase in the nuclear charge, which results in greater attraction for electrons.

*The second electron gain enthalpy refers to a process in which the electron is added to a negative ion.* For example:



Since a negative ion  $\text{O}^{-}$  and an electron repel each other, energy is required and not released by the process. Therefore the second electron gain enthalpy is negative in this case.

### **Factors influencing the magnitude of electron affinity**

The magnitude of EA is influenced by a number of factors such as (i) *Atomic size*; (ii) *Effective nuclear charge*; and (iii) *Screening effect by inner electrons*.

#### ***Example***

Which of the following will have the most negative electron gain enthalpy and which has the least negative? P, S, Cl, F.

Explain your answer.

### ***Solution***

Electron gain enthalpy generally becomes more negative across a period as we move from left to right. Within a group, electron gain enthalpy becomes less negative down a group. However, adding an electron to the 2p orbital leads to greater repulsion than adding an electron to the larger 3p orbital. Hence the element with most negative electron gain enthalpy is chlorine; the one with the least negative electron gain enthalpy is phosphorus.

### **(iv) Electronegativity**

*Electronegativity may be defined as the tendency of an atom in a molecule to attract towards itself the shared pair of electrons.* The main factors, which the electronegativity depends, are effective nuclear charge and atomic radius. Greater the effective nuclear charge greater is the electronegativity. Smaller the atomic radius greater is the electronegativity.

In a period electronegativity increases in moving from left to right. This is due to the reason that the nuclear charge increases whereas atomic radius decreases as we move from left to right in a period. Halogens have the highest value of electronegativity in their respective periods.

In a group electronegativity decreases on moving down the group. This is due to the effect of the increased atomic radius. Among halogens fluorine has the highest electronegativity. In fact fluorine is the most electronegative element and is given a value of 4.0 (Pauling's scale) whereas cesium is the least electronegative element (E.N. = 0.7) because of its largest size and maximum screening effect. In other words, cesium is the most electropositive element and hence is the most metallic element in the periodic table.

The main differences between Electron gain enthalpy (electro affinity) and electronegativity are given below :

<b>Electron gain Enthalpy</b>	<b>Electronegativity</b>
It is the tendency of an isolated gaseous atom to attract an electron.	It is the tendency of an atom in a molecule to attract the shared pair of electrons.
It is measured in electron volts/atom or kcal/mole or kj/mole.	It is a number and has no units.
It is the property of an isolated atom.	It is property of a bonded atom.
An atom has an absolute value of electron gain enthalpy.	An atom has a relative value of electronegativity depending upon its bonding state. For example, sp-hybridized carbon is more electronegative than sp <sup>2</sup> -hybridized carbon which, in turn, is more electronegative than sp <sup>3</sup> -hybridized carbon.
It does not change regularly in a period or group.	It changes regularly in a period or a group.

Electronegativity of an element is important in determining the bond character. If two atoms have the same electronegativities the bond between the two will be covalent, while a large difference in electronegativity leads to ionic bond. Between the extremes the purely covalent bond and purely ionic, the bonds will have different degrees of ionic character. As a rough estimate it is seen that a difference of 1.7 in electronegativities, the bond has 50% ionic character. If the difference is less than 1.7, the bond is considered covalent, and greater than 1.7 it is considered ionic.

**Table 4.7 Pauling's Electronegativity coefficients (for the most common oxidation states of the elements)**

					H 2.1
Li	Be F	B	C	N	O
1.0	1.5 4.0	2.0	2.5	3.0	3.5
Na 0.9 3.0					Cl
K Br 0.8 2.8					
Rb 0.8 2.5					I
Cs 0.7					

#### **4.5 Anomalous periodic properties in terms of screening constant, stability etc.**

According to Hund's rule atoms having half-filled or completely filled orbitals are comparatively more stable and hence more energy is needed to remove an electron from such atoms. The ionization potentials of such atoms are, therefore, relatively higher than expected normally from their position in the periodic table.

##### ***Example***

A few irregularities that are seen in the increasing values of ionization potential along a period can be explained on the basis of the concept of half-filled and completely filled orbitals, e.g., Be and N in the second period and Mg and P in the third period have slightly higher values of ionization potentials than those normally expected. This is explained on the basis of extra stability of the completely-filled 2s-orbital

in Be(Be $\rightarrow 2s^2$ ) and 3s-orbital in Mg (Mg $\rightarrow 3s^2$ ) and of half-filled 2p-orbital in N (N $\rightarrow 2s^2 2p^3$ ) and 3p-orbital in P (P $\rightarrow 3s^2 3p^3$ ).

Another example for irregularity in Ionization potential is observed in the case of B and Be.

Ionization energy of boron (B  $\rightarrow 2s^2 2p^1$ ) is lower than that of beryllium (Be  $\rightarrow 2s^2$ ) [B = 8.3 eV, Be = 9.3 eV], since in case of boron we have to remove a  $2p^1$  electron to get B $^+$  [B ( $2s^2 2p^1$ )  $\rightarrow$  B $^+$ ( $2s^2$ ) + e $^-$ ] while in case of Be we have to remove a  $2s^1$  electron of the same main energy level to have Be $^+$  ion. [Be ( $2s^2$ )  $\rightarrow$  Be $^+$ ( $2s^1$ ) + e $^-$ ].

There is an exception to the vertical trend of ionization potential. This exception occurs in the case of those elements whose atomic numbers are greater than 72. Thus the ionization potentials of the elements from Ta<sub>73</sub> to Pb<sub>82</sub> are greater than those of the elements of the same sub-group above them as shown below : (First ionization potential values are given in electron volts, eV).

**Table 4.8**

<b>V B</b>	<b>VI B</b>	<b>VII B</b>	<b>VIII</b>			<b>I B</b>	<b>II B</b>	<b>III A</b>	<b>IV A</b>
Nb <sub>41</sub>	Mo <sub>42</sub>	Tc <sub>43</sub>	Ru <sub>44</sub>	Rh <sub>45</sub>	Pd <sub>46</sub>	Ag <sub>47</sub>	Cd <sub>48</sub>	In <sub>49</sub>	Sn <sub>50</sub>
6.8	7.1	7.2	7.3	7.4	8.3	7.5	8.9	5.7	7.3
Ta <sub>73</sub>	W <sub>74</sub>	Re <sub>75</sub>	Os <sub>76</sub>	Ir <sub>77</sub>	Pt <sub>78</sub>	Au <sub>79</sub>	Hg <sub>80</sub>	Tl <sub>81</sub>	Pb <sub>82</sub>
7.7	7.8	7.8	8.7	9.2	9.0	9.2	10.4	6.1	7.4

The reason for the abnormal behaviour (i.e. an increase in the value of I<sub>1</sub> from Nb  $\rightarrow$  Ta, Mo  $\rightarrow$  W, ....., Sn  $\rightarrow$  Pb) shown by the elements from Ta<sub>73</sub> to Pb<sub>82</sub> is due to the lanthanide contraction as a result of which there occurs an increase in the nuclear charge without a corresponding increase in size through the rare earths. In fact, the size actually decreases in this region.

### Periodic Variations

Similarly in moving down a group electron affinity values generally decrease, e.g. E<sub>Cl</sub> > E<sub>Br</sub> > E<sub>I</sub>. This is due to the steady increase in the atomic radius of the elements.

### Exceptions

There are, however, some exceptions to this general rule as is evident from the following examples:

It is known that  $E_F < E_{Cl}$  ( $E_F = 322 \text{ kJ mol}^{-1}$ ,  $E_{Cl} = 349 \text{ kJ mol}^{-1}$ ). The lower value of  $E$  for F is probably due to the electron-electron repulsion in relatively compact  $2p$ -orbital of F-atom.

**In period,** electron affinity values generally increase on moving from left to right in a period in the periodic table.

### Exceptions

There are, however, exceptions also to this general rule; e.g.

Be and Mg have their EA values equal to zero. Since Be and Mg have completely filled  $s$ -orbitals ( $\text{Be} \rightarrow 2s^2$ ,  $\text{Mg} \rightarrow 3s^2$ ), the additional electron will be entering the  $2p$ -orbital in case of Be and  $3p$ -orbital in case of Mg which are of considerably higher energy than the  $2s$ - and  $3s$  orbitals respectively.

### Questions

#### A. Choose the Best Answer

1. The elements with atomic numbers 31 belongs to :  
(a) d-block              (b) f-block  
(c) p-block              (d) s-block
2. Representative elements are those which belong to :  
(a) s and d-blocks    (b) s and p-blocks    (c) p and d-blocks  
(d) d and f-blocks
3. The most electronegative element of the periodic table is :  
(a) Iodine    (b) Fluorine    (c) Chlorine    (d) Oxygen
4. Which of the following forms stable gaseous negative ion.  
(a) F              (b) Cl              (c) Br              (d) I
5. The elements having highest ionization energies within their periods are called :  
(a) Halogens    (b) Noble gases    (c) Alkali metals  
(d) Transition elements



## s - BLOCK ELEMENTS

	1		
①		2	
②	Li	Be	d
③	Na	Mg	3
④	K	Ca	
⑤	Rb	Sr	
⑥	Cs	Ba	
⑦	Fr	Ra	
	$ns^1$	$ns^2$	

$ns^{1-2}$

1 → Alkali metals

2 → Alkaline earth metals

## 5. GROUP 1 s - BLOCK ELEMENTS

### OBJECTIVES

- Know about the occurrence and isotopes of hydrogen.
- Understand the nature and application of different isotopes of hydrogen.
- Differentiate ortho and para forms of hydrogen.
- Gain knowledge about the application of heavy water.
- Know about the preparation, properties and uses of hydrogen peroxide.
- Understand the special feature of liquid hydrogen used as a fuel - hydrogen economy.
- Analyse general properties of alkali metals.
- Know about the basic nature of oxides and hydroxides.
- Learn the extraction of alkali metal - lithium and sodium.
- Recognise the properties and understands the uses of lithium and sodium.

Hydrogen is the first element in the periodic table. It has the simplest electronic configuration  $1s^1$ . It contains one proton in the nucleus and one electron.

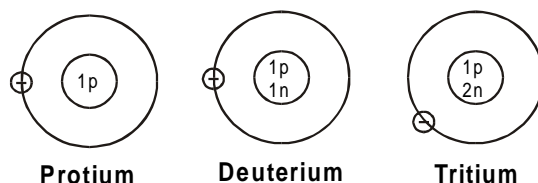
Isotopes:- Atoms of the same element having same atomic number but different mass number are called isotopes.

There are three isotopes for hydrogen with mass numbers 1, 2 and 3, each possessing an atomic number of one.

**Table 5.1 Isotopes of hydrogen**

S. No	Name	Symbol	Atomic number	Mass number	Number of		Percentage abundance
					Protons	Neutrons	
1.	Protium or hydrogen	${}_1\text{H}^1$	1	1	1	0	99.984
2.	Deuterium or heavy hydrogen	${}_1\text{H}^2$	1	2	1	1	0.016
3.	Tritium	${}_1\text{H}^3$	1	3	1	2	$10^{-15}$

The structure of the three isotopes of hydrogen are



**1. Protium or ordinary hydrogen:** It is the common form of hydrogen. It consists of one proton in its nucleus and one electron revolving around it. It constitutes 99.984% of total hydrogen available in nature. Its mass number is one.

**2. Deuterium or heavy hydrogen:**  ${}_1\text{H}^2$  or  ${}_1\text{D}^2$ . It occurs naturally in very small traces. The proportion present in naturally occurring hydrogen is in the approximate ratio: D: H~ 1:6000. Its nucleus consists of a proton and a neutron. However only a solitary electron is revolving around the nucleus. Its chemical properties are similar to those of protium but their reaction rates are different.

**3. Tritium,  ${}_1\text{H}^3$  or  ${}_1\text{T}^3$ :** It occurs in the upper atmosphere only where it is continuously formed by nuclear reactions induced by cosmic rays. Unlike deuterium, it is radioactive, with a half-life of ~ 12.3 years. Its nucleus consists of one proton and two neutrons.

They will have same similar chemical properties, however, their reaction rates will be different and their physical properties differ appreciably.

### Methods of Preparation of deuterium

**1. By Diffusion Process:** It is possible to obtain deuterium directly from hydrogen gas by taking advantage of different rates of diffusion of the two isotopes. The lighter hydrogen diffuses more quickly than deuterium through a porous partition under reduced pressure. Lower the pressure, higher is the efficiency of the process.

The process of diffusion has been carried out in various diffusion chambers called Hertz diffusion units. Each diffusion units consists of a porous membrane.

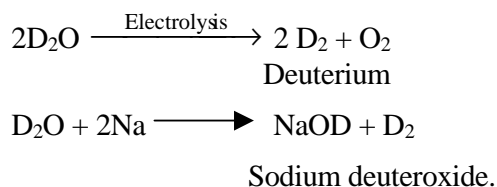
When the mixture is led into the diffusion units under reduced pressure

by the help of mercury diffusion pumps, the heavier deuterium diffuses less readily while lighter hydrogen diffuses at faster rates. This process is repeated several times till hydrogen gets collected on the left while deuterium on the right. The efficiency of this process could be increased by increasing the number of diffusion units.

**2. By fractional distillation of liquid hydrogen:** By fractional distillation of liquid hydrogen, it is possible to result in enrichment of the last fraction in deuterium because deuterium boils at 23.5K while hydrogen boils at lower temperature of 20.2K.

**3. By electrolysis of heavy water:** As water contains about one part of heavy water in 6000 parts, at first, the concentration of heavy water is increased by fractional electrolysis of water containing an alkali between nickel electrodes. For example 1 ml of heavy water is obtained from about 20 litres by this method.

From heavy water, it is possible to get deuterium by decomposing it with sodium, red hot iron or tungsten or by its electrolysis containing sodium carbonate.



Deuterium obtained can be further obtained in purified state by the diffusion process.

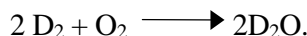
### Physical properties

Like hydrogen, deuterium is a colourless, odourless and tasteless gas which is insoluble in water and bad conductor of heat and electricity. The values of boiling point, melting point, vapour pressure, dissociation energy and latent heat of fusion are found to be lower for protium than deuterium.

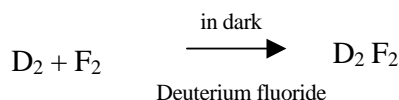
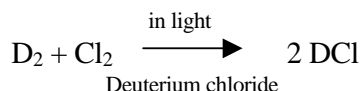
### Chemical properties

By virtue of its larger mass, deuterium reacts slower than hydrogen.

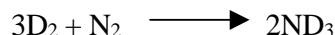
**1. Burning in oxygen:** Like hydrogen, it is combustible and burns in oxygen or air to give deuterium oxide which is also known as heavy water.



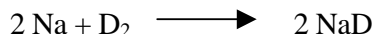
**2. Reaction with halogens:** Like hydrogen, it combines with halogens under suitable conditions to form their deuterides.



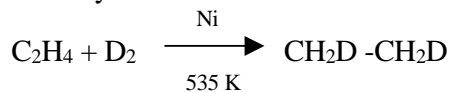
**3. Reaction with nitrogen:** Like hydrogen, it combines with nitrogen in the presence of a catalyst to form nitrogen deuteride which are also known as heavy ammonia or deuterio ammonia.



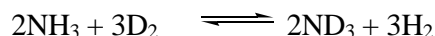
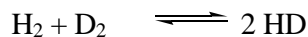
**4. Reaction with metals:** Like hydrogen, it reacts with alkali metals at high temperatures (633K) to form deuterides

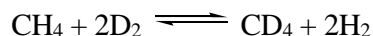


**5. Addition reactions:** Like hydrogen, it gives addition reactions with unsaturated compounds. For example, a mixture of deuterium and ethylene when passed over heated nickel, gives Ethylene deuteride which is saturated hydrocarbon like ethane.



**6. Exchange reactions:** Deuterium and hydrogen atoms undergo ready exchange with  $\text{H}_2$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  and  $\text{CH}_4$  deuterium slowly exchanges their hydrogens partially or completely at high temperatures.





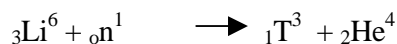
### Uses of deuterium

1. It is used as tracers in the study of mechanism of chemical reactions.
2. High speed deuterons are used in artificial radioactivity.
3. Its oxide known as heavy water ( $\text{D}_2\text{O}$ ) which is employed as moderator in nuclear reactor to slow down the speed of fast moving neutrons.

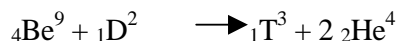
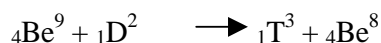
**Tritium  ${}_1\text{H}^3$ :** It is a rare isotope of hydrogen. Its traces are found in nature due to nuclear reactions induced by cosmic rays.

Tritium is prepared by

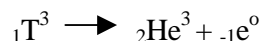
- i) By bombarding lithium with slow neutrons



- ii) By bombarding beryllium with deuterons



**Properties :** It is radioactive with a half-life of 12.4 years. It decays into helium -3 with the emission of beta radiation.



### Uses

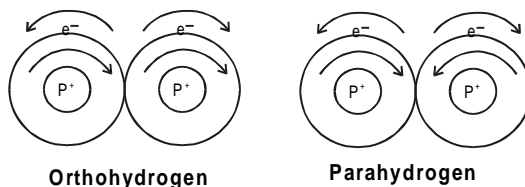
- (i) It is used as a radioactive tracer in chemical research.
- (ii) It is used in nuclear fusion reactions.

## 5.1 Ortho and Para hydrogen

The nucleus of the hydrogen atom spins about an axis like a top. When two hydrogen atoms combine, they form molecular hydrogen.

Thus depending on the direction of the two protons in the nucleus the

following two types of hydrogen molecules are known. Hydrogen molecule in which both the protons in the nuclei of both H-atoms are known to spin in same direction is termed as ortho hydrogen. If the protons in the nuclei of both H-atoms spin in opposite direction, it is termed as parahydrogen.



At room temperature ordinary hydrogen consists of about 75% ortho and 25% para form. As the temperature is lowered, the equilibrium shifts in favour of para hydrogen. At 25K. There is 99% para and 1% ortho hydrogen. The change in the proportion of the two forms of hydrogen requires a catalyst such as platinum or atomic hydrogen or silent electric discharge.

The para form was originally prepared by absorbing ordinary hydrogen in activated charcoal in a quartz vessel kept at a temperature of 20K. The charcoal absorbs almost pure para hydrogen. By this method, pure para hydrogen can be isolated.

### Conversion of para into ortho hydrogen

Ortho hydrogen is more stable than para hydrogen. The para form is transformed into ortho form by the following methods.

- i. By treatment with catalysts like platinum or iron
- ii. By passing an electric discharge
- iii. By heating to 800°C or more.
- iv. By mixing with paramagnetic molecules like O<sub>2</sub>, NO, NO<sub>2</sub>.
- v. By mixing with nascent hydrogen or atomic hydrogen.

**Properties:** Ortho and para hydrogen are similar in chemical properties but differ in some of the physical properties.

(i) Melting point of para hydrogen is 13.83K while that of ordinary hydrogen is 13.95 K.

(ii) Boiling point of para hydrogen 20.26K while that of ordinary hydrogen is 20.39K.

(iii) The vapour pressure of liquid para hydrogen is higher than that of ordinary liquid hydrogen.

(iv) The magnetic moment of para hydrogen is zero since the spins neutralise each other while in the case of ortho, it is twice that of a proton.

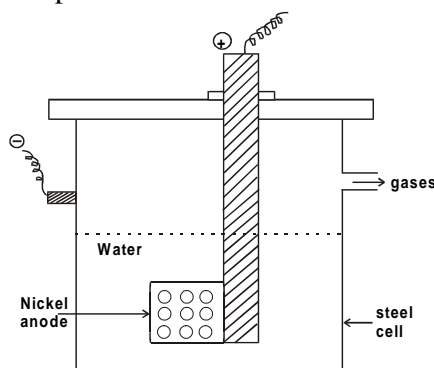
(v) Para hydrogen possesses a lower internal molecular energy than ortho form.

## 5.2 Heavy water

It is also called as deuterium oxide. The oxide of heavy hydrogen (deuterium) is called heavy water. Heavy water was discovered by Urey in 1932. By experimental data he showed that 'ordinary water',  $\text{H}_2\text{O}$  contains small proportion of heavy water,  $\text{D}_2\text{O}$  (about 1 part in 5000).

**Preparation:** The main source of heavy water is the ordinary water from which it is isolated. Generally it is prepared by exhaustive electrolysis.

**Principle:** The heavy water is isolated either by prolonged electrolysis or by fractional distillation of water containing alkali. Taylor, Eyring and First in 1933 formulated the electrolysis of water in seven stages using  $\text{N}/2\text{-NaOH}$  solution and strip nickel electrodes.



The cell consists of a steel cell 18 inches long and 4 inches in diameter. The cell itself serves as the cathode while the anode consists of a cylindrical sheet of nickel with a number of holes punched in it. A large number of



such cells are used for electrolysis of water in several stages. The gases obtained from each stage are separately burnt and the water thus formed is returned to the previous stage. The heavy water gradually concentrates in the residue left behind. The process usually consists of five stages.

A partial separation of heavy water from ordinary water can be affected by fractional distillation. This method utilises the small difference in boiling points of protium oxide ( $\text{H}_2\text{O}$ ) and deuterium oxide ( $\text{D}_2\text{O}$ ).

#### Comparison of water and heavy water

Property	$\text{H}_2\text{O}$	$\text{D}_2\text{O}$
Density at $20^\circ\text{C}$	0.998	1.017
Freezing point	$0^\circ\text{C}$	$3.82^\circ\text{C}$
Boiling point	$100^\circ\text{C}$	$101.42^\circ\text{C}$
Maximum density	1.000 ( $4^\circ\text{C}$ )	1.1073 ( $11.6^\circ\text{C}$ )
Specific heat at $20^\circ\text{C}$	1.00	1.01
Surface tension at $20^\circ\text{C}$	72.8 dynes/cm	67.8 dynes/cm
Dielectric constant	82.0	80.5
Viscosity at $20^\circ\text{C}$	10.09 millipoises	12.6 millipoises

The solubilities of substances in heavy water also differ from those in ordinary water. Thus sodium chloride is about 15% less soluble in heavy water than in ordinary water.

#### Physical Properties

Heavy water is a colourless, odourless and tasteless mobile liquid. Higher viscosity of heavy water is responsible for lower solubility of ionic solids like  $\text{NaCl}$  and smaller mobilities of ions.

#### Chemical Properties

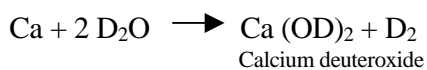
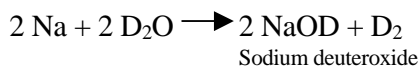
The difference in chemical behaviour between  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  is very slight. However, the reaction velocity in general is slightly less in case of  $\text{D}_2\text{O}$  reactions.

#### Important reactions of heavy water

##### 1. With metals

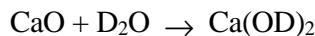
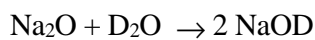
$\text{D}_2\text{O}$  reacts slowly with alkali and alkaline earth metals liberating heavy

hydrogen.



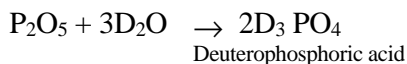
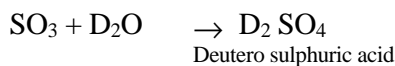
2. With metallic oxides

Metals like sodium and calcium dissolve in  $\text{D}_2\text{O}$  and form heavy alkalies.



3. With acid anhydrides

$\text{D}_2\text{O}$  forms corresponding acids containing heavy hydrogen.



4. Upon electrolysis, heavy water containing dissolved  $\text{P}_2\text{O}_5$ , decomposes into deuterium and oxygen which are liberated at the cathode and anode respectively.

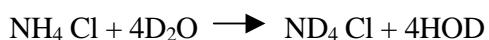


5. With salt and other compounds they form deuterates.



7. Exchange reactions

When compounds containing hydrogen are treated with  $\text{D}_2\text{O}$ , hydrogen undergoes an exchange for deuterium.



## Biological Properties

In general heavy water, retards the growth of living organisms like plants and animals. The tobacco seeds do not grow in heavy water. Also, pure heavy water kills small fish, tadpoles and mice when fed upon it. Certain moulds have been found to develop better in heavy water.

#### Uses of heavy water

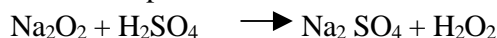
1. As a neutron moderator, in nuclear reactors.
2. It is used as a tracer compound in the study of reactions occurring in living organisms.
3. It is used for the preparation of deuterium.

### 5.3 Hydrogen peroxide

Hydrogen peroxide was first prepared by L.J. Thenard, in 1813 by the action of dilute acid on barium peroxide. Traces of  $\text{H}_2\text{O}_2$  are found in atmosphere and in certain plants.

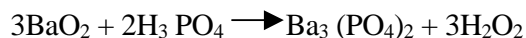
#### Laboratory preparation of hydrogen peroxide

1. By the action of dilute sulphuric acid on sodium peroxide. Calculated quantity of  $\text{Na}_2\text{O}_2$  is added in small proportions to a 20% ice cold solution of sulphuric acid.



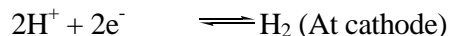
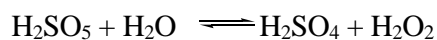
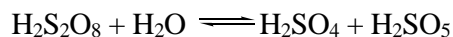
30% solution of  $\text{H}_2\text{O}_2$  is obtained by this process.

2. Pure  $\text{H}_2\text{O}_2$  is obtained by reacting  $\text{BaO}_2$  with an acid



3.  $\text{H}_2\text{O}_2$  is manufactured by the electrolysis of 50% sulphuric acid followed by vacuum distillation. The distillate is 30% solution of pure  $\text{H}_2\text{O}_2$ .

#### Reactions



#### Concentration of hydrogenperoxide solution

The impurities like organic material or metallic ions, may catalyse its explosive decomposition.

i) By careful evaporation of the solution obtained above on a water bath preferably under reduced pressure using fractionating column.

ii) By distillation under reduced pressure at temperatures below 330K, the concentration up to 90% solution is used till crystallisation formed.

### **Strength of Hydrogenperoxide**

The strength of a sample of hydrogen peroxide solution is expressed in terms of the volumes of oxygen at S.T.P that one volume of  $\text{H}_2\text{O}_2$  gives on heating.

### **Properties**

#### **Physical**

$\text{H}_2\text{O}_2$  is a colourless, odourless, syrupy liquid in the anhydrous state. It is miscible with water, alcohol, and ether in all proportions.

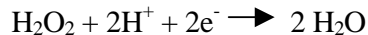
#### **Chemical**

Pure  $\text{H}_2\text{O}_2$  is unstable and decomposes on standing. On heating when water and oxygen are formed.



### **Oxidizing Properties**

$\text{H}_2\text{O}_2$  is a powerful oxidizing agent. It functions as an electron acceptor.



(In acidic solution)



(In alkaline solution)

i) It oxidises PbS to  $\text{PbSO}_4$



ii) It oxidizes ferrous salts into ferric salts .



Due to its oxidizing property, it is a valuable bleaching agent, powerful but harmless disinfectant and germicide. Delicate materials like silk, wool, hair which will be destroyed by chlorine, are bleached with  $\text{H}_2\text{O}_2$ .

### Reducing Properties

With powerful oxidizing agents,  $\text{H}_2\text{O}_2$  acts as a reducing agent. Moist silver oxide, acidified  $\text{KMnO}_4$ , ozone, chlorine and alkaline solutions of ferricyanides are reduced.



### Uses

- i) It destroys bacteria and hence it is used as an antiseptic and germicide for washing wounds, teeth and ears.
- ii) It destroys the colour of some organic compounds and is used in bleaching delicate things like hair, wool, silk ivory and feathers.
- iii) It is used as an oxidizing agent.
- iv) It is also used as a propellant in rockets.

## 5.4 Liquid hydrogen as a fuel

The hydrogen atom has become a model for the structure of atom. Hydrogen as a substance however, has an equally important place in chemistry. Hydrogen is normally a colourless, odourless gas composed of  $\text{H}_2$  molecules. Approximately 40% of the hydrogen produced commercially is used to manufacture ammonia and about the same amount is used in petroleum refining. But the future holds an even greater role for hydrogen as a fuel.

Liquid hydrogen,  $\text{H}_2$ , is a favourable rocket fuel. On burning, it produces more heat per gram than any other fuel. In its gaseous form, hydrogen may become the favourite fuel of the twenty first century. When hydrogen burns in air, the product is simply water. Therefore, the burning of hydrogen rather than fossil fuels (natural gas, petroleum, and coal) has important advantages.

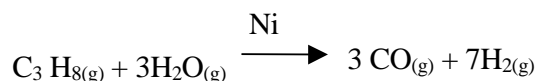
The burning of fossil fuels is a source of environmental pollutants. They become the source of acid rain and discharge a large amount of toxic gases like  $\text{SO}_2$  and  $\text{CO}_2$ .

Controlling carbondioxide emissions into the atmosphere is a difficult

challenge, but the answer might lie in the conversion to a hydrogen economy, hydrogen would become a major energy barrier. Automobiles, for example may be modified to burn hydrogen. At present, in USA they use car using a modified piston engine and has a hydrogen storage unit in the tank. This proves that it is possible to develop hydrogen-burning cars.

Hydrogen is not a primary energy source. But it is a convenient and non-polluting fuel, but it would have to be obtained from other energy sources.

1) It is produced by heating propane and steam at high temperature and pressure in presence of the catalyst nickel.



2) Pure hydrogen may be produced by reacting carbonmonoxide with steam in the presence of a catalyst to fix CO<sub>2</sub> and H<sub>2</sub>. The CO<sub>2</sub> is removed by dissolving it in a basic aqueous solution.

3) Hydrogen can be obtained directly from water that is decomposed by some form of energy. For example, electricity from solar photovoltaic collectors can be used as a source of energy to decompose water by electrolysis. Researchers use solar energy to convert water directly to hydrogen and oxygen.

## 5.5 Alkali Metals

### Position of alkali metals in the periodic table

Alkali metals occupy the group I of the periodic table. Elements lithium, sodium, potassium, rubidium, caesium and francium constitute alkali metals. They are named so from the Arabic word 'Alquili' meaning 'plant ashes'. Ashes of plants are composed mainly of sodium and potassium carbonates.

### General characteristics

1. The alkali metals are shiny white and soft.
2. They can be readily cut with a knife.
3. They are extremely reactive metals and form strong alkaline oxides

and hydroxides.

4. The last metal of this group, francium is radioactive.
5. Since the alkali metals are extremely reactive they occur only as compounds in nature.
6. All the alkali metals exhibit an oxidation state of +1. This is because the metals can easily lose their single outermost electron.
7. The alkali metals give characteristic colour in bunsen flame. The colours given by Li, Na and K are crimson red, yellow, lilac respectively. This is because when the alkali metal or any of its compounds are heated in a bunsen flame, the  $ns$  electron gets excited to higher energy levels and while returning to their ground state the excitation energy absorbed by them is released as light in the visible region.

**Table 5.2 Electronic configuration of alkalimetals**

Element	Symbol	Atomic number	Electronic configuration
Lithium	Li	3	[Helium] $2s^1$
Sodium	Na	11	[Neon] $3s^1$
Potassium	K	19	[Argon] $4s^1$
Rubidium	Rb	37	[Krypton] $5s^1$
Caesium	Cs	55	[Xenon] $6s^1$
Francium	Fr	87	[Radon] $7s^1$

### **Gradation in Physical Properties**

**1. Density:** In general, these elements have high density due to the close packing of atoms in their metallic crystals. Lithium has low density due to the low atomic weight of the atom. Density of the elements increases on moving down the group due to the increase in the mass of the atoms with increasing atomic number. However, K is lighter than Na probably due to an unusual increase in atomic size.

**2. Atomic volume:** Atomic volume increases on moving down the group from Li to Cs. Hence there is an increase in atomic and ionic radii in the same order.

**3. Melting and boiling points :** All alkali metals have low melting and boiling point due to the weak bonding in the crystal lattice. The weak interatomic bonds are attributed to their large atomic radii and to the presence of one valence electron. With the increase in the size of the metal atoms, the repulsion of the non-bonding electron gets increased and therefore melting and boiling points decrease on moving down the group from Li to Cs.

**4. Ionization energy :** The first ionization energies of alkali metals are relatively low and decrease on moving down from Li to Cs.



As the atomic radius gets increased on moving down the group, the outer electron gets farther and farther away from the nucleus and therefore ionization energy decreases.

The second ionization energies of alkali metals are fairly high. This implies that the loss of the second electron is quite difficult, because it has to be pulled out from the noble gas core.

**5. Electropositive character :** As alkali metals have low ionization energies, they have a great tendency to lose electrons forming unipositive ions. Therefore they



have strong electropositive character. Electropositive character increases as we go down the group. The alkali metals are so highly electropositive that they emit electrons when irradiated with light. This effect is known as photoelectric effect. Due to this property, Cs and K are used in photoelectric cells.

**6. Oxidation state:** All the alkali metals have only one electron in their outermost valence shell. As the penultimate shell being complete, these elements lose one electron to get the stable configuration of the nearest inert gas. Thus, they are monovalent elements showing an oxidation state of +1.

**7. Reducing properties :** As alkali metals have low ionization energy, they lose their valence electrons readily and thus bring about reduction reaction. Therefore these elements behave as good reducing agents.



## 5.6 Extraction of Lithium and Sodium

Extraction of Lithium - Electrolysis of Lithium chloride.

Lithium metal is obtained by the electrolysis of moisture free lithium chloride in a crucible of thick porcelain using gas-coke splinter anode and iron wire cathode. For the preparation of the metal on a large scale, a fused mixture of equal parts of lithium and potassium chloride is used, as it melts at a lower temperature of 720 K.

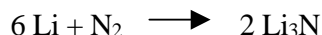
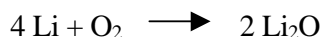
Lithium is also obtained by the electrolysis of a concentrated solution of lithium chloride in pyridine or acetone.

### Properties of Lithium

**Physical :** Lithium is a silvery white metal and it is the lightest of all solid elements. It's vapours impart calamine red colour to the flame. It is a good conductor of heat and electricity. It gives alloys with number of metals and forms amalgam.

### Chemical

1) With air: Lithium is not affected by dry air but in moist air it is readily oxidized. When heated in air above 450K, it burns to give lithium monoxide and lithium nitride



2) It decomposes cold water forming lithium hydroxide and hydrogen



3) Lithium is a strongly electropositive metal and displaces hydrogen from acid with the formation of corresponding lithium salts. Dilute and concentrated hydrochloric and dilute sulphuric acid react readily while concentrated sulphuric acid reacts slowly. With nitric acid, the action is violent and metal melts and catches fire.

### Uses

- 1) For the manufacture of alloys.
- 2) As a deoxidizer in the preparation of copper and nickel.
- 3) Lithium citrate and salicylate are used in the treatment of gout.

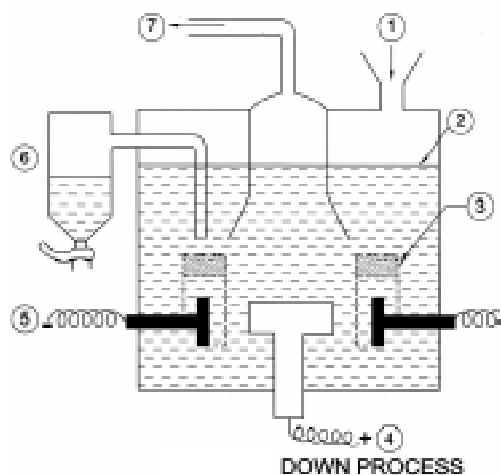
- 4)  $\text{LiAlH}_4$  is used as an reducing agent.
- 5) Its compounds are used in glass and pottery manufacture.

### Extraction of Sodium

**Down's process :** It is now manufactured by electrolysis of fused sodium chloride.

Down's electrolytic cell, consists of an iron box through the bottom of which rises a circular carbon anode. The anode is surrounded by a ring shaped iron cathode enclosed in a wire gauze shell which also acts as a partition and separates the two electrodes.

On electrolysis, chlorine is liberated at the anode and let out through an exit at the top. Sodium is liberated at the cathode and remains in the wire-gauze shell. Level of molten sodium rises and it overflows into a receiver.



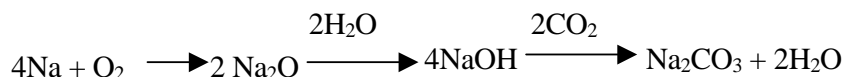
1	$\text{NaCl}$
2	FUSED $\text{NaCl}$
3	WIRE GAUZE SHELL
4	GRAPHITE ANODE
5	IRON CATHODE
6	RING-SHAPED SODIUM
7	CHLORINE

### Physical properties

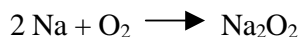
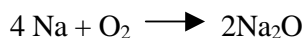
- 1) It is a silvery white metal when freshly cut but is rapidly tarnished in air. It forms tetragonal crystals.
- 2) It is a soft metal.
- 3) It is a good conductor of electricity.
- 4) It dissolves in liquid ammonia forming an intense blue solution.

### Chemical

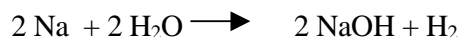
**1) Action of air :** In moist air a layer of sodium oxide, hydroxide and carbonate is formed on its surface which loses its lustre.



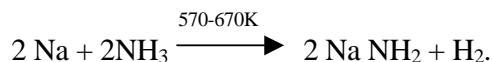
When heated in air, it burns violently to form the monoxide and the peroxide.



**2) Action of water :** It decomposes water vigorously, liberating hydrogen and forming sodium hydroxide.

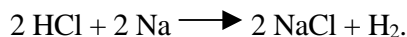


**3) Action of ammonia:** Sodium gives sodamide with ammonia liberating hydrogen.



Sodium dissolved in liquid ammonia is used as a reducing agent in organic chemistry.

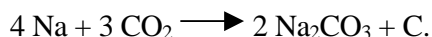
**4) Action of acids:** It displaces hydrogen from acids



**5) Reducing action:** Reduces many compounds when heated with them in the absence of air



Reduces carbondioxide when heated forming carbon and sodium carbonate.



**6) With Mercury :** When heated with mercury, sodium forms an amalgam of varying composition  $\text{Na}_2\text{Hg}$ ,  $\text{Na}_3\text{Hg}$ ,  $\text{NaHg}$  etc.

#### Uses

- 1) For the preparation of sodium peroxide, sodamide and sodium cyanide, tetraethyl lead etc.
- 2) Sodium amalgam is employed as a reducing agent.
- 3) As a deoxidizing agent in the preparation of light alloys and some rare earth metals from their oxides.
- 4) It acts as a catalyst in the polymerisation of isoprene ( $\text{C}_5\text{H}_8$ ) into artificial rubber.
- 5) As a reagent in organic chemistry.

#### Questions

##### A. Choose the best answer

1. Atoms of the same element having same atomic number but different mass number are called  
(a) isotopes (b) isobars (c) isotones (d) isomerism
2. Deuterium nucleus consists of  
(a) 2 protons only (b) one neutron  
(c) one proton and one neutron (d) 2 protons and one neutron
3. Deuterium with oxygen gives  
(a) oxydeuterium (b) water (c) heavy water (d) all the above
4. Tritium is prepared by bombarding lithium with  
(a) deuterons (b) mesons (c) slow neutrons (d) all helium nucleus
5. At room temperature ordinary hydrogen consists of about  
(a) 25% para and 75% ortho (b) 75% para and 25% ortho  
(c) 99% para and 1% ortho (d) 1% para and 99% ortho
6.  $\text{D}_2\text{O}$  reacts with  $\text{P}_2\text{O}_5$  and gives  
(a)  $\text{DPO}_4$  (b)  $\text{D}_2\text{PO}_4$  (c)  $\text{D}_3\text{PO}_3$  (d)  $\text{D}_3\text{PO}_4$
7. \_\_\_\_\_ is used for the preparation of deuterium  
(a) deuterium oxide (b) heavy water  
(c) both a and b (d) deuterium peroxide

8.  $\text{H}_2\text{O}_2$  is a powerful \_\_\_\_\_ agent  
(a) dehydrating (b) oxidising (c) reducing (d) desulphurising
9. \_\_\_\_\_ is used as a propellant in nucleus  
(a)  $\text{H}_2\text{O}_2$  (b)  $\text{D}_2\text{O}$  (c)  $\text{ND}_3$  (d)  $\text{CH}_2 = \text{CH}_2$
10. The oxidation state of alkali metals is  
(a) +2 (b) 0 (c) +1 (d) +3
11. When heated in bunsen flame, lithium gives \_\_\_\_\_ colour  
(a) yellow (b) blue (c) lilac (d) crimson red
12. On moving down the group, density of the alkali metals  
(a) increases (b) decreases  
(c) increases and then decreases (d) decreases and then increases
13. If the element can lose an electron readily, they are said to be  
(a) electronegative (b) electropositive  
(c) electronative (d) electrovalent

**B. Fill in the blanks**

1. The first element in the periodic table is \_\_\_\_\_.
2. \_\_\_\_\_ is the common form of hydrogen.
3. The half-life of tritium is \_\_\_\_\_.
4. Deuterium reacts with ammonia to form \_\_\_\_\_.
5. The rare isotope of hydrogen is \_\_\_\_\_.
6. \_\_\_\_\_ is employed in nuclear reactor to slow down the speed of fast moving neutrons.
7. The magnetic moment of para hydrogen is \_\_\_\_\_.
8. Deuterium with salt and other compounds forms \_\_\_\_\_.
9. Hydrogen peroxide was first prepared by \_\_\_\_\_ in \_\_\_\_\_.
10. Pure  $\text{H}_2\text{O}_2$  is \_\_\_\_\_.
11. The Arabic word 'Alquili' means \_\_\_\_\_.
12. The electronic configuration of potassium is \_\_\_\_\_.
13. All alkali metals have \_\_\_\_\_ melting and boiling points.
14. On moving down the group of alkali metals, ionization energy \_\_\_\_\_.
15. \_\_\_\_\_ is the lightest of all solid elements.

**C. Write in one or two sentences**

1. What are isotopes? Mention the isotopes of hydrogen.
2. Write a short note on tritium.
3. How does deuterium react with nitrogen?
4. How does deuterium react with metals?
5. Mention the uses of deuterium.

6. How is tritium prepared?
7. How do you convert para hydrogen to ortho hydrogen?
8. How does heavy water react with metals?
9. How is hydrogen peroxide prepared in the laboratory?
10. How is hydrogen peroxide solution concentrated?
11. Write about the reducing property of hydrogen peroxide.
12. Mention two important uses of  $\text{H}_2\text{O}_2$ .
13. Why alkali metals have low melting and boiling points?
14. Why alkali metals have strong electropositive character?

**D. Explain briefly on the following**

1. How is deuterium obtained by diffusion process?
2. Write about the exchange reactions of deuterium.
3. What are ortho and para hydrogen? Explain.
4. Differentiate between ortho and para hydrogen.
5. Explain the preparation of heavy water.
6. Compare water and heavy water.
7. Explain the oxidizing property of hydrogen peroxide.
8. Explain how liquid hydrogen can be used as a fuel.
9. How is lithium extracted from its ore?

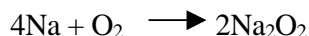
**Problem**

An element occupies group number 1 and period number 3. This element heated in air gives compound A. With water it gives compound B - a strong base. With ammonia gives compound C, which is used as a reducing agent in organic chemistry. Identify the element A, B and C.

**Solution**

(i) As per the position in the periodic table this element occupying group number 1 and period number 3 is sodium.

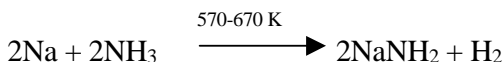
(ii) When heated in air, it forms sodium peroxide (A)



(iii) With water, sodium gives sodium hydroxide (B)



(iv) With ammonia, sodium gives sodamide (I)



The element is sodium.

The compound A is sodium peroxide.

The compound B is sodium hydroxide.

The compound C is sodamide.

### Problems

1. An isotope of hydrogen reacts with oxygen to give compound (A), which is used as a moderator in nuclear reactor. Like hydrogen, this isotope also undergoes addition reaction. It reacts with ethylene to give compound B, which is a saturated hydrocarbon. Identify the element A and B. A is radioactive.
2. An isotope of hydrogen is prepared by bombarding beryllium with deuterons. It decays to an element A, with the emission of beta radiation. Identify the isotope and the element A.
3. A deuterium compound (A) which is used as a moderator in nuclear reactor reacts with Ca to form compound B. A reacts with  $\text{SO}_2$  to give compound C. Upon electrolysis compound A gives deuterium molecule. Identify A, B and C.
4. An element occupies group number 1 and period number 2. This element burns with air and forms compound A. With water, it gives compound B, with hydrogen it forms an ionic compound C. Identify the elements, A, B and C.

### SUMMARY

Hydrogen is the first element in the periodic table. It exists in 3 isotopes. Protium, deuterium and tritium. The preparation properties of deuterium are dealt in detail.

Depending on the spins of the nucleus of hydrogen atom in a molecule, two types ortho and para hydrogen are known. It can be converted from one to another form.

One of the important compound of deuterium is heavy water, which is isolated from ordinary water. It reacts with metals, metallic oxides, acid anhydrides etc. It also undergo exchange reaction.

In 1813, L.J. Thenard prepared hydrogen peroxide by the action of dilute acid on barium peroxide. Traces of it are found in atmosphere. Pure  $\text{H}_2\text{O}_2$  is unstable. It acts as a powerful oxidizing agent.

The use of liquid hydrogen as a fuel is explained in this chapter.

Group 1 elements are known as alkalimetals. There is mostly regular gradation in properties like density, atomic volume, melting and boiling point, ionization energy etc. along the group.

The extraction of lithium and sodium and its properties are explained in detail.

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2. Inorganic Chemistry, P.L. Soni.



## 6. GROUP 2 s - BLOCK ELEMENTS

### OBJECTIVES

- Understands the general characteristics of alkaline earth metals
- Know the comparison of alkali and alkaline earth metals.
- Understand the extraction of magnesium by electrolytic process, its properties and uses.
- Recognise the different compounds of alkaline earth metals.
- Understand and learn in detail about the preparation, properties and uses of CaO, plaster of paris and  $MgSO_4$ .

**6.1** The second group of the periodic table contains Beryllium (Be), Magnesium (Mg), Calcium (Ca), Strontium (Sr), Barium (Ba) and Radium (Ra). These elements are also known as "Alkaline Earth Metals". The word earth was applied in old days to a metallic oxide and because the oxides of calcium, strontium and barium produced alkaline solutions in water and, therefore these metals are called the alkaline earth metals. Radium corresponds to all the alkaline earth metals in its chemical properties but being radioactive, it is studied along with other radioactive elements.

Like the alkali metals, they are very reactive and hence never occur in nature in free form and react readily with many non metals.

### Electronic configuration

Element	At No.	Electronic	Configuration of Valence Shell
Beryllium	4	$1s^2 2s^2$	$2s^2$
Magnesium	12	$1s^2 2s^2 2p^6 3s^2$	$3s^2$
Calcium	20	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$	$4s^2$
Strontium	38	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 4p^6 5s^2$	$5s^2$
Barium	56	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2$	$6s^2$
Radium	88	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 5d^{10} 5f^{14} 6s^2 6p^6 7s^2$	$7s^2$

The electronic configurations show that for each element, the neutral atom has two electron after inert gas core and two electrons are in a

completed s-subshell. Thus, the outer electronic configuration of each element is  $ns^2$  where n is the number of the valence shell. It can be expected that the two electrons can be easily removed to give the inert gas electronic configuration. Hence these elements are all bivalent and tend to form ionic salts. Thus ionic salts are less basic than group 1. Due to their alike electronic structure, these elements resemble closely in physical and chemical properties.

The variation in physical properties are not as regular as for the alkalimetals because the elements of this group do not crystallise with the same type of metallic lattice.

These elements have been sufficiently soft yet less than the alkalimetals as metallic bonding in these elements has been stronger than in first group alkali elements.

Beryllium is unfamiliar, partly because it is not very abundant and partly because it is difficult to extract. Magnesium and calcium are abundant and among the eight most common elements in the earth's crust. Strontium and barium are less abundant but are well known, while radium is extremely scarce and its radioactivity is more important than its chemistry.

### **Metallic properties**

The alkaline earth metals are harder than the alkali metals. Hardness decreases, with increase in atomic number. They show good metallic lustre and high electrical as well as thermal conductivity because the two s-electrons can easily move through the crystal lattice.

### **Melting and Boiling Points**

Both melting and boiling points do not show regular trends because atoms adopt different crystal structures. They possess low melting and boiling points. These are, however, higher than those of alkali metals because the number of bonding electrons in these elements is twice as great as group 1 elements.

### **Atomic radius**

The atoms of these elements are somewhat smaller than the atoms of the corresponding alkali metals in the same period. This is due to higher

nuclear charge of these atoms which tends to draw the orbital electrons inwards. Due to the smaller atomic radius, the elements, are harder, have higher melting points and higher densities than the elements of group 1. Atomic radius is seen to increase on moving down the group on account of the presence of an extra shell of electron at each step.

### **Ionic radius**

The ions are also large but smaller than those of the elements in group 1. This is due to the fact that the removal of two orbital electrons in the formation of bivalent cations  $M^{2+}$ , ( $Be^{2+}$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Sr^{2+}$ , etc) increases the effective nuclear charge which pulls the electrons inwards and thus reduces the size of the ions. The ionic radius is seen to increase on moving down the group 2.

### **Atomic volume**

Due to the addition of an extra shell of electrons to each element from Be to Ra, the atomic volume increases from Be to Ra.

### **Ionisation Energy**

As the alkaline earth metals are having smaller size and greater nuclear charge than the alkali metals, the electrons are more tightly held and hence the first ionisation energy would be greater than that of the alkali metal.

The second ionisation energy has been to be nearly double than that of the first ionisation energy.

It is interesting to observe that although the  $IE_2$  of the alkaline earth metals is much higher than the  $IE_1$  they are able to form,  $M^{2+}$  ions. This is due to their high heat of hydration in aqueous solution and high lattice energy in the solid state. As the atomic size gets increased from Be to Ba, the values of  $IE_1$  and  $IE_2$  of these elements would decrease on going down the group, ie, Be to Ba.

As among second group elements beryllium has the highest ionisation energy. It has the least tendency to form  $Be^{2+}$  ion.

Thus its compounds with nitrogen, oxygen, sulphur and halogens are covalent whereas the corresponding compounds of Mg, Ca, Sr and Ba are ionic.

The total energy required to produce gaseous divalent ion for second group elements is over four times greater than the amount needed to ionise alkali metals. This very high energy requirement is more than offset by the hydration energy or the lattice energy being more than four times greater.

### **Oxidation states**

Because of the presence of two s-electrons in the outermost orbital, being high heat of hydration of the dipositive ions and comparatively low value of  $IE_2$ , the alkaline earth metals have been bivalent. The divalent ion is having no unpaired electron, hence their compounds are diamagnetic and colourless, provided their anions have been also colourless.

### **Flame colouration**

These elements and their compounds impart characteristic colours to flame. Thus, barium - apple green, calcium - brick red, strontium - crimson red, radium - crimson red.

The reason for imparting the colour to flame is that when elements or their compounds are put into flame, the electrons get energy and excite to higher energy levels. When they return to the ground state they emit the absorbed energy in the form of radiations having particular wavelength.

Beryllium and magnesium atoms are smaller and their electrons being strongly bound to the nucleus are not excited to higher energy levels. Therefore they do not give the flame test.

### **Diagonal relationship between Beryllium and Aluminium**

In case of beryllium, a member of second period of the periodic table, which resembles more with Aluminium group (13 group) than the member of its own group (2nd). The anomalous behaviour of beryllium is mainly ascribed to its very small size and partly due to its high electronegativity. These two factors tend to increase the polarising power of  $Be^{2+}$  tends to form ions to such extent that it is significantly equal to the polarising power of  $Al^{3+}$  ions. Thus the two elements resemble very much.

## **6.2 Magnesium**

The magnesium comes from the name of the mineral magnesite, which in turn is believed to stem from the name Magnesia. The British chemist Humphry Davy discovered the pure element magnesium in 1808.

Due to its low density, it is considered to be a structural unit.

### Important Ores

Magnesium does not occur in the native state. In the combined state it occurs very abundantly in the earth crust.

Magnesite, $\text{MgCO}_3$	Dolomite, $\text{MgCO}_3, \text{CaCO}_3$
Epsomsalt, $\text{MgSO}_4, 7\text{H}_2\text{O}$	Carnallite $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$

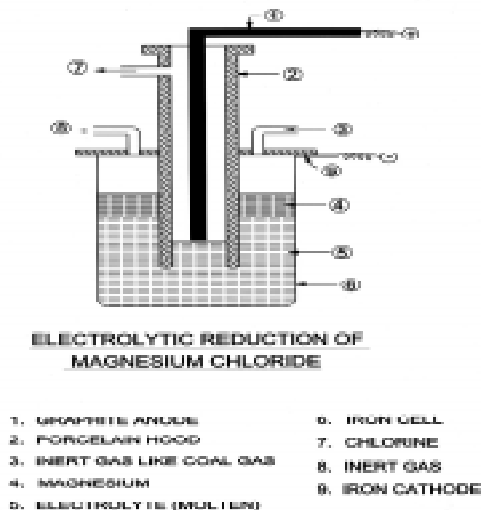
However magnesium ion  $\text{Mg}^{2+}$ , is the third most abundant dissolved ion in the oceans, after  $\text{Cl}^-$  and  $\text{Na}^+$ . The oceans are the best sources for magnesium. It is widely distributed in the vegetable kingdom being present in chlorophyll, the green colouring matter of the leaves.

### Metallurgy

Magnesium is prepared on a large scale by the electrolysis of either fused magnesium chloride or magnesia.

#### 1. Electrolysis of fused magnesium chloride

The purified carnallite ore is the principal source for this process. A mixture of equal quantities of carnallite and  $\text{NaCl}$  is fused to a clear liquid at 973K. The alkali chloride prevents hydrolysis of magnesium chloride and increases the conductivity of the fused mass.



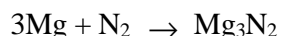
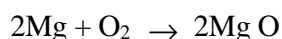
The electrolysis of the fused mass is carried out in an atmosphere of coal gas in air tight iron cell which can hold 6-7 tonnes of the electrolyte. The temperature of the electrolyte bath is maintained at 970K. The iron cell itself acts as a cathode unlike the anode consists of a carbon or graphite rod surrounded by a porcelain tube through which the liberated chlorine escapes. Molten magnesium being lighter than the electrolyte, rises to the surface and is periodically removed with perforated ladle. The electrolysis is carried out in an atmosphere of coal gas so as to avoid the oxidation of molten magnesium. The metal thus obtained is 99.9% pure. It may be further purified by remelting with a flux of anhydrous magnesium chloride and sodium chloride.

### Physical

Pure magnesium metal is a relatively active silvery white metal. At slightly below its melting point, it is malleable and ductile and can be drawn into wire or rolled into ribbon in which form it is generally sold. It is a very light metal.

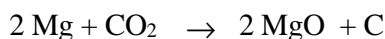
### Chemical Properties

1. **Action of Air :** It does not tarnish in dry air but a layer of white oxide is formed on its surface in moist air.
2. **With air on burning :** It burns in air or oxygen with a dazzling light rich in ultraviolet rays, forming magnesium oxide and magnesium nitride.



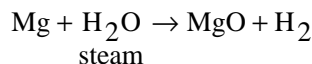
3. **With CO<sub>2</sub>**

It continues to burn in CO<sub>2</sub>,



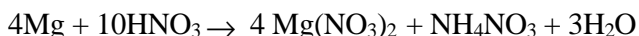
4. **Action of Water**

When heated with steam it burns brilliantly producing magnesium oxide and hydrogen.



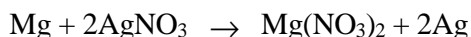
## 5. Action of Acids

Dilute HCl or H<sub>2</sub>SO<sub>4</sub> gives hydrogen with magnesium. With dilute HNO<sub>3</sub>, part of the hydrogen liberated is oxidised by nitric acid, which itself is reduced to a variety of products depending upon the concentration. With concentrated HNO<sub>3</sub>, it gives ammonium nitrate.



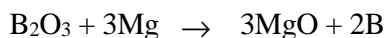
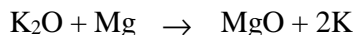
## 6. Displacement of Metals

It is a strongly electropositive metal and hence Mg displaces nearly all the metals from the solutions of their salts eg.



## 7. Reducing Action

Mg has great affinity for oxygen and it liberates sodium, potassium, boron and silicon from their oxides at high temperatures.



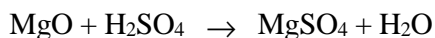
## Uses of Magnesium

1. In flashlight photography, pyrotechnics and in fireworks.
2. As a reducing agent in the preparation of boron and silicon and deoxidiser in metallurgy.

## 6.3 Compounds of alkaline earth metals

### Magnesium sulphate, epsom salt, MgSO<sub>4</sub>·7H<sub>2</sub>O

It is prepared by dissolving magnesium oxide or carbonate in dilute sulphuric acid.

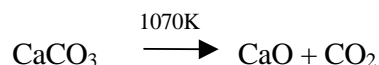


### Uses

- 1) As a purgative
- 2) In dyeing and tanning processes and in dressing cotton goods.
- 3) Platinised MgSO<sub>4</sub> is used as a catalyst.

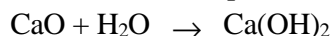
### Calcium oxide, CaO, quicklime

It is prepared by burning limestone in specially designed kilns.



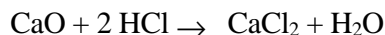
### Properties

1. Lime is a white porous solid
2. On adding water it gives a hissing sound and becomes very hot. The fine powder obtained is known as slaked lime and consists of calcium hydroxide  $\text{Ca(OH)}_2$ . This process is called slaking of lime.



The paste of lime in water is called milk of lime whereas the filtered and clear solution is known as lime water.

3. With chlorine it gives bleaching powder  $\text{CaOCl}_2 \cdot \text{H}_2\text{O}$
4. With carbon dioxide, it forms calcium carbonate while with sulphur dioxide, calcium sulphite is obtained.
5. Moist hydrochloric acid gas reacts with it to give calcium chloride but there is no action with the dry gas.

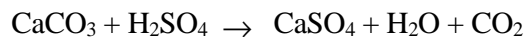


### Uses

1. For the manufacture of calcium chloride, cement, mortar and glass.
2. For drying gases and alcohol.
3. As milk of lime, used in refining sugar and white washing.
4. As lime water, used as a reagent in laboratory and in medicine.

### Calcium sulphate, $\text{CaSO}_4$

It occurs as Anhydrite,  $\text{CaSO}_4$  and Gypsum  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . It may be prepared by adding dilute sulphuric acid to the solution of a calcium salt.



### Uses of Gypsum

It is used

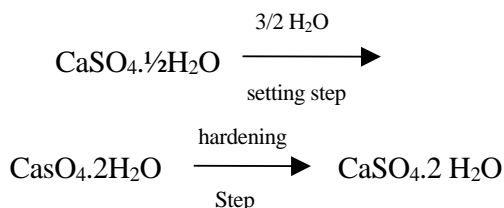
1. For preparing plasters
2. As a retardant for the setting of cement



### Plaster of Paris

When Gypsum is heated to about 393K it loses  $1\frac{1}{2}$  molecules of water and forms plaster of paris with the formula  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ , Calcium Sulphate hemihydrate. The substance is known as plaster of paris because the large deposits of Gypsum used for the manufacture of plaster are at Montmeite (Paris).

When plaster of paris is wetted with, it forms a plastic mass which sets in from 5 to 15 minutes to a white porous hard mass. A slight expansion occurs during the setting so that it will take sharp impression of a mould. The process of setting takes place in two steps, the setting step and the hardening step. The final product of setting is gypsum.



The setting step may be catalysed by NaCl while it is retarded by borax or alum.

**Uses :** It is used

1. In surgery for plastering the fractured bones.
2. In making moulds for statues, in dentistry etc.
3. In making false ceilings.

### Questions

#### A. Choose the best Answer

1. Among the following, which is known as 'alkaline earth metal'.  
(a) Sodium      (b) Calcium      (c) Lithium      (d) Potassium
2. Alkaline earth metals are  
(a) monovalent      (b) trivalent      (c) divalent      (d) zerovalent
3. Among alkaline earth metals \_\_\_\_\_ is having the highest ionization energy.  
(a) Beryllium      (b) magnesium      (c) Calcium      (d) Barium

4. The colour given by barium in flame is  
(a) Brick red (b) Apple Green (c) Red (d) Blue
5. The third most abundant dissolved ion in the ocean is  
(a) Beryllium (b) Barium (c) Calcium (d) Magnesium
6. Quick lime is  
(a) Calcium oxide (b) Calcium hydroxide  
(c) Calcium nitrate (d) Calcium sulphate
7. The formula of bleaching powder is  
(a)  $\text{CaCl}_2 \cdot \text{H}_2\text{O}$  (b)  $\text{CaOCl}_2 \cdot \text{H}_2\text{O}$   
(c)  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (d)  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$
8. Plaster of paris is  
(a)  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (b)  $\text{CaCl}_2$   
(c)  $\text{CaSO}_4$  (d)  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
9. The compound used in making moulds for statues is  
(a) Epsom salt (b) Calcium sulphide  
(c) Plaster of paris (d) Gypsum
10. The element used in pyrotechnics is  
(a) Magnesium (b) Barium (c) Calcium (d) Beryllium

**B. Fill in the Blanks**

1. The general electronic configuration of alkaline earth metals is \_\_\_\_\_.
2. The ionic radius \_\_\_\_\_ on moving down the group 2.
3. In flame, calcium gives \_\_\_\_\_ colour.
4. Beryllium resembles more with an element in 13th group \_\_\_\_\_.
5. Magnesium comes from the name of the mineral \_\_\_\_\_.
6. \_\_\_\_\_ is present in chlorophyll.
7. Magnesium is prepared by the electrolysis of fused \_\_\_\_\_.
8. With air, Magnesium forms \_\_\_\_\_ and \_\_\_\_\_.
9. The formula of epsom salt is \_\_\_\_\_.
10. Epsom salt is used as \_\_\_\_\_.

**C. Match the following**

- |               |  |
|---------------|--|
| 1. Magnetite  | $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$                  |
| 2. Dolomite   | $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$ |
| 3. Epsom salt | $\text{MgCO}_3$  |
| 4. Carnallite | $\text{MgCO}_3 \cdot \text{CaCO}_3$                        |
| 5. Gypsum     | $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$                  |

**Problem**

An element occupies group number 2 and period number 3. This element reacts with oxygen and nitrogen to form compound A and B. It is a strong electropositive metal so it displaces Ag from  $\text{AgNO}_3$  solution. With concentrated nitric acid, it forms compound C. Identify the element, compound A, B and C.

**D. Write in one or two sentence**

1. Why the oxides of Group 2 metals have high melting points?
2. Why there is increase in the ionisation potential for forming  $\text{M}^{3+}$  ion for group 2 metals?
3. Why the ionization potential of  $\text{M}^{2+}$  is not very much greater than  $\text{M}^+$ ?
4. Why a precipitate of  $\text{Mg}(\text{OH})_2$  is not formed when aqueous ammonia,  $\text{NH}_4\text{OH}$  is added to a solution of  $\text{MgCl}_2$ ?
5. List the carbonates and hydroxide of alkaline earth metals in order of their increasing stability and their solution.
6. Why do beryllium halides fume in air?
7. Why group 2 elements are harder than alkali metals?
8. Beryllium halides are covalent whereas magnesium halides are ionic. Why?
9. Why are monoxides of alkaline earth metals are very stable?
10. The basic strength of the oxides of group 2 elements increases from Be to Ba. Why?

**D. Explain briefly on the following**

1. What are alkaline earth metals? Why are they called so?
2. In what respects Be and Mg differ from all the other metals of group 2.

## **p - BLOCK ELEMENTS**

### ***Learning Objectives***

- ✎ *Understand the general trends in the chemistry of elements of groups 13,14,15,16,17 and 18.*
- ✎ *Understands the preparation, properties and the uses of potash alum.*
- ✎ *Knowledge about know about silicones.*
- ✎ *Understand the extraction of lead, properties and the uses of lead.*
- ✎ *Understands the preparation, properties, uses and the structure of halides, oxides, oxyacids and hydrides of phosphorus.*
- ✎ *Recognize the anomalous behavior of Fluorine.*
- ✎ *Understand about interhalogen compounds.*
- ✎ *Know about the isolation of noble gases.*
- ✎ *Recognises the preparation, properties and the structure of xenon compounds.*
- ✎ *Appreciates the application of noble gases.*

## PERIODIC TABLE

		$ns^2np^{1-5}$					18	
		13	14	15	16	17	He	①
d		B	C	N	O	F	Ne	②
12		Al	Si	P	S	Cl	Ar	③
		Ga	Ge	As	Se	Br	Kr	④
		In	Sn	Sb	Te	I	Xe	⑤
		Tl	Pb	Bi	Po	At	Rn	⑥
								⑦
		$ns^2np^1$	$ns^2np^2$	$ns^2np^3$	$ns^2np^4$	$ns^2np^5$	$ns^2np^6$	

- |                     |                     |
|---------------------|---------------------|
| 13 → Boron group    | 17 → Halogen family |
| 14 → Carbon group   | 18 → Noble gases    |
| 15 → Nitrogen group |                     |
| 16 → Oxygen group   |                     |

p-block elements grouped with s-block elements are called as main group elements or representative elements. There are 44 main group elements. p-block elements occupy groups 13-18 of the periodic table including inert gases. p-block elements play dominant part in all natural processes. Aluminium plays vital role in aircraft and as conductors. Carbon is the backbone of all organic compounds. Silicon chips play a vital part in computers. Nitrogen acts as a building block of life. Molecular oxygen is a cell fuel.

## General characteristics of p-block elements

1. The general electronic configuration of p-block elements is  $ns^2 np^{1-6}$ .
2. These elements include metals and non-metals with a few semi metals (Metalloids)
3. Most of them form covalent compounds.
4. These elements possess relatively higher ionisation energy and the value tends to increase along the period but decrease down the group.
5. Most of the elements show negative (except some metals) as well as positive oxidation states (except Fluorine).
6. One of the familiar characteristic of p-block elements is to show inert pair effect i.e. the tendency of being less availability for ns electron in bonding. The inert pair effect increases down the group with the increase in atomic number.

## Group 13 elements – The Boron family

The group 13(IIIA) elements are Boron, aluminium, gallium, indium and thallium.

- Boron is a relatively rare element, accounting for only about 0.001% of the earth's crust by mass.
- Aluminium is the most important of 13<sup>th</sup> group elements.
- Gallium is remarkable for its unusually low melting point (29.7°C) and therefore generally exist as a liquid at room temperature. Its most important use is in making gallium arsenide. This is a semi conductor material employed in the manufacture of diode lasers for laser printers, compact – disc players and fibre optic communication devices.
- Indium is also used in making semi conductor devices, such as transistors and electrical resistance thermometers called thermistors.
- Thallium is extremely toxic and has no commercial use.

### 3.1 GENERAL TRENDS

**Electronic configurations:** The general electronic configuration of the various elements of this family is  $ns^2 np^1$ .

**Table 3.1 Electronic configuration of group 13 elements**

Element	Atomic Number	Electronic Configuration	Group Number	Period Number
Boron	5	[He] $2s^2 2p^1$	13	2
Aluminium	13	[Ne] $3s^2 3p^1$	13	3
Gallium	31	[Ar] $3d^{10} 4s^2 4p^1$	13	4
Indium	49	[Kr] $4d^{10} 5s^2 5p^1$	13	5
Thallium	81	[Xe] $4f^{14} 5d^{10} 6s^2 6p^1$	13	6

#### 3.1.1 Potash Alum, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$

Potash Alum is manufactured from alunite or alum stone.

**From Alunite:** Alunite or alum stone is  $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 4Al(OH)_3$ . It is finely powdered and boiled with dilute sulphuric acid, the aluminium hydroxide part changes into aluminium sulphate. When a little more potassium sulphate in calculated amount is added, the alum is crystallised.

#### Properties

1. Potash alum is a white crystalline solid.
2. It is soluble in water but insoluble in alcohol.
3. The aqueous solution is acidic due to the hydrolysis of  $Al_2(SO_4)_3$ .
4. When heated, it melts at 365K and on further heating loses the whole of its water of crystallisation and swells up. The swollen mass so produced is called **burnt alum**.

#### Uses

1. It is used in purification of water, water proofing of textiles and in dyeing and paper industry.
2. It is also employed to arrest bleeding.

### 3.2 GROUP - 14 ELEMENTS - THE CARBON FAMILY

The group 14 (IVA) elements – carbon, silicon, germanium, tin and lead are especially important both in industry and in living organisms.

- Carbon is an essential constituent of the molecules on which life is based.
- Silicon is the second most abundant element in the earth's crust.
- Both silicon and germanium are used in making modern solid – state electronic devices.
- Tin and lead have been known and used since ancient times.

#### General Trends

**Electronic configuration:** The elements of this group possess  $ns^2 np^2$  electronic configuration.

Element	Atomic Number	Electronic Configuration	Group Number	Period Number
Carbon	6	[He] $2s^2 2p^2$	14	2
Silicon	14	[Ne] $3s^2 3p^2$	14	3
Germanium	32	[Ar] $3d^{10} 4s^2 4p^2$	14	4
Tin	50	[Kr] $4d^{10} 5s^2 5p^2$	14	5
Lead	82	[Xe] $4f^{14} 5d^{10} 6s^2 6p^2$	14	6

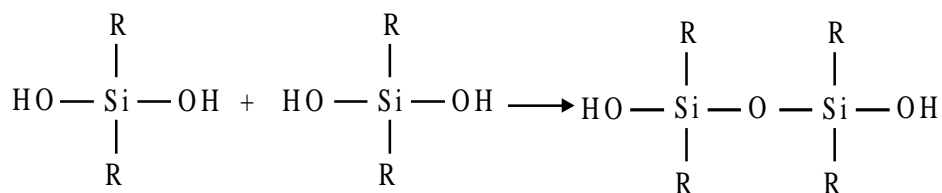
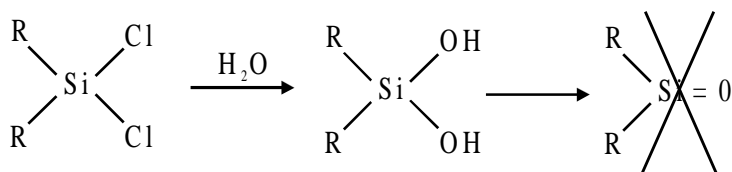
**Table 3.2 Electronic Configuration of Group 14 elements**



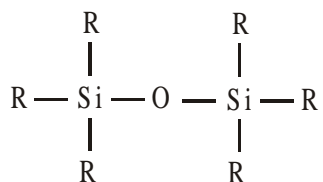
### 3.2.1 Silicones – structure and uses

The silicones are a group of organosilicon polymers. They have a wide variety of commercial uses.

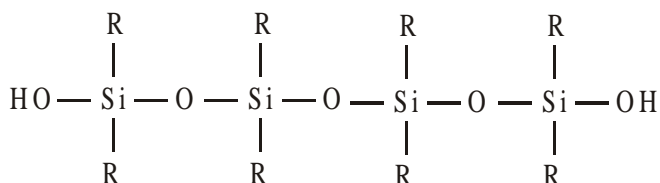
The complete hydrolysis of  $\text{SiCl}_4$  yields silica  $\text{SiO}_2$ , which has a very stable three-dimensional structure. The fundamental research of F.S. Kipping on the hydrolysis of alkyl-substituted chlorosilanes led, not to the expected silicon compound analogous to a ketone, but to long-chain polymers called silicones.



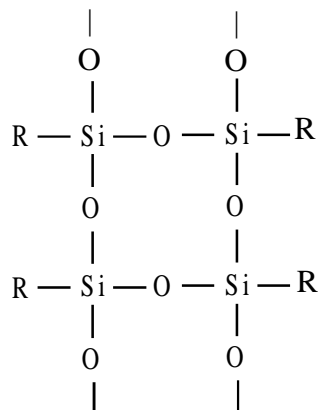
The starting materials for the manufacture of silicones are alkyl-substituted chlorosilanes. Thus the hydrolysis of trialkylmonochlorosilane  $\text{R}_3\text{SiCl}$  yields hexaalkylsiloxane.



The dialkyldichlorosilane  $\text{R}_2\text{SiCl}_2$  on hydrolysis gives rise to straight chain polymers and, since an active OH group is left at each end of the chain, polymerisation continues and the chain increases in length.



The hydrolysis of alkyl trichlorosilane  $\text{RSiCl}_3$  gives a very complex cross-linked polymer.



### Uses

- 1) Silicones act as excellent insulators for electric motors and other appliances as they can withstand high temperatures.
- 2) Straight chain polymers of 20 to 500 units are used as silicone fluids. They are water repellent because of the organic side group. These polymers are used in waterproofing textiles, as lubricants and as polish.
- 3) Silicone rubber retain their elasticity even at low temperatures and resist chemical attack. They are mixed with paints to make them damp-resistant.
- 4) Silicone resins, a cross-linked polymer used as non-stick coating for pans and are used in paints and varnish.
- 5) Silicone oils are highly stable and non-volatile even on heating. Hence used for high temperature oil bath, high vacuum pump etc.

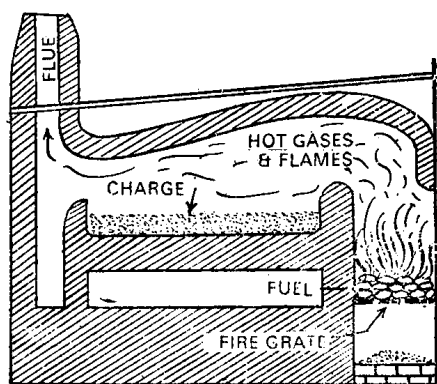
### 3.2.2 Metallurgy of Lead

#### Ores

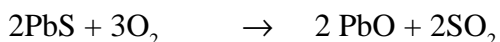
1. Galena  $\text{PbS}$
2. Cerrusite  $\text{PbCO}_3$
3. Anglesite  $\text{PbSO}_4$
4. Lead ochre  $\text{PbO}$

**Extraction:** Lead is mainly extracted from the sulphide ore galena. Galena contains lead sulphide and small quantities of silver.

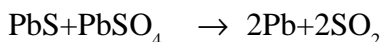
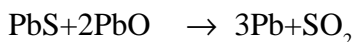
1. **Concentration:** The ore is concentrated by froth floatation process.
2. **Smelting in a Reverberatory furnace:** The concentrated ore is roasted in a reverberatory furnace at a moderate temperature. The temperature of furnace is controlled by regulating the air supply. During roasting, galena is partly oxidized to lead monoxide and partly to lead sulphate.



**Fig. 3.1 A reverberatory furnace**

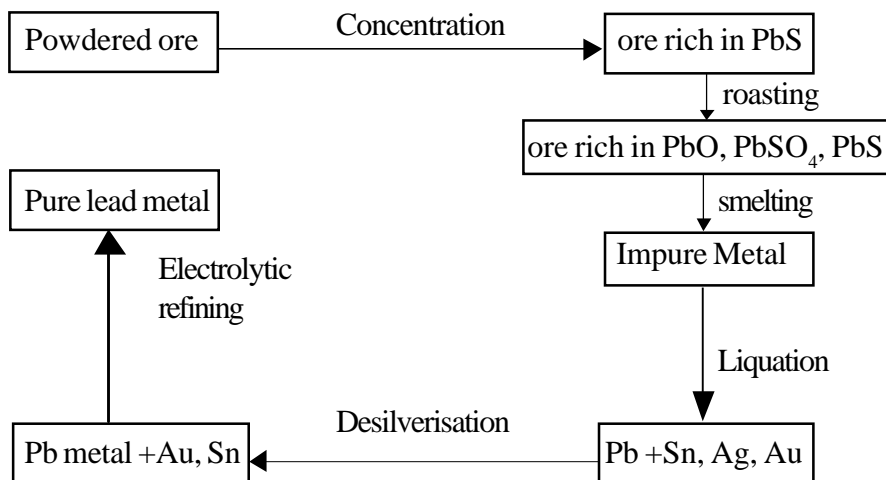


More of galena is then added. The temperature is raised and simultaneously the air supply is reduced. Lead sulphide reacts with the two oxidised products giving lead.



Thus in this process roasting and smelting are carried out in the same furnace, at two different temperatures.

About 90% of lead is obtained as metal, the rest passes into slag. Lead is recovered from the slag by heating with lime and powdered coke.



## Purification of Lead

Lead extracted by the above method contains impurities such as silver, copper, tin, bismuth, gold and iron. It is refined by the following processes.

### a. Liquation

The impure metal is heated on a sloping hearth. Lead melts and flows down the slope. The infusible impurities remain on the hearth.

### b. Desilverisation

Silver is removed by either Pattinson's process or Park's process.

### c. Electrolytic refining

Very pure lead is obtained by this process.

Anode – Impure lead

Cathode – Very pure lead

Electrolyte – Lead fluosilicate + Hydrofluosilicic Acid



The metallic impurities which are more electropositive than lead, such as iron and tin, go into the solution while the rest of the impurities are thrown down as anode mud.

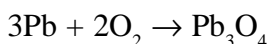
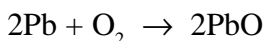
## Physical properties

1. Lead is a bluish grey metal with a bright luster.
2. It is soft and can be cut with a knife and drawn into a wire and rolled into a sheet.
3. It is not a good conductor of heat and electricity.
4. It marks paper.

## Chemical properties

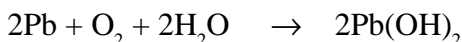
### 1. Action of air

- i) It is unaffected by dry air but in moist air a layer of lead carbonate or lead hydroxide is deposited on its surface which protects it from further action of air.
- ii) When heated in air or oxygen, lead is oxidized to litharge (PbO) and red lead (Pb<sub>3</sub>O<sub>4</sub>)



### 2. Action of water

Lead is not attacked by pure water in the absence of air, but water containing dissolved air has a solvent action on it due to the formation of lead hydroxide (a poisonous substance). This phenomenon is called **Plumbo solvency**.

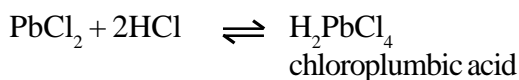
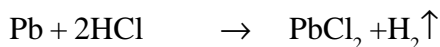


### 3. Action of acids

- i) Dilute H<sub>2</sub>SO<sub>4</sub> and HCl have no action on lead.
- ii) Hot Conc. H<sub>2</sub>SO<sub>4</sub> liberates SO<sub>2</sub> but the reaction is retarded by the formation of an insoluble layer of lead sulphate.



- iii) Concentrated HCl evolves hydrogen and also forms Chloroplumbic acid



**Uses:** Lead is used

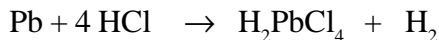
1. For making lead pipes,
2. For making telegraph and telephone wires,
3. In making bullets and lead accumulators,
4. In lead chambers, for the manufacture of sulphuric acid,
5. For making alloys like solder, pewter and type metal,
6. For preparing tetraethyl lead ( $\text{Pb}(\text{C}_2\text{H}_5)_4$ ) which is used as an additive to petrol to prevent knocking.

### **Problem**

An element **A** belongs to 14<sup>th</sup> group and occupies period number 6. **A** reacts with conc. HCl. to give **B** an acid. **A** is used to prepare **C** which is used as an antiknock in automobiles. Identify the element **A** and the compounds **B** and **C** Write the reactions.

### **Solution**

1. As per the position in the periodic table, the element A is lead.
2. Lead with Conc. HCl gives **B**



∴ Compound **B** is chloroplumbic acid.

3. Compound **C** is tetraethyl lead.

### **3.3 GROUP – 15 ELEMENTS – THE NITROGEN FAMILY**

The group 15 (VA) elements are nitrogen, phosphorus, arsenic, antimony and bismuth.

- Nitrogen is a gas. It makes up 78% of the earth's atmosphere by volume.
- Phosphorus is the most abundant element of 15<sup>th</sup> group, accounting for 0.10% of the mass of the earth's crust.
- Arsenic is also used to make pesticides and semi conductors, such as GeAs.
- Bismuth is a silvery solid. Bismuth compounds are present in some pharmaceuticals such as Pepto–bismol.
- The natural abundance of As, Sb and Bi in the earth's crust is relatively low.

## General trends

**Electronic configuration:** All these elements have general electronic configuration of  $ns^2 np^3$ .

**Table 3.3 Electronic configuration of group 15 elements**

Element	Atomic Number	Electronic Configuration	Group Number	Period Number
Nitrogen	7	[He] $2s^2 2p^3$	15	2
Phosphorus	15	[Ne] $3s^2 3p^3$	15	3
Arsenic	33	[Ar] $3d^{10} 4s^2 4p^3$	15	4
Antimony	51	[Kr] $4d^{10} 5s^2 5p^3$	15	5
Bismuth	83	[Xe] $4f^{14} 5d^{10} 6s^2 6p^3$	15	6

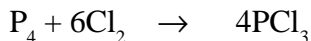
### 3.3.1 Compounds of Phosphorus

#### a) Halides of Phosphorus

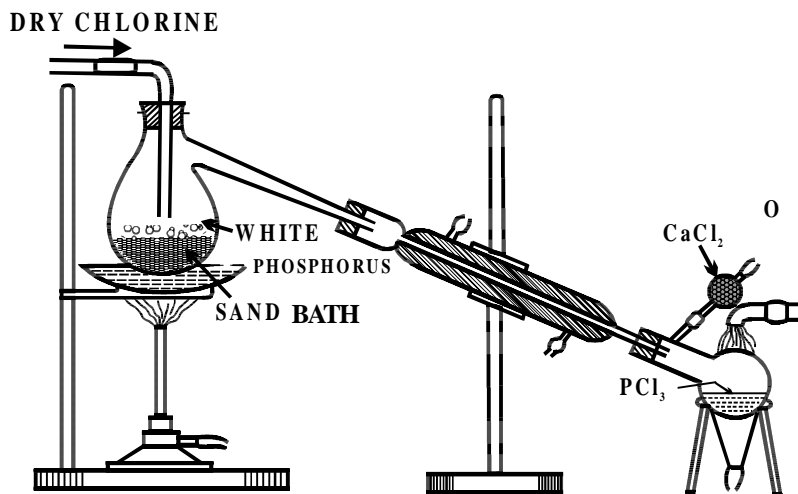
Phosphorus combines with all the halogens forming phosphorus halides which are all covalent compounds. Phosphorus chlorides are more important. Tri and pentachlorides of phosphorus are most common.

#### I. Phosphorus Trichloride, $\text{PCl}_3$

**Preparation:**  $\text{PCl}_3$  is prepared by heating white phosphorus in a current of dry chlorine.



Dry white phosphorus is placed in the retort and gently heated on a water bath. A current of pure, dry chlorine is led over the phosphorus. The phosphorus trichloride formed being volatile distills over and is collected in a water cooled receiver.



**Fig. 3.2 Laboratory Preparation of PCl<sub>3</sub>**

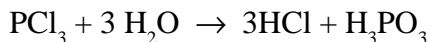
The phosphorus trichloride obtained as above contains some PCl<sub>5</sub> as impurity. This is removed by distilling the PCl<sub>3</sub> over white phosphorus.

### Physical properties

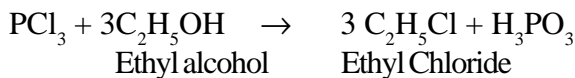
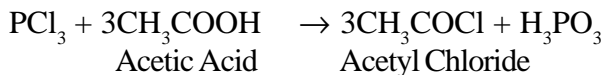
1. Colourless low boiling liquid
2. It fumes in moist air
3. It has pungent odour.

### Chemical Properties

1. It is violently hydrolysed by water giving phosphorus acid and hydrochloric acid gas.

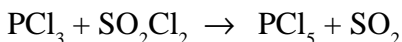
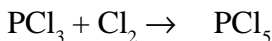


In a similar manner it reacts with organic compounds containing hydroxyl (OH) group, such as acids and alcohols.

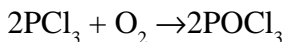


2. It reacts with chlorine or sulphuryl chloride forming phosphorus pentachloride.

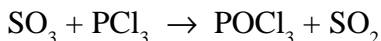




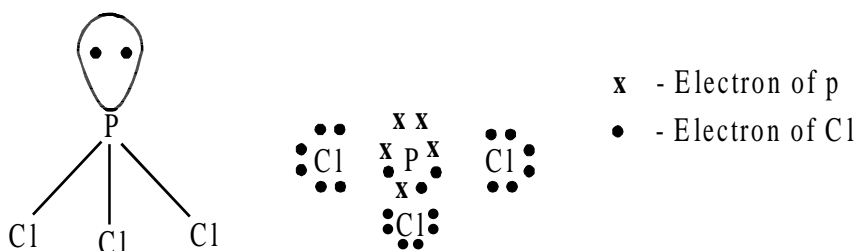
3. It readily combines with oxygen forming phosphorus oxychloride



4. It reacts with  $\text{SO}_3$  to form phosphorus oxychloride and  $\text{SO}_2$

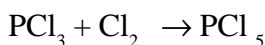


**Structure:**  $\text{PCl}_3$  molecule has a pyramidal shape, which arises from  $\text{sp}^3$  hybridisation of phosphorus atom. One of the tetrahedral positions is occupied by a lone pair of electrons.



## II. Phosphorus pentachloride, $\text{PCl}_5$

**Preparation:** Phosphorus pentachloride is usually prepared by the action of an excess of chlorine on phosphorus trichloride.

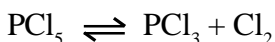


### Physical properties

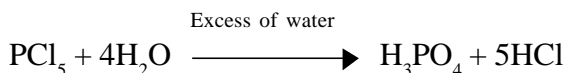
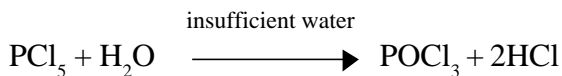
1. Phosphorus pentachloride is a yellowish white crystalline solid.
2. It sublimes on heating at 473 K and melts at 318 K under pressure.

### Chemical properties

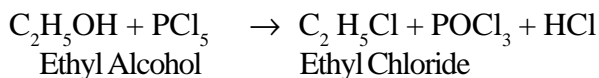
1. Phosphorus pentachloride dissociates on heating into phosphorus trichloride and chlorine.



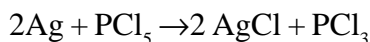
2. It is violently hydrolysed by water giving phosphorus oxychloride or phosphoric acid depending upon the quantity of water.



3. It reacts with compounds containing hydroxyl groups forming chloro derivatives. In all these cases, the hydroxyl group is replaced by chlorine.

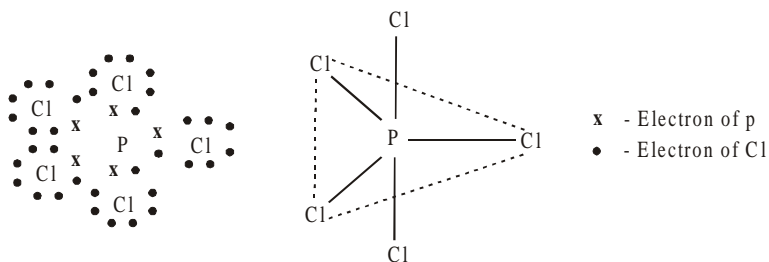


4. It reacts with metals on heating to give corresponding chlorides.



### Structure

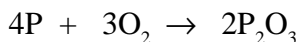
$\text{PCl}_5$  molecule has trigonal bipyramidal shape in vapour state which arises from  $\text{sp}^3\text{d}$  hybridisation of phosphorus atom.



### b) Oxides of phosphorus

#### I. Phosphorus trioxide $\text{P}_2\text{O}_3$ or $\text{P}_4\text{O}_6$

It is obtained by the combustion of phosphorus in a limited supply of air.

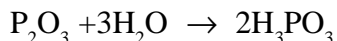


#### Physical properties

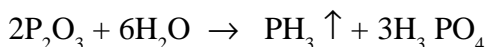
1. It is a white waxy substance
2. It has a garlic odour.

#### Chemical properties

1. It reacts with cold water, gives phosphorus acid.

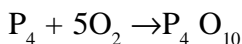


2. It reacts with hot water vigorously to form inflammable phosphine.



## II. Phosphorus pentoxide $\text{P}_2\text{O}_5$ or $\text{P}_4\text{O}_{10}$

Phosphorus pentoxide can be prepared by burning phosphorus with sufficient supply of air.

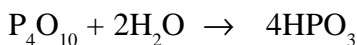


### Physical properties

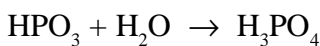
It is a white solid and an acidic oxide.

### Chemical properties

1. It reacts with moisture to form metaphosphoric acid.



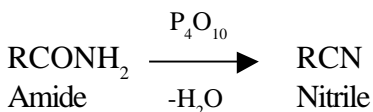
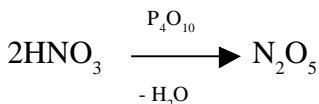
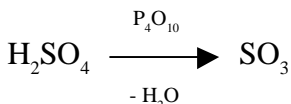
When the solution is boiled, the metaphosphoric acid is changed to orthophosphoric acid.



or



2. Phosphorus pentoxide extracts water from many inorganic compound including sulphuric acid, nitric acid and several organic compounds. It is therefore, used as a powerful dehydrating agent.

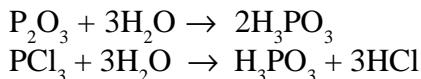


**Use:** It is used as a dehydrating agent.

## c) Oxy-Acids of Phosphorus

### I. Phosphorus acid - $\text{H}_3\text{PO}_3$

It is prepared by the action of cold water on phosphorus (III) oxide or phosphorus (III) chloride.

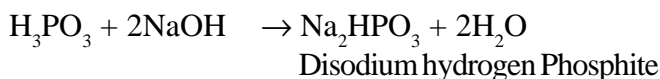
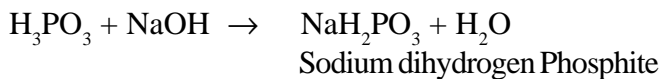


#### Physical properties

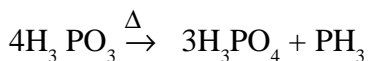
It is a white crystalline solid with garlic taste.

#### Chemical Properties

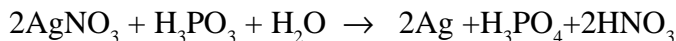
1. **Acidic nature:** It is a dibasic acid and gives salts of two types.



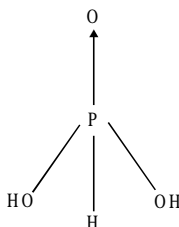
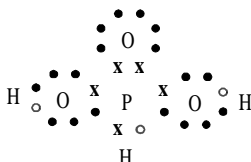
2. When it is heated it undergoes auto-oxidation and reduction to form phosphoric acid and phosphine.



3. It is a powerful reducing agent because it has P-H bond. It reduces silver nitrate solution into silver.



#### Electronic structure



x - Electron of P  
• - Electron of Cl  
o - Electron of H

**Use:** It is used as a reducing agent

## II. Ortho phosphoric Acid, $\text{H}_3\text{PO}_4$

### Preparation

1. It is prepared by dissolving phosphorus pentoxide in water and boiling the solution.



2. **Laboratory preparation:** In the laboratory orthophosphoric acid can be prepared by boiling a mixture of red phosphorus with 50% nitric acid in a flask fitted with a reflux condenser on a water bath till no more oxides of nitrogen are liberated.

Iodine acts as a catalyst. The product is evaporated below 453 K and then cooled in a vacuum desiccator surrounded by freezing mixture when crystals of orthophosphoric acid are deposited.

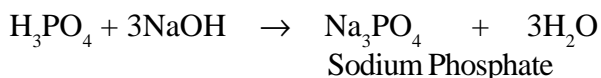
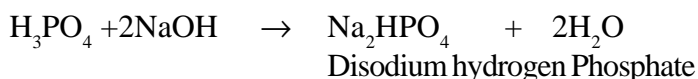
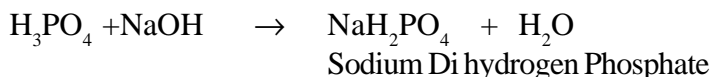


### Physical properties

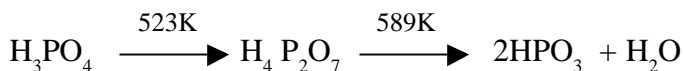
1. It is a deliquescent crystalline solid.
2. It is soluble in water.

### Chemical properties

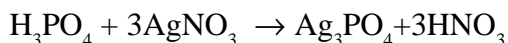
1. It is a tribasic acid. It combines with alkalies like NaOH to form three series of salts.



2. On heating it gives pyrophosphoric acid at 523 K and at 589 K gives metaphosphoric acid



3. On reaction with silver nitrate, it gives yellow precipitate of silver phosphate.

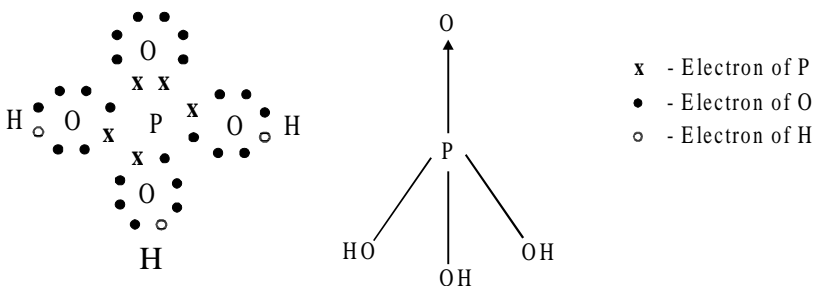


## Uses

1. It is used in the preparation of HBr and HI as a substitute for sulphuric acid.
2. It is used as souring agent in the preparation of soft drinks.
3. It is used in the preparation of phosphate salts of sodium, potassium and ammonium.
4. It is used in the manufacture of phosphatic fertilisers.

## Structure

Being a tribasic acid, the structure of phosphoric acid is represented as



## III. B. Pyrophosphoric acid, $\text{H}_4\text{P}_2\text{O}_7$

**Preparation:** Pyrophosphoric acid is prepared by heating orthophosphoric acid to 523 K – 533 K.

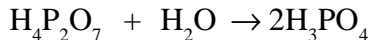


### Physical Properties

It is a colourless crystalline solid.

### Chemical Properties

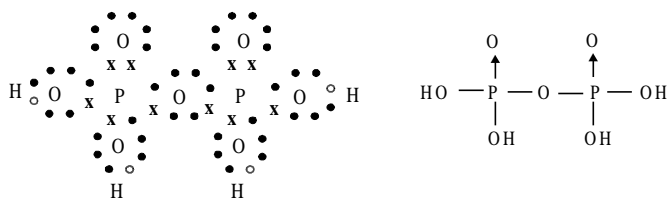
1. It is reconverted to orthophosphoric acid on boiling with water



2. When heated strongly, it yields metaphosphoric acid



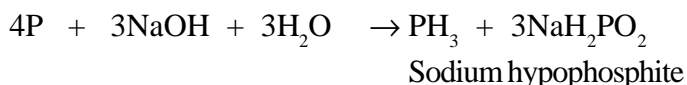
**Structure:** The Structure of pyrophosphoric acid is represented as:



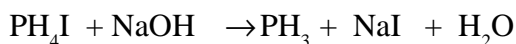
#### d) Phosphine - $\text{PH}_3$

Phosphine is the best known hydride of phosphorus.

**Laboratory preparation:** It is usually obtained by boiling white phosphorus with 30-40% solution of caustic soda in an inert atmosphere of  $\text{CO}_2$ .



Phosphine so obtained is impure. It is passed into an aqueous solution of hydrogen iodide,  $\text{PH}_4\text{I}$  is formed.  $\text{PH}_4\text{I}$  is heated with  $\text{KOH}$  or  $\text{NaOH}$ , pure phosphine is obtained.

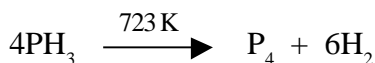


#### Physical properties

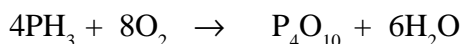
Phosphine is colourless gas with rotten fish odour.

#### Chemical properties

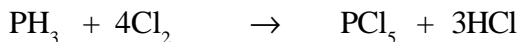
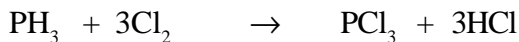
**1. Dissociation:** Phosphine dissociates at about 723 K and gives red phosphorus.



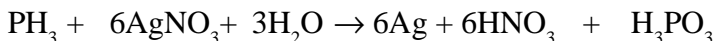
**2. Action of air:** It burns with oxygen and produces phosphorus pentoxide.



**3. Action of chlorine:** Phosphine burns in chlorine spontaneously forming  $\text{PCl}_3$  and  $\text{PCl}_5$ .



**4. Reducing properties:**  $\text{PH}_3$  is a powerful reducing agent. When it is passed through the salt solutions, corresponding metal is formed.

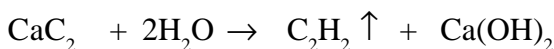
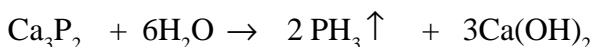


## Uses

### 1. Smoke screens

When  $\text{PH}_3$  burns it produces smoke which is dense enough to serve as smoke screens.

**2. Holme's signal :** Containers which have a perforated bottom and a hole at the top are filled with calcium phosphide and calcium carbide. These are thrown into the sea. Water enters the container through the bottom and reacts with calcium carbide and calcium phosphide to give acetylene and phosphine. Phosphine gets ignited spontaneously as it comes in contact with air and also ignites acetylene. Thus a bright red flame is produced which is accompanied by huge smoke due to the burning of phosphine. This serves as a signal to the approaching ships.



## Problem

An element 'A' occupies group number 15 and period number 3 reacts with chlorine to give **B** which further reacts with chlorine to give **C** at 273 K. Both B and C are chlorinating agent for organic compounds. **C** is a better chlorinating agent because it chlorinates metals also. **B** reacts with  $\text{SO}_3$  and reduces it to  $\text{SO}_2$ . **B** has a pyramidal shape. **C** has trigonal bipyramidal shape by  $\text{sp}^3\text{d}$  hybridisation. Identify the element A and the compounds B and C. Write the reactions.

1. The element which occupies group number 15 and period number 3 is phosphorus. Therefore A is phosphorus. Phosphorus reacts with chlorine



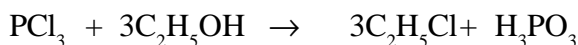
to give  $\text{PCl}_3$ . Therefore compound B is phosphorus trichloride and it has a pyramidal shape.



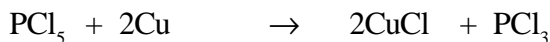
- $\text{PCl}_3$  further reacts with  $\text{Cl}_2$  to give  $\text{PCl}_5$ . Therefore, the compound C is phosphorus pentachloride and it has a trigonal bipyramidal shape.



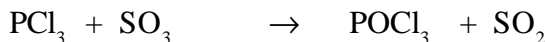
- $\text{PCl}_3$  and  $\text{PCl}_5$  are chlorinating agents for organic compounds. So, both reacts with  $\text{C}_2\text{H}_5\text{OH}$  gives  $\text{C}_2\text{H}_5\text{Cl}$ .



- $\text{PCl}_5$  is a better chlorinating agent. So it chlorinates copper.



- $\text{PCl}_3$  reacts with  $\text{SO}_3$  and reduces it to  $\text{SO}_2$ .



### 3.4 Group 16 THE 'OXYGEN' FAMILY

The group 16 (VI A) elements are oxygen, sulphur, selenium, tellurium and polonium. The first four elements are collectively called CHALCOGENS or ore forming elements, because many metal ores occur as oxides and sulphides.

- Oxygen the most abundant element, is an important constituent of atmosphere and ocean. It constitutes 46.6% earth's crust.
- Sulphur is less abundant and occurs in free and combined states. Sulphur is also known as Brim stone.
- Polonium, a radioactive element that occurs in trace amounts in uranium ores. Its name from Poland, the home country of Marie Curie who discovered the element in 1898.

#### General Trends

##### Electronic configuration

All of these elements have  $ns^2np^4$  configuration, just two electrons short of an octet configuration.

**Table 3.4 Electronic configuration of Group 16 elements**

Element	Atomic Number	Electronic Configuration	Group Number	Period Number
Oxygen	8	[He] $2s^2 2p^4$	16	2
Sulphur	16	[Ne] $3s^2 3p^4$	16	3
Selenium	34	[Ar] $3d^{10} 4s^2 4p^4$	16	4
Tellurium	52	[Kr] $4d^{10} 5s^2 5p^4$	16	5
Polonium	84	[Xe] $4f^{14} 5d^{10} 6s^2 6p^4$	16	6

**3.5 GROUP 17 - THE HALOGEN FAMILY**

Group 17 of the periodic table contains the elements fluorine, chlorine, bromine, iodine and astatine. These are collectively known as HALOGENS. It is derived from two Greek words Halo and Gens meaning “Salt producer”. Because most of them exist in Sea water.

**General Trends**

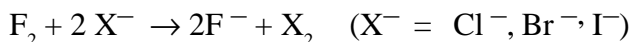
**Electronic Configuration:** All these elements possess  $ns^2 np^5$  configuration.

**Table 3.5 Electronic Configuration of group 17 elements**

Element	Atomic Number	Electronic Configuration	Group Number	Period Number
Fluorine	9	[He] $2s^2 2p^5$	17	2
Chlorine	17	[Ne] $3s^2 3p^5$	17	3
Bromine	35	[Ar] $3d^{10} 4s^2 4p^5$	17	4
Iodine	53	[Kr] $4d^{10} 5s^2 5p^5$	17	5
Astatine	85	[Xe] $4f^{14} 5d^{10} 6s^2 6p^5$	17	6

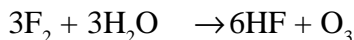
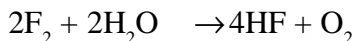
## Chemical Properties

**1. Oxidising power:** An important feature of the halogen is their oxidising property which is due to high electron affinity of halogen atoms. The oxidising power decreases from fluorine to iodine. Fluorine is the strongest oxidising agent. It oxidises other halide ions to halogens in solution or when dry.



Halogen of low atomic number oxidises the halide ion of higher atomic number.

**2. Solubility:** Halogens, being non-polar molecules, do not dissolve to a considerable extent in a polar solvent like water. However, fluorine reacts with water readily forming a mixture of  $\text{O}_2$  and  $\text{O}_3$ .



Chlorine, bromine and Iodine are more soluble in organic solvents such as  $\text{CCl}_4$ ,  $\text{CHCl}_3$  and produce yellow, brown and violet colour.

### 3. Hydrides of the Halogens (Hydrogen halides):

- All halogens react with hydrogen to form volatile covalent hydrides of formula  $\text{HX}$ .
- These hydrides are called hydracids.
- The activity of halogens towards hydrogen decreases from fluorine to iodine. Hydrogen combines explosively with fluorine even in dark. It combines with chlorine in the presence of sunlight and with bromine on heating. Hydrogen combines with iodine on heating and in presence of a catalyst.
- Hydracids are the reducing agents.
- Except  $\text{HF}$ , all hydrogen halides are gases.  $\text{HF}$  is a liquid because of inter molecular hydrogen bonding.

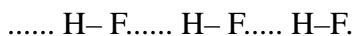


- The acidic character of  $\text{HX}$  are in the following order.



## Anomalous Nature of Fluorine

1. Fluorine is the most reactive element among halogen. This is due to the minimum value of F–F bond dissociation energy.
2. Fluorine decomposes cold dilute alkalis liberating  $\text{OF}_2$  and with conc. alkali,  $\text{O}_2$  is liberated. Under similar conditions, the other halogens will give rise to the hypohalites and halates respectively.
3. It has the greatest affinity for hydrogen, forming HF which is associated due to the hydrogen bonding. Hydrofluoric acid is a weak acid whereas the other hydrohalic acids are strong acids.

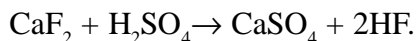


4. It differs markedly from the other halogens in that it can form two types of salts with metals.  $\text{NaF}$  and  $\text{NaHF}_2$ .
5. The salts of HF differ from the corresponding salts of other hydric acids.  $\text{AgF}$  is soluble in water while the other  $\text{AgX}$  are insoluble.
6. Being strongly electronegative it can have only a negative oxidation state while the other halogens can have negative as well as positive oxidation state.
7. HF attacks glass while others do not.
8. Fluorine, because of the absence of d-orbitals in its valence shell does not form any polyhalides. Thus we have  $\text{I}_3^-$ ,  $\text{Br}_3^-$ ,  $\text{Cl}_3^-$  ions but no  $\text{F}_3^-$  ion.

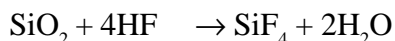
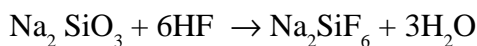
## ETCHING ON GLASS

### Etching glass

Industrially, hydrogen fluoride is obtained by heating fluorspar ( $\text{CaF}_2$ ) with concentrated  $\text{H}_2\text{SO}_4$  in a lead vessel.



HF distils over and the vapours are condensed in water in a lead receiver. Aqueous HF thus obtained is stored in wax bottles. It cannot be stored in glass or silica bottles as it attacks silicates and silica.



The action of hydrofluoric acid on silica and silicates is used for etching glass. The glass article is first covered with a film of wax. The design to be etched is now drawn on the waxed surface and is then exposed to the action of hydrofluoric acid. Now the glass can be very soon etched. The wax is finally washed off with turpentine.

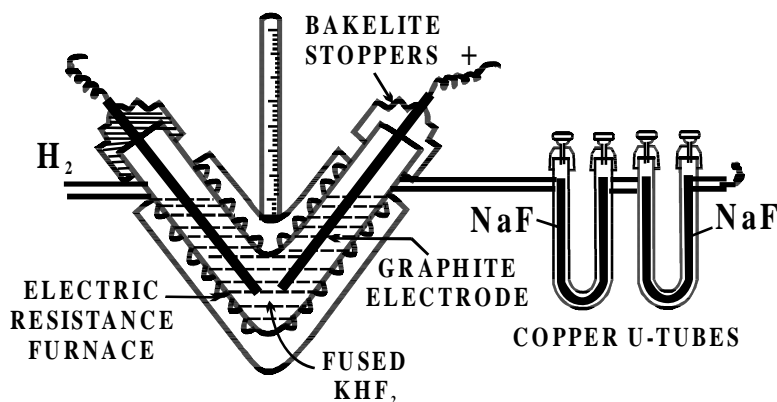
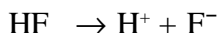
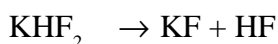
### 3.5.1 ISOLATION OF FLUORINE

Symbol - F    Atomic number - 9    Period Number : 2

Valency - 1    Atomic mass - 19    Group Number : 17

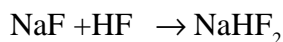
Fluorine does not occur free in nature. It occurs in the combined form.

**Dennis' Method:** This was devised by Dennis, Veeder and Rochow in 1931. In this fluorine is prepared by the electrolysis of fused sodium or potassium hydrogen fluoride (perfectly dry). Electrolysis is carried out between graphite electrodes in a V-shaped electrically heated copper tube. The ends of the tube are covered with copper caps into which the graphite electrodes are fixed with bakelite cement. The copper tube is thickly lagged to prevent loss of heat.



**Fig. 3.3 Preparation of fluorine**

Fluorine liberated at the anode is passed through the U-tube containing sodium fluoride. This removes the hydrogen fluoride vapours coming with fluorine.



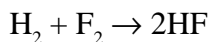
### Physical Properties

1. Fluorine is a gas and has pale greenish yellow colour.
2. It has extremely pungent and penetrating odour.
3. It is heavier than air.

### Chemical Properties

Fluorine is the most active member of halogen family.

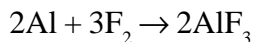
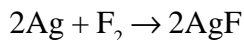
1. **Action with Hydrogen:** Hydrogen explodes violently in fluorine even in the dark.



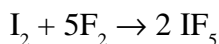
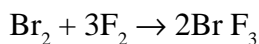
2. **Action with non-metals:** Non-metals like carbon, silicon and phosphorus burn in fluorine forming fluorides.



3. **Action with metals:** It reacts with metals forming corresponding fluorides.



4. **Formation of Interhalogen compounds:** It forms a variety of inter halogen compounds with other halogens.



## Uses

1. Fluorine is used in the manufacture of a series of compounds known as freons. These non-toxic, non-combustible and volatile liquids are used as refrigerants in refrigerators, deep freezers and air conditioners. The most common, freon is known as dichlorodifluoro methane  $\text{CF}_2\text{Cl}_2$ .
2.  $\text{CaF}_2$  is used as flux in metallurgy.
3.  $\text{NaF}$  is used as a preservative to prevent fermentation and also for preventing dental cavities.
4.  $\text{SF}_6$  is used as an insulating material in high voltage equipment.
5. Teflon is used as container to store hydrofluoric acid.
6.  $\text{UF}_6$  is used in the separation of  $\text{U}^{235}$  from  $\text{U}^{238}$ .

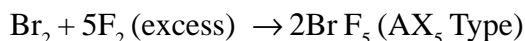
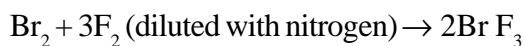
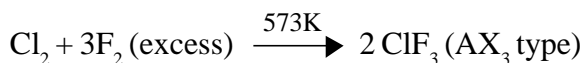
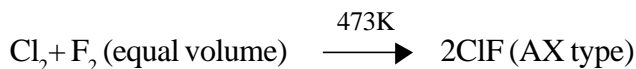
## INTERHALOGEN COMPOUNDS OR INTERHALOGENS

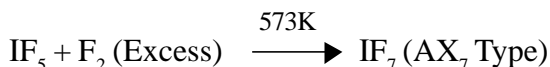
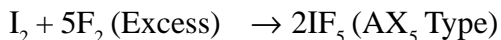
Each halogen combines with another halogen to form several compounds known as interhalogen compounds. The less electronegative element is written first. In naming also, the less electronegative element is mentioned first.

They are divided into four types.

$\text{AX}$	$\text{AX}_3$	$\text{AX}_5$	$\text{AX}_7$
$\text{ClF}$ $\text{BrF}$ $\text{BrCl}$ $\text{ICl}$ $\text{IBr}$	$\text{ClF}_3$ $\text{BrF}_3$ $\text{ICl}_3$	$\text{BrF}_5$ $\text{IF}_5$	$\text{IF}_7$

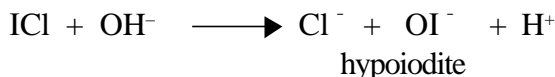
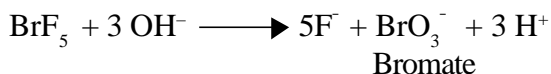
They can all be prepared by direct combination or by the action of a halogen on a lower interhalogen, the product formed depends on the conditions.





The bonds are essentially covalent because of the small electronegativity difference, and the melting and boiling points increase as the difference in electronegativity increases.

The interhalogens are generally more reactive than the halogens (except F) because the A-X bond is weaker than the X-X bond in the halogens. The reactions are similar to those of the halogens. Hydrolysis gives halide and oxyhalide ions, the oxyhalide ion being formed from the larger halogen present.

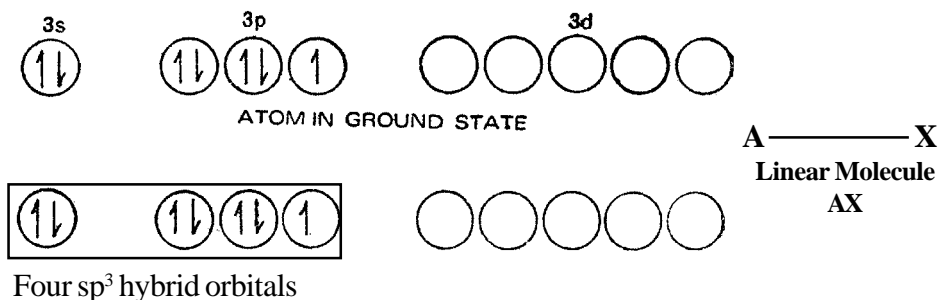


### Structures of interhalogen compounds

Interhalogen compounds are generally covalent compounds in which the larger halogen forms the central atom.

**1. Type AX.** As expected, the compounds of the type AX are linear. Thus ClF, BrF, BrCl, IBr and ICl are all **linear** in structure.

Electronic structure of Chlorine atom, in the ground state and hybridised state is represented as in Fig. 3.4.



**Figure 3.4 Linear structure of the interhalogen compounds of the type AX**



Although the spatial arrangement of the four electron pairs ( $bp = 1$  and  $lps = 3$ ) round the central chlorine atom is tetrahedral, due to the presence of three lone pairs of electrons in three hybrid orbitals, the shape of AX molecule gets distorted and become linear.

**2. Type  $AX_3$**  Compounds of the type  $AX_3$  have trigonal bipyramidal structure, Fig. 3.5 for the  $ClF_3$  molecule.

Bipyramidal structure arises out of  $sp^3d$  hybridisation involved in the formation of this compound, as illustrated in the Fig. 3.6. The three dotted arrows indicate electrons contributed by the three fluorine atoms (without lone pair it is T-shaped).

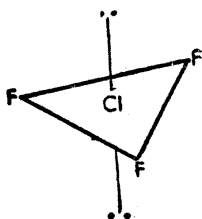


Fig. 3.5 Bi pyramidal structure of  $ClF_3$  molecule

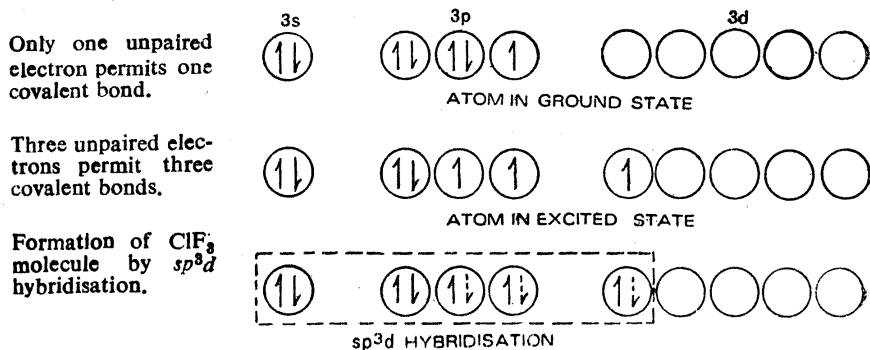


Fig. 3.6  $sp^3d$  hybridisation involved in the formation of  $ClF_3$  molecule

**3. Type  $AX_5$  ( $IF_5$ ,  $BrF_5$ , etc.)** These compounds are formed by  $sp^3d^2$  hybridisation and hence have an **octahedral** structure, as shown in Fig. 3.7 for the formation of  $IF_5$  molecule (without lone pair it is square pyramidal).

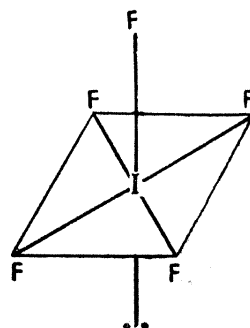
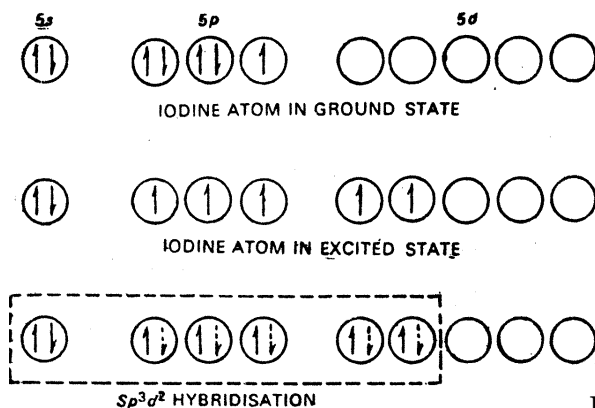


Fig. 3.7 Structure of  $IF_5$

4. **Type  $AX_7$  ( $IF_7$ ).** This compound has a pentagonalbipyramidal structure since this is formed by  $sp^3d^3$  hybridisation.

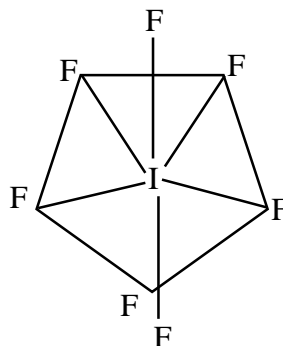
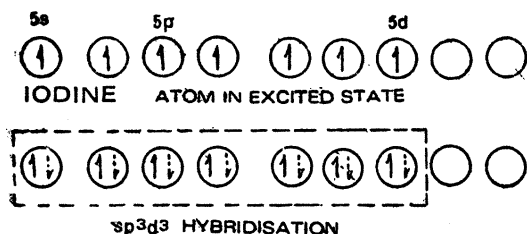


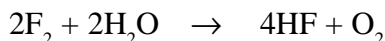
Fig. 3.8 Structure of  $IF_7$

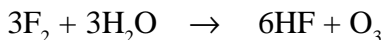
### Problem

An element **A** occupies group number 17 and period number 2, shows anomalous behaviour. **A** reacts with water forms a mixture of **B**, **C** and acid **D**. **B** and **C** are allotropes. **A** also reacts with hydrogen violently even in dark to give an acid **D**. Identify **A**, **B**, **C** and **D**. write the reactions.

### Solution

- The element **A** that occupies group number 17 and period number 2 is fluorine.
- Fluorine reacts with water and forms a mixture of **B** and **C**





Therefore, **B** is Oxygen and **C** is Ozone.

iii) Fluorine reacts with hydrogen to give **D**.



**D** is Hydrofluoric acid.

### 3.6 GROUP 18 NOBLE GASES OR INERT GASES

Group 18 of the periodic table consists of helium, neon, argon, krypton, xenon and radon. All these are gases under ordinary conditions of temperature and pressure. All of them (except Rn) are present in air in traces. Rn is obtained from radio active disintegration of radium.

On account of their very minute quantities in atmosphere, they were named as **rare gases**. Due to their chemical inactivity these were named as **inert gases**. A number of xenon compounds and two krypton fluorides were prepared and thus they were named as **noble gases**.

#### Electronic Configuration

All these elements possess  $ns^2 np^6$  configuration. The differentiating electron enters into p-sub shell and thus are included in p-block elements.

**Table 3.6 Electronic Configuration of Group 18 elements**

Element	Atomic Number	Electronic Configuration	Group Number	Period Number
Helium	2	$1s^2$	18	1
Neon	10	$1s^2 2s^2 2p^6$	18	2
Argon	18	$1s^2 2s^2 2p^6 3s^2 3p^6$	18	3
Krypton	36	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$	18	4
Xenon	54	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$	18	5
Radon	86	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6$	18	6

## ISOLATION OF NOBLE GASES

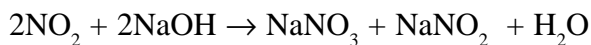
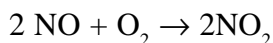
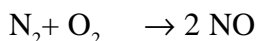
The noble gases are isolated from air by removing oxygen and nitrogen from air free from carbon-di-oxide, water vapour, dust particles, etc., This can be accomplished by either chemical methods or physical methods. In the chemical method, the unwanted gases are removed by means of compound formation while in the physical method, these are removed by the fractional evaporation of liquid air.

### CHEMICAL METHOD

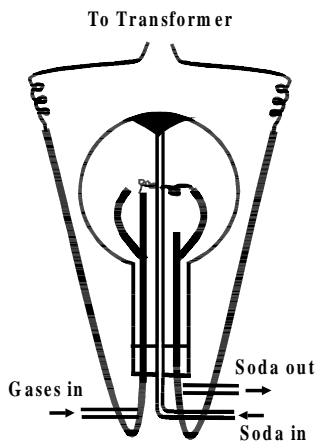
The first step in this method is to isolate the noble gases mixed together, from the atmosphere by passing repeated electric sparks in air so as to remove nitrogen and oxygen as nitrogen dioxide ( $\text{N}_2 + 2\text{O}_2 \rightarrow 2\text{NO}_2$ ). The second step is to separate the various constituents from one another taking advantage of the fact that they can be adsorbed on activated charcoal at different temperatures.

#### Step 1 Removal of oxygen and nitrogen of the atmosphere as Nitrogen dioxide

**Ramsay - Raleigh's method:-** A mixture of air and oxygen is constantly admitted into a glass globe of about 50 litres capacity. Two platinum electrodes are introduced and a discharge from a transformer of about 6000 - 8000 volts is passed by the action of which nitrogen and oxygen rapidly combine to form oxides of nitrogen. The oxides are dissolved out in a solution of sodium hydroxide continuously circulated through the flask.



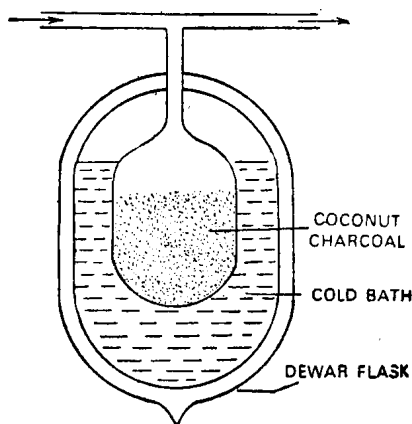
Oxygen if any is removed by introducing alkaline pyrogallol in the globe. The supply of air and electric discharge is shut after some time and the remaining mixture of noble gases is pumped out.



**Fig. 3.9 Chemical method for isolation of noble gases**

### **Step 2 Separation of noble gases (DEWAR'S METHOD)**

The mixture of noble gases obtained by the above method is separated into individual constituents by the use of coconut charcoal which adsorbs different gases at different temperatures.



**Fig. 3.10 Separation of noble gases (Dewar's method)**

The mixture of noble gases is passed into a double-walled bulb containing coconut charcoal and placed in a low temperature bath at 173K. It is allowed to remain in contact with the charcoal for about half an hour. At 173K, only argon,

krypton and xenon are adsorbed by the charcoal while helium and neon remain unadsorbed. These are pumped out and collected.

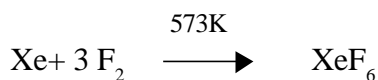
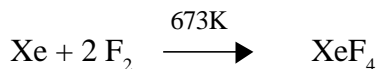
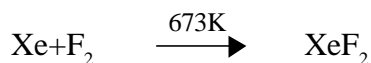
The mixture of helium and neon is kept in contact with coconut charcoal at 93K which completely adsorbs neon leaving free helium.

The charcoal at 173K containing argon, krypton and xenon is placed in contact with another charcoal at the temperature of the liquid air when argon diffuses into the other charcoal.

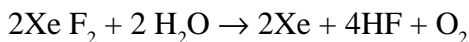
The temperature of the first charcoal (temp. 173K) still containing krypton and xenon is raised to 183K when krypton is set free while xenon remains adsorbed in the charcoal. When it is heated, xenon is recovered.

### **XENON FLUORIDE COMPOUNDS**

Xenon forms three binary fluorides  $\text{XeF}_2$ ,  $\text{XeF}_4$ , and  $\text{XeF}_6$  by the direct union of elements under appropriate experimental conditions.



**PROPERTIES:**  $\text{XeF}_2$ ,  $\text{XeF}_4$  and  $\text{XeF}_6$  are colourless crystalline solids subliming readily at 298K. They are powerful fluorinating agents. They are readily hydrolysed by even traces of water. For example.



**Structure:** The structure of the three xenon fluorides can be deduced from VSEPR theory.  $\text{XeF}_2$  and  $\text{XeF}_4$  have the linear and square planar structure respectively.  $\text{XeF}_6$  has 7 electron pairs (6 bonding and one lone pair) and thus has a distorted octahedral structure in the gas phase.

## USES OF NOBLE GAS

### (A) HELIUM

1. Because of its lightness and non-inflammability helium is used to filling balloons for meteorological observations.
2. Because of its lightness it is used in inflating aeroplane tyres.
3. Helium oxygen mixture is used by deep-sea divers in preference to nitrogen oxygen mixtures. It is much less soluble in blood than  $N_2$ . This prevents “**bends**” which is the pain caused by formation of nitrogen bubbles in blood veins when a diver comes to the surface.
4. A mixture of oxygen and helium is used in the treatment of asthma.
5. Liquid helium (b.pt 4.2K) is used as cryogenic agent for carrying out various experiments at low temperatures.
6. It is used to produce and sustain powerful super conducting magnets which form essential part of modern NMR Spectrometers and Magnetic Resonance Imaging system (MRI) for clinical diagnosis.

### (B) NEON

1. Neon is used in discharge tubes and fluorescent bulbs for advertisement display purposes.
2. Mixed with helium it is used to protect electrical instruments from high Voltages.
3. It is also used in beacon lights for safety of air navigation as the light possesses fog and storm-penetrating power.
4. Neon light is used in botanical gardens as it stimulates growth and helps the formation of chlorophyll.

### (C) ARGON

1. Mixed with 26% percent nitrogen it is used in gas filled electric lamps.
2. It is also used in radio valves and tubes.

### (D) KRYPTON AND XENON

1. Krypton and xenon are also used in filling incandescent metal filament electric bulbs.
2. They are also used to a small extent in discharge tubes.

### (E) RADON

1. It is used in radioactive research and in radiotherapy for treatment of cancer.

## SELF EVALUATION

### A. Choose the correct answer

- Which of the following does not belong to group 13?  
a) B      b) Al      c) Ge      d) In
- Which of the following is most abundant in earth's crust?  
a) C      b) Si      c) Ge      d) Sn
- An element which was burnt in limited supply of air to give oxide **A** which on treatment with water gives an acid. **B**. Acid **B** on heating gives acid **C** which gives yellow precipitate with  $\text{AgNO}_3$  solution **A** is  
a)  $\text{SO}_2$       b)  $\text{NO}_2$       c)  $\text{P}_2\text{O}_3$       d)  $\text{SO}_3$
- The compound with garlic odour is  
a)  $\text{P}_2\text{O}_3$       b)  $\text{P}_2\text{O}_5$       c)  $\text{H}_3\text{PO}_3$       d)  $\text{H}_3\text{PO}_4$
- The shape of  $\text{PCl}_5$  is  
a) pyramidal      b) trigonal bipyramidal  
c) linear      d) tetrahedral
- The compound used as smoke screen  
a)  $\text{PCl}_3$       b)  $\text{PCl}_5$       c)  $\text{PH}_3$       d)  $\text{H}_3\text{PO}_3$
- Which shows only -1 oxidation state?  
a) fluorine      b) bromine      c) chlorine      d) iodine
- One can draw the map of building on a glass plate by  
a) HI      b) HF      c) HBr      d) HCl
- Among the halogen acid, the weakest acid is  
a) HF      b) HCl      c) HBr      d) HI
- Halogens belong to the group number  
a) 14      b) 15      c) 17      d) 18



11. The noble gases are unreactive because they
  - a) have same number of electrons    b) have an atomicity of one
  - c) are gases with low densities       d) have stable electronic configuration.
12. The shape of  $\text{XeF}_4$  is
  - a) tetrahedral    b) octahedral    c) square planar    d) pyramidal
13. Which is not known?
  - a)  $\text{XeF}_6$             b)  $\text{XeF}_4$             c)  $\text{XeO}_3$             d)  $\text{ArF}_6$
14. The lightest gas which is non-inflammable is
  - a) He                b)  $\text{H}_2$                 c)  $\text{N}_2$                 d) Ar
15. Which of the following has highest first ionisation energy?
  - a) He                b) Ne                c) Ar                d) Kr.

**B. Answer in one or two sentences**

16. Write a note on plumbo solvency.
17.  $\text{H}_3\text{PO}_3$  is diprotic. Why?
18. Draw the structure of a)  $\text{PCl}_5$     b)  $\text{H}_3\text{PO}_3$
19. Prove that  $\text{P}_2\text{O}_5$  a powerful dehydrating agent.
20. Why  $\text{H}_2\text{O}$  is a liquid while  $\text{H}_2\text{S}$  is a gas?
21. Why the compounds of fluorine with oxygen are called fluorides of oxygen and not oxides of fluorine?
22. Fluorine atom is more electronegative than iodine atom yet, HF has lower acid strength than HI. Explain?
23. What are interhalogen compounds? How are they formed?
24. Discuss the oxidising power of fluorine.
25. How is  $\text{XeF}_6$  prepared?
26. Why do noble gases form compounds with fluorine and oxygen only?

27. Write the uses of Neon?

**C. Answer not exceeding 60 words**

28. What are silicones? How are they prepared? Mention its uses?

29. Give an account of manufacture of lead. Describe its important properties and uses.

30. How are the following compounds prepared from phosphorus?

a)  $P_2O_3$       b)  $P_2O_5$       c)  $PCl_3$       d)  $PCl_5$       e)  $PH_3$

31. How fluorine is isolated from their fluorides? Describe its important properties and uses.

32. Give a detailed account of the interhalogen compounds with special reference to the compounds involving iodine. Draw their structures.

33. Describe in detail how noble gases are isolated from air?

34. Give an account of various types of compounds which are formed by xenon?

**D. Practice Problems**

1. An element **A** belongs to 14<sup>th</sup> group is a metal, which can be cut with a knife. It is not a good conductor of heat and electricity. **A** in pure state does not react with water but air dissolved water forms hydroxide. Identify **A**.

2. An element **A** occupies group number 15 and period number 3, exhibits allotropy and it is tetra atomic. **A** reacts with caustic soda to give **B** which is having rotten fish odour. **A** reacts with chlorine to give **C** which has a smell of garlic. Identify **A**, **B** and **C**. Write the reactions.

3. An element **A** occupies group number 15 and period number 3, reacts with chlorine to give compound **B**. The compound **B** on hydrolysis gives a dibasic acid **C**. The compound **C** on heating undergoes auto oxidation and reduction to give a tribasic acid **D**. Identify the element **A**, compound **B**, **C** and **D**. Write the reactions.

4. An element **A** occupies group number 17 and period number 2, is the most electronegative element. Element **A** reacts with another element **B**, Which occupies group number 17 and period number 4, to give a compound **C**.

Compound **C** undergoes  $sp^3d^2$  hybridisation and has octahedral structure. Identify the elements **A** and **B** and the compound **C**. Write the reactions.

## SUMMARY

- Groups 13-18 of the periodic table are known as p-block elements.
- Group 13 is known as boron family. Potash alum is manufactured from alunite.
- Group 14 is known as carbon family. Silicones are organo silicon polymers. Lead is extracted from galena.
- Group 15 is known as nitrogen family. Phosphorus forms oxides, halides, oxyacids and hydrides.
- Group 16 is known as oxygen family.
- Group 17 is known as halogen family. Fluorine has different behaviour than other halogens. Halogens are extremely reactive and as such they are found in the combined state only. Fluorine is the most electronegative of all elements.  $F_2$  is obtained by electrolysis of their halide salts.
- Group 18 is known as rare gases or inert gases, with closed valence shell electronic configuration exhibit low chemical reactivity. Xenon can form compounds with fluorine.

## References

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# PHYSICAL CHEMISTRY

## 8. THE SOLID STATE - I

### OBJECTIVES

- *Definition of a crystalline solid.*
- *Difference between crystalline and an amorphous materials.*
- *Definition of a unit cell.*
- *Study of Sodium Chloride and Cesium Chloride unit cells.*
- *Definition of Miller Indices.*
- *Learn to identify the important planes in a cubic system in terms of Miller indices.*
- *To recognizes different types of cubic crystal system.*

### 8.1 Crystalline solids

Some solids, like sodium chloride, sulphur and sugar, besides being incompressible and rigid, have also characteristic geometrical forms. In these solids the atoms or molecules are arranged in a very regular and orderly fashion in a three dimensional pattern. Such substances are called **crystalline solid**.

The X-ray diffraction studies reveal that their ultimate particles (viz., molecules, atoms or ions) are arranged in a definite pattern throughout the entire three-dimensional net-work of a crystal. This definite and ordered arrangement of molecules, atoms or ions (as the case may be) extends over a large distance. This is termed as **long-range order**.

The outstanding characteristics of a crystalline solid are its sharp melting point. Crystalline solids are **anisotropic** since they exhibit different physical properties in all directions e.g., the electrical and thermal conductivities are different in different directions.

### Amorphous solids

There is another category of solids such as glass, rubber and plastics, which possess properties of incompressibility and rigidity to a certain extent but do not have definite geometrical forms. Such substances are called **amorphous solids**

Amorphous solids (from the Greek words for 'with out form') neither have ordered arrangement nor sharp melting point like crystals but when heated, they become pliable until they assume the properties usually related to liquids. These solids lack well-defined faces and shapes. Many amorphous solids are mixture of molecules that do not stick together well. Most others are composed of large complicated molecules. Amorphous solids are therefore regarded as super cooled liquids with high material becomes rigid but there the forces of attraction holding the molecules together are so great that the material becomes rigid but there is no regularity of structure. Thus, amorphous solids do not melt at specific temperatures. Instead they soften over a temperature range as intermolecular forces of various strengths are overcome.

Amorphous solids are **isotropic** as they exhibit same physical properties in all the directions.

**Difference between Crystalline and Amorphous Solids.** Crystalline and amorphous solids differ from one another in the following respects

### **1. Characteristic geometry**

A crystalline solid has a definite and regular geometry due to definite and orderly arrangement of molecules or atoms in three-dimensional space. An amorphous solid, on the other hand, does not have any pattern of arrangement of molecules or atoms and, therefore, does not have any definite geometrical shape. It has been found that even if some orderly arrangement of molecules or atoms exists in a few amorphous solids, it does not extend more than a few Angstrom units. Thus unlike crystalline solids, amorphous solids do not have a long range order.

### **2. Melting points**

As a solid is heated, its molecular vibrations increase and ultimately become so great that molecules break away from their fixed positions. They now begin to move more freely and have rotational motion as well. The solid now changes into liquid state. The temperature at which this occurs is known as the melting point.

A crystalline substance has a sharp melting point, i.e., it changes abruptly into liquid state. An amorphous substance, on the contrary, does not have a sharp melting point. For example, if glass is heated gradually, it softens and starts to flow without undergoing a definite and abrupt

change into liquid state. The amorphous solids are, therefore, regarded as liquids at all temperatures. There is some justification for this view because it is known from X-ray examination that amorphous substances do not have well-ordered molecular or atomic arrangements. Strictly speaking, solid state refers to crystalline state, i.e., only a crystalline material can be considered to be a true solid.

### 3. Isotropy and Anisotropy

Amorphous substances differ from crystalline solids and resemble liquids in another important respect. The properties such as electrical conductivity, thermal conductivity, mechanical strength and refractive index are the same in all directions. Amorphous substances are, therefore, said to be isotropic. Liquids and gases are also isotropic. Crystalline solids, on the other hand, are anisotropic, i.e., *their physical properties are different in different directions*. For example, the velocity of light passing through a crystal varies with the direction in which it is measured. Thus, a ray of light entering such a crystal may split up into two components each following a different path and travelling with a different velocity. This phenomenon is known as **double refraction**. Thus, anisotropy in itself is a strong evidence for the existence of ordered molecular arrangements in such materials. This can be shown on reference to Fig. 8.1 in which a simple two-dimensional arrangement of only two different kinds of atoms is depicted.

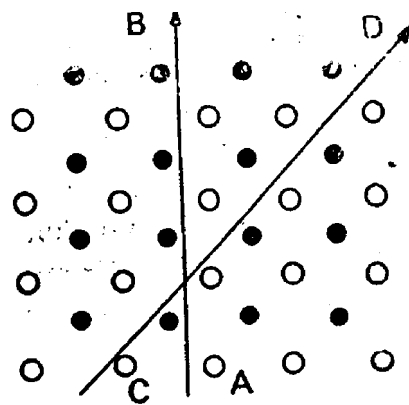


Fig. 8.1 Anisotropic behaviour of crystals

If the properties are measured along the direction indicated by the slanting line CD, they will be different from those measured in the direction indicated by the vertical line AB. The reason is that while in the first case, each row is made up of alternate type of atoms, in the second case, each row is made up of one type of atoms only. In amorphous solids as well as in liquids and gases, atoms or molecules are arranged at random and in a disorderly manner and, therefore, all directions are identical and all properties are alike in all directions.

### **Size and shape of crystals**

Several naturally occurring solids have definite crystalline shapes, which can be recognized easily. There are many other solid materials, which occur as powders or agglomerates of fine particles and appear to be amorphous. But when an individual particle is examined under a microscope, it is also seen to have a definite crystalline shape. Such solids, in which the crystals are so small that can be recognized only under a powerful microscope, are said to be **microcrystalline**. The size of a crystal depends on the rate at which it is formed: the slower the rate the bigger the crystal. This is because time is needed by the atoms or molecules to find their proper positions in the crystal structure. Thus, large transparent crystals of sodium chloride, silver chloride, lithium chloride, etc., can be prepared by melting these salts and allowing them to cool very slowly at a uniform rate. It is for this reason that crystals of most of the minerals formed by geological processes are often very large.

Crystals possess the following characteristic features:

i). **Faces:** Crystals are bound by plane faces. The surfaces usually planar and arranged on a definite plane (as a result of internal geometry), which bound crystals are called faces.

Faces are of two types:

*Like:* A crystal having all faces alike e.g. Fluorspar.

*Unlike:* A crystal having all faces not alike e.g. Galena.

ii) **Form:** All the faces corresponding to a crystal are said to constitute a form.

iii) **Edges:** The intersection of two adjacent faces gives rise to the formation of edge.

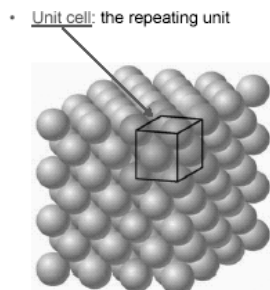
iv) Interfacial Angle: The angle between the normals to the two intersecting faces is called interfacial angle.

Although the size of the faces or even faces of the crystals of the same substance may vary widely with conditions of formation, etc., yet the interfacial angles for any two corresponding faces of the crystals remain invariably the same throughout.

Although the external shape is different yet the interfacial angles are same. The measurement of interfacial angles in crystals is, therefore, important in the study of crystals. The subject is known as **crystallography**.

## 8.2 Unit Cell

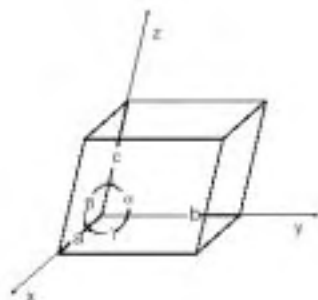
Crystals are built up of a regular arrangement of atoms or ions in three dimensions. *The smallest structure of which the crystalline solid (or crystal) is built by its repetition in three dimensions is called as unit cell.* A unit cell may be considered as the brick of a wall depends upon the shape of brick, the shape of crystal also depends upon the shape of unit cell. Therefore, a unit cell is the fundamental elementary pattern of a crystalline solid. The characterization of the crystal involves the identification of its unit cell.



### Characteristic parameters of unit cell

1. Crystallographic axes: The lines drawn parallel to the lines of intersection of any three faces of the unit cell which do not lie in the same plane are called crystallographic axes.
2. Interfacial angles: The angles between the three crystallographic axes are known as interfacial angles.
3. Primitives: The three sides  $a$ ,  $b$  and  $c$  (as shown in figure ) of a unit cell are known as primitives or characteristic intercepts.





Crystallographic axes : OX, OY, OZ

Interfacial angles :  $\alpha$ ,  $\beta$ ,  $\gamma$

Primitives (distances) : a, b, c

The unit cell is characterized by the distances a, b and c and angles  $\alpha$ ,  $\beta$  &  $\gamma$ .

The size (edge length) of a unit cell depends on the size of the atoms or ions and their arrangement. Because a unit cell is representative of the entire structure, the ratio of ions in the unit cell is the same as the ratio in the overall structure.

There are seven classes of unit cells. 1. *Cubic* , 2. *Triclinic*, 3. *Monoclinic*, 4. *Orthorhombic*, 5. *Tetragonal*, 6. *Hexagonal* and 7. *Rhombohedral*.

Packing arrangement variations exist in each of the classes, yet here we will only explore the cubic system because it is the simplest.

### **Cubic unit cells**

Three types of cubic unit cells are discussed in this chapter. Each unit cell is defined by one type of atom. Consequently, whichever atom you choose when defining that unit cell is the **only** atom used in defining the unit cell. (Ignore all other types.)

#### **Simple cubic**

The most simple unit cell is known as a simple cubic unit cell. This is where one atom occupies each of the eight corners of a cube. The distance from atom to atom along the lattice is the same in every direction, and the angle between each of axes is  $90^\circ$ .

### Body-centred cubic

The next unit cell is known as the body-centred cubic. In this form of crystal, there is an atom at each corner of the unit cell and also there is an additional atom in the center of the cube. This packing can fit more atoms into less space than the simple cubic unit cell.

### Face-centred cubic

A slightly more tightly packed unit cell is the face-centred cubic unit cell. In this form of crystal, there is an atom at each corner of the unit cell. And there is an atom at the center of each of the six faces of the cubic unit cell. This crystal packing form has an even higher density than the body-centred cubic unit cell.

Atoms or ions are shared between adjacent unit cells. The lattice position of the atom or ion determines the number of unit cells involved in the share. There are four different lattice positions an atom or ion can occupy.

Body: Not shared

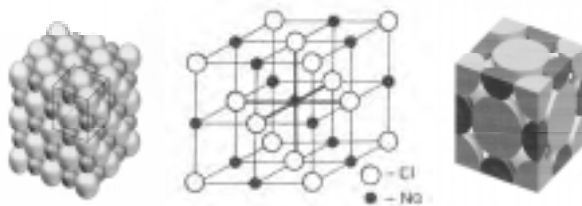
Face: Shared by two unit cells

Edge: Shared by four unit cells

Corner: Shared by eight unit cells.

### Sodium chloride crystal

Space lattice of sodium chloride is known to consist of a face-centered cubic lattice of  $\text{Na}^+$  ions interlocked with a similar lattice of  $\text{Cl}^-$  ions. A unit cell of this combined lattice is shown in figure. This unit cell repeats itself in three dimensions throughout the entire crystal. The yellow spheres indicate chloride ions and red spheres represent sodium ions. The lattices are constituted entirely by ions are known as **ionic lattices**. All electrovalent compounds show such lattices.



There are four units of NaCl in each unit cube with atoms in the positions

Cl: 0 0 0;             $\frac{1}{2}$   $\frac{1}{2}$  0;     $\frac{1}{2}$  0  $\frac{1}{2}$ ;    0  $\frac{1}{2}$   $\frac{1}{2}$  ;  
 Na:  $\frac{1}{2}$   $\frac{1}{2}$   $\frac{1}{2}$ ;        0 0  $\frac{1}{2}$ ;        0  $\frac{1}{2}$  0;     $\frac{1}{2}$  0 0;

As will be seen figure, the unit cell of sodium chloride consists of 14 chloride ions and 13 sodium ions. Each chloride ion is surrounded by 6 sodium ions and similarly, each sodium ion is surrounded by 6 chloride ions.

Notice that the particles at corners, edges and faces do not lie wholly within the unit cell. Instead these particles are shared by other unit cells. A particle at a corner is shared by eight unit cells, one at the centre of face is shared by two and one at the edge is shared by four. The unit cell of sodium chloride has 4 sodium ions and 4 chloride ions as shown below;

No. of Sodium ions

$$\begin{aligned}
 &= 12 \text{ (At edge centers)} \times (1/4) + 1 \text{ ( At body center)} \times 1 \\
 &= \frac{N_{ec}}{4} + \frac{N_b}{1} + \frac{N_F}{2} + \frac{N_C}{8} \\
 &= 12 \times \frac{1}{4} + 1 \times 1 = \mathbf{3 + 1 = 4}
 \end{aligned}$$

No. of Chloride ions

$$\begin{aligned}
 &= 8 \text{ (At corners)} \times (1/8) + 6 \text{ ( At face centre)} \times (1/2) \\
 &= 8 \times (1/8) + 6 \times (1/2) = \mathbf{1 + 3 = 4}
 \end{aligned}$$

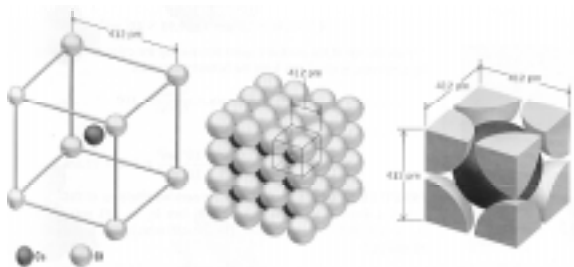
Thus, number of NaCl units per unit cell is 4.

The sodium chloride structure is also called rock-salt structure.

Representative crystals having the NaCl arrangements includes: LiH, NaI, KCl, RbF, RbI, PbS etc.

### Cesium Chloride structure

The cesium chloride, CsCl, structure has body-centred cubic system and is shown in figure. The body-centred cubic arrangement of atoms is not a close packed structure. There is one molecule per primitive cell, with atoms at the corners (000) and body-centred positions  $\frac{1}{2}$   $\frac{1}{2}$   $\frac{1}{2}$  of the simple cubic space lattice.



1. The  $\text{Cl}^-$  ions are at the corners of a cube where as  $\text{Cs}^+$  ion is at the centre of the cube or vice versa
2. Each  $\text{Cs}^+$  ion is connected eight  $\text{Cl}^-$  ions and each  $\text{Cl}^-$  ion is connected eight  $\text{Cs}^+$  ions i.e., 8:8 coordination. Thus each atom is at the center of a cube of atoms of the opposite kind, so that the coordination number is eight.

The unit cell of cesium chloride has one  $\text{Cs}^+$  ion and one  $\text{Cl}^-$  ion as shown below

No. of  $\text{Cl}^-$  ions

$$= 8(\text{At corners}) \times 1/8 (\text{common to eight unit cell})$$

$$= 8 \times 1/8 = \mathbf{1}$$

No. of  $\text{Cs}^+$  ion = 1 (At the body center)  $\times$  1

$$= 1 \times 1 = \mathbf{1}$$

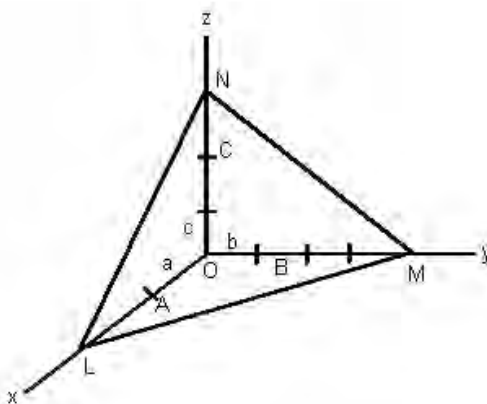
Thus number of CsCl units per unit cell is 1.

Representative crystals having the CsCl arrangements include: CsBr, CsI, TlBr, TlI,  $\text{NH}_4\text{Cl}$  etc.

### 8.3 Miller Indices

The geometry of a crystal may be completely defined with the help of coordinate axes all meeting at a point (origin). The number and inclination of these crystal intercept them at definite distances from the origin or are parallel to some of the axes, i.e., intercepting at infinity. The law of rational indices or intercepts states that it is possible to choose along the three coordinate axes unit distances (a, b, c) not necessarily of the same length such that the ratio of the intercepts of any plane in the crystal is given by (1a : mb : nc) where l, m and n are simple integers like 1, 2, 3 or fractions of whole numbers.

For example consider plane LMN in the crystal shown in Fig. 8.2.



**Fig. 8.2 The intercepts of a crystallographic plane**

This plane has intercepts OL, OM and ON along the x-, y- and z-axes at distances  $2a$ ,  $4b$  and  $3c$  respectively, when  $OA = a$ ,  $OB = b$  and  $OC = c$  are the chosen unit distances along the three coordinates. These intercepts are in the ratio of  $2a : 4b : 3c$  wherein 2, 4, 3 are simple integral whole numbers.

The coefficients of  $a$ ,  $b$  and  $c$  (2, 4 and 3 in this case) are known as the Weiss indices of a plane. It may be borne in mind that the Weiss indices are not always simple integral whole numbers as in this case. They may have fractional values as well as infinity (an indefinite quantity). Weiss indices are, therefore, rather awkward in use and have consequently been replaced by miller indices. Taking the reciprocals of Weiss indices and multiplying throughout by the smallest number in order to make all reciprocals as integers obtain the **Miller indices** of a plane. The Miller indices for a particular family of planes are usually written **(h, k, l)** where  $h$ ,  $k$  and  $l$  are positive or negative integers or zero.

Consider a plane which in Weiss notation is given by  $2a : 4b : 3c$ . Taking reciprocals of coefficients of  $a$ ,  $b$  and  $c$ , we get the ratio  $1/2$ ,  $1/4$ ,  $1/3$ . Multiplying by 12 in order to convert them into whole numbers, we get 6, 3, 4. These numbers are called the Miller indices of the plane, and the plane is designated as the (634) plane. In (634) plane,  $h = 6$ ,  $k = 3$  and  $l = 4$ .

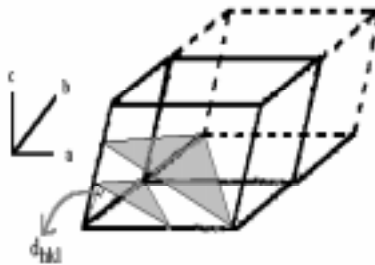
Similarly the Miller's indices for the plane which the Weiss notation is given by  $\infty a : 2b : c$ . Taking reciprocals of coefficients of  $a$ ,  $b$  and  $c$ , we get the ratio  $1/\infty, 1/2, 1/1$ , i.e.,  $0, 1/2, 1$ . Multiplying by 2 in order to convert them into whole numbers, we get  $0, 1, 2$ . The plane is designated as the  $(012)$  plane in which,  $h = 0, k = 1$  and  $l = 2$ .

The distances between parallel planes in a crystal are designated as  $d_{hkl}$ . For different cubic lattices these interplanar spacings are given by the general formula

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Where  $a$  is the length of the cube side while  $h$ ,  $k$  and  $l$  are the Miller indices of the plane.

#### Definition of Miller Indices in three dimensions



#### A pair of planes with Miller indices (213)

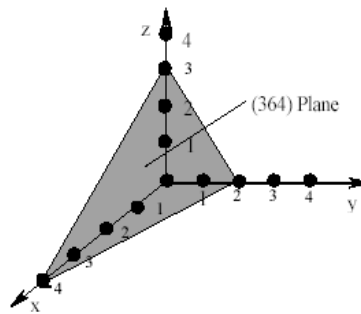
The **Miller indices** of a face of a crystal are inversely proportional to the intercepts of that face on the various axes.

The **Miller indices** of this particular family of planes are given by the reciprocals of the fractional intercepts along each of the cell directions. E.g.  $1/2 \times a, 1 \times b, 1/3 \times c$ .

The procedure for determining the miller indices for a plane is as follows:

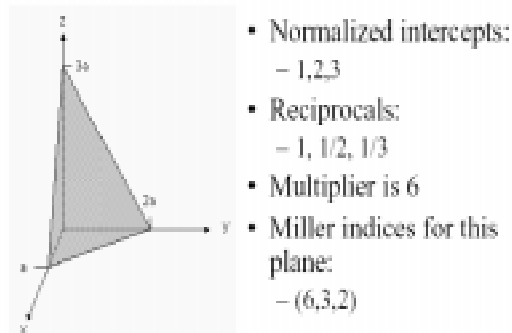
1. Prepare a three-column table with the unit cell axes at the tops of the columns.
2. Enter in each column the intercept (expressed as a multiple of  $a$ ,  $b$  or  $c$ ) of the plane with these axes.

3. Invert all numbers.
4. Clear fractions to obtain h, k and l.



Consider the x-, y-, z- axes in the above figure with the dots representing atoms in a single crystal lattice. To determine the Miller indices, one finds the intercepts on the three axis. The intercepts are:  $x = 4$ ,  $y = 2$  and  $z = 3$ . Then the reciprocals are taken, ie.,  $\frac{1}{4}$ ,  $\frac{1}{2}$ ,  $\frac{1}{3}$  and finally these fractions are reduced to the smallest integers, ie., 3, 6, 4 by 12. These are the Miller indices represented as (364).

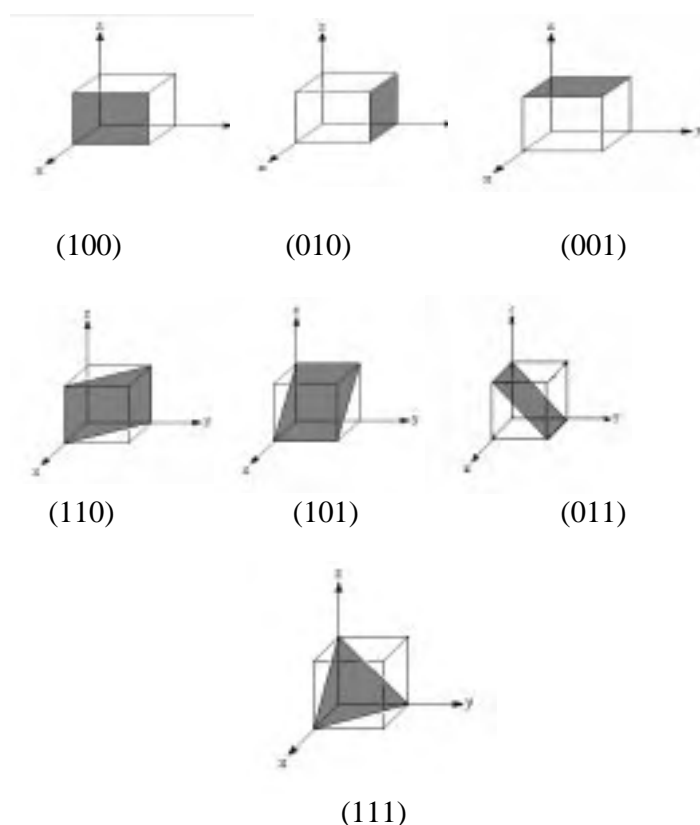
### Miller Indices: Example



Let us look at the most common planes in a cube, shown below in figure. As an example the front crystal face shown here intersects the x-axis but does not intersect the y- or z-axes but parallel to y and z axis. The front crystal face intersects only one of the crystallographic axes(x-axes). So the miller indices for the plane is (100). The side plane has intercepts

$x = \infty$ ,  $y = 1$ ,  $z = \infty$  because the plane is parallel to the  $x$ - and  $z$ -axes, forming the Miller indices gives (010). The top plane has intercepts  $x = \infty$ ,  $y = \infty$ ,  $z = 1$  because the plane is parallel to the  $x$ - and  $y$ - axes, forming the Miller indices gives (001).

The (110) plane intercepts  $x=1$ ,  $y=1$  and  $z = \infty$  which is parallel to  $z$ -axis. Similarly the other two planes are (101) and (011). The (111) plane intercepts all the three axes  $x=1$ ,  $y=1$  and  $z=1$ .



**Example 1:** Calculate the Miller indices of crystal planes which cut through the crystal axes at (i)  $(2a, 3b, c)$  (ii)  $(a, b, c)$  (iii)  $(6a, 3b, 3c)$  and (iv)  $(2a, -3b, -3c)$ .

**Solution :** following the procedure given above, we prepare the tables as follows:



(i)	a	b	c	
	2	3	1	intercepts
	$\frac{1}{2}$	$\frac{1}{3}$	1	reciprocals
	3	2	6	clear fractions

Hence, the Miller indices are (326).

(ii)	a	b	c	
	1	1	1	intercepts
	1	1	1	reciprocals
	1	1	1	clear fractions

Hence, the Miller indices are (111).

(iii)	a	b	c	
	6	3	3	intercepts
	$\frac{1}{6}$	$\frac{1}{3}$	$\frac{1}{3}$	reciprocals
	1	2	2	clear fractions

Hence, the Miller indices are (122).

(iv)	a	b	c	
	2	-3	-3	intercepts
	$\frac{1}{2}$	$-\frac{1}{3}$	$-\frac{1}{3}$	reciprocals
	3	-2	-2	clear fractions

Hence, the Miller indices are (322).

Note: The negative sign in the Miller indices is indicated by placing a bar on the integer. The Miller indices are enclosed within parentheses.

**Example 2:** How do the spacings of the three planes (100), (110) and (111) of cubic lattice vary?

Applying the formula

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

$$d_{(100)} = \frac{a}{\sqrt{1^2 + 0 + 0}} = a$$

$$d_{(110)} = \frac{a}{\sqrt{1^2 + 1^2 + 0}} = \frac{a}{\sqrt{2}}$$

$$d_{(111)} = \frac{a}{\sqrt{1^2 + 1^2 + 1^2}} = \frac{a}{\sqrt{3}}$$

$$\begin{aligned}\text{Thus } d_{(100)} : d_{(110)} : d_{(111)} &= 1 : 1/\sqrt{2} : 1/\sqrt{3} \\ &= 1 : 0.707 : 0.577\end{aligned}$$

**Example 3:** A metallic element exists as a cubic lattice. Each edge of the unit cell is  $2.88\text{\AA}$ . The density of the metal is  $7.20\text{ g cm}^{-3}$ . How many unit cells there will be in 100g of the metal?

**Solution:** Volume of unit cell  $= (2.88\text{\AA})^3 = 23.9 \times 10^{-24}\text{ cm}^3$

$$\begin{aligned}\text{Volume of 100 g of the metal} &= \frac{m}{\rho} \\ &= 100 = 13.9\text{ cm}^3\end{aligned}$$

$$\begin{aligned}\text{Number of unit cells in this volume} &= \frac{13.9\text{ cm}^3}{23.9 \times 10^{-24}\text{ cm}^3} = 5.82 \times 10^{23}\end{aligned}$$

**Example 4:** Calculate the number(n) of atoms contained within (i) a primitive cubic unit cell (ii) a body –centred cubic unit cell and (iii) a face-centred cubic (f.c.c) unit cell

**Solution:** (i) The primitive unit cell consists of one atom at each of the 8 corners; each atom is thus shared by 8 unit cells. Hence  $n = 8 \times (1/8) = 1$

(ii) The b.c.c unit cell consists of 8 atoms at the 8 corners and one atom at the centre. At each corner only  $1/8^{\text{th}}$  of the atom is within the unit cell. Thus the contribution of the 8 corners is  $8 \times (1/8) = 1$  while that of the body-centred atom is 1. Hence,  $n = 1+1 = 2$

(iii) The 8 atoms at the corners contribute  $8 \times (1/8) = 1$  atom. There is one atom each of the 6 faces, which is shared by 2 unit cells each. Therefore, the contribution face-centred atoms  $= 6 \times (1/2) = 3$  Hence,  $n = 1+3 = 4$ .

**Example 5 :** At room temperature, pollonium crystallizes in a primitive cubic unit cell. If  $a = 3.36\text{\AA}$ , calculate the theoretical density of pollonium; its atomic mass is  $209\text{ g mol}^{-1}$ .

**Solution:** A primitive cubic unit cell contains atoms only at the 8 corners with each corner contributing  $1/8^{\text{th}}$  of an atom. Hence  $n = 8 \times (1/8) = 1$ .

$$\text{Volume } V = a^3 = (3.36\text{\AA})^3$$

$$\begin{aligned} \text{From Eq. 1} \quad \rho &= \frac{nM_m}{N_0 V} \\ &= \frac{(1) 209 \text{ g mol}^{-1}}{(6.022 \times 10^{23} \text{ mol}^{-1}) (3.36 \times 10^{-8} \text{ cm})^3} \\ &= 9.15 \text{ g cm}^{-3} \end{aligned}$$

### Questions

#### A. Choose the best answer

- The structure of sodium chloride crystal is:
  - body centred cubic lattice
  - face centred cubic lattice
  - octahedral
  - square planar
- The number of atoms in a face centred cubic unit cell is:
  - 4
  - 3
  - 2
  - 1
- The 8:8 type of packing is present in:
  - CsCl
  - KCl
  - NaCl
  - MgF<sub>2</sub>
- In a simple cubic cell, each point on a corner is shared by
  - 2 unit cells
  - 1 unit cells
  - 8 unit cells
  - 4 unit cells
- An amorphous solid is :
  - NaCl
  - CaF<sub>2</sub>
  - glass
  - CsCl
- Each unit cell of NaCl consists of 4 chlorine ions and:
  - 13 Na atoms
  - 4 Na atoms
  - 6 Na atoms
  - 8 Na atoms
- In a body centred cubic cell, an atom at the body of centre is shared by:
  - 1 unit cell
  - 2 unit cells
  - 3 unit cells
  - 4 unit cells

8. In the sodium chloride structure, formula per unit cell is equal to  
(a) 2                      (b) 8                      (c) 3                      (d) 4
9. In a face centred cubic cell, an atom at the face centre is shared by:  
(a) 4 unit cell (b) 2 unit cells (c) 1 unit cells (d) 6 unit cells

**Answers:**

- 1) b    2) a    3) a    4) c    5) c    6) b    7) a    8) d    9) b

**B. Fill in the Blanks :**

1. In NaCl ionic crystal each  $\text{Na}^+$  ion is surrounded by -----  $\text{Cl}^-$  ions and each  $\text{Cl}^-$  ion is surrounded by -----  $\text{Na}^+$  ions.
2. The coordination number of  $\text{Cs}^+$  in CsCl crystal is -----
3. ----- solids do not possess sharp melting points and can be considered as ----- liquids.
4. A body centred unit cell has an atom at the each vertex and at ----- of the unit cell.
5. The three types of cubic unit cells are -----, ----- and -----
6. A crystal may have a number of planes or axes of symmetry but it possesses only one ----- of symmetry.
7. Amorphous solids that exhibit same physical properties in all the directions are called -----.
8. Crystalline solids that exhibit different physical properties in all directions are called -----.
9. The number of atoms in a single unit cell of cubic close packed sphere is -----
10. In a bcc, an atom of the body centre is shared by ----- unit cell.
11. The Weiss indices of a plane are  $1/2, 1/2, 1/2$ . Its miller indices will be ----- and the plane is designated as -----.
12. A plane is parallel to x & z axes and makes unit intercepts along y-axis. Its Weiss indices are ----- . Its Miller indices are ----- . The plane is designated as -----.

**Answers :**

- (1) 6, 6    (2) 8    (3) Amorphous, supercooled (4) Centre  
(5) simple cubic, bcc, fcc    (6) Centre    (7) isotropic  
(8) Anisotropic    (9) 4    (10) 1    (11) 2, 2, 2; (222) plane  
(12)  $\infty, 1, \infty$  ; 0, 1, 0 ; (010) plane

**C. Write in one or two sentence :**

1. What governs the packing of particles in crystals?
2. What is meant by 'unit cell' in crystallography?
3. How many types of cubic unit cell exists?
4. What are Miller Indices?
5. Mention the number of sodium and chloride ions in each unit cell of NaCl
6. Mention the number of cesium and chloride ions in each unit cell of CsCl

**D. Explain briefly on the following :**

1. Define and explain the following terms  
a) Crystalline solids b) Amorphous solids c) Unit cell
2. Give the distinguishing features of crystalline solids and amorphous solids.
3. Explain the terms Isotropy and Anisotropy.
4. What is the difference between body centred cubic and face centred cubic?
5. Draw a neat diagram for sodium chloride structure and describe it accordingly.
6. Draw a neat diagram for Cesium chloride structure and describe it accordingly.

**Problems**

1. How many atoms are there per unit cell in (i) simple cubic arrangement of atoms, (ii) body centred cubic arrangement of atoms, and (iii) face-centred cubic arrangement of atoms?  
Ans: (i) : 1, (ii) : 2 and (iii) : 4
2. How do the spacings of the three planes (100), (101) and (111) of simple cubic lattice vary?  
Ans: 1 :  $1/\sqrt{2}$  :  $1/\sqrt{3}$
3. How do the spacings of the three planes (001), (011) and (111) of bcc lattice vary?  
Ans:  $1/2$  :  $1/\sqrt{2}$  :  $1/2\sqrt{3}$
4. How do the spacings of the three planes (010), (110) and (111) of fcc lattice vary?  
Ans:  $1/2$  :  $1/2\sqrt{2}$  :  $1/\sqrt{3}$

## 9. GASEOUS STATE

### OBJECTIVES

- *To recognise the measurable properties of gases like  $P, V, T$  and mass.*
- *To learn various gas laws and ideal gas equation*
- *To learn different units of gas constant 'R'.*
- *To understand the Dalton's law of partial pressures & Graham's law of diffusion.*
- *To analyse the deviation of ideal behaviour and to know Vanderwaal's equation of state.*
- *To understand and deduce the relationship between critical phenomena and vanderwaal's constants.*
- *To understand Joule - Thomson effect and the role of inversion temperature.*
- *To know methods of liquefaction of gases and adiabatic demagnetisation.*

### 9.1 Properties of gases

Matter is known to exist in three states - solid, liquid and gas. A substance may be made to exist in any one of the three states by varying the temperature or pressure or both. Dynamic motion of molecules therefore is an inherent property in gaseous and liquid states of matter. The energy of motion known as kinetic energy is present in the gaseous molecules. Therefore the basic theory which explains the behaviour of gases is called as kinetic theory of gases.

A gaseous state can be described in terms of four parameters which are known as **measurable properties** such as the volume,  $V$ ; Pressure,  $P$ ; Temperature,  $T$  and Number of moles,  $n$  of the gas in the container.

#### Pressure effect

A gas may be considered to consist of a large number of molecules moving haphazardly all around in a vessel. Due to their constant motion, the molecules may not collide against one another very frequently, but can strike against the walls of the containing vessel. The molecular collisions are regarded as ideal (ie) perfectly elastic, so that there is no loss of energy in these collisions. **Pressure is defined as force per unit area.** This

depends upon the number of molecules that strike per unit area of the walls of the container in one second. The greater the number of molecules striking per unit area of the walls in one second, the greater would be the pressure exerted by the gas. Thus for example, when we pump air into a bicycle tube, the number of molecules within the tube increases and hence the number of collisions of the molecules with the walls per second increases and the pressure goes up.

### **Temperature effect**

The kinetic energy of molecules is given by  $\frac{1}{2}mv^2$  where  $m$  is the mass of the molecule and  $v$  is the velocity of its motion. When a gas is heated, its temperature increases. Although the mass of the molecule remains constant, its velocity increases. This causes an increase in kinetic energy. Therefore the molecules strike the wall of the containing vessel more frequently. In this case there is no change in the number of molecules, but the number of collisions against the walls of the container in a given time increases. Therefore the pressure of the gas increases with rise in temperature when the amount and its volume remain constant.

### **Volume effect**

The volume of the container is considered as the volume of the gas sample. This is considered from the postulates of kinetic theory of gases. That is, the volume of gas molecules themselves are negligible compared to the container volume. Volume of gas is determined by its pressure, temperature and number of moles at any instant.

### **Number of moles (n) effect**

Effects of pressure and volume of a gas bear a direct proportionality with number of moles. When 'n' increases the number of molecules colliding against the wall of container increases. This effect increases the pressure of the gas. When the amount of gas increases the volume occupied by themselves also, increases.

## **9.2 The gas laws**

### **Boyle's law**

Robert Boyle in 1662, studied the effect of change of pressure on the volume of a given mass of gas at constant temperature. According to

Boyle's law, for given mass of a gas at constant temperature, the pressure (P) is inversely proportional to its volume (V).

$$P \propto \frac{1}{V} \quad (\text{at constant temperature})$$

(or)

$$PV = \text{constant.}$$

Thus if  $V_1$  is the volume occupied by a given mass of a gas at pressure  $P_1$  and  $V_2$  is the volume when pressure changes to  $P_2$ , then as the temperature remains constant, according to Boyle's law

$P_1 V_1 = P_2 V_2 = \text{Constant}$
---------------------------------------

### Charle's Law

The variation in the volume of a gas with temperature at constant pressure is given by charle's law. The law may be stated as,

For a given mass of gas, at constant pressure, its volume (V) varies directly as its absolute temperature (T).

$V \propto T$	(or)	$\frac{V}{T} = \text{Constant}$
---------------	------	---------------------------------

Based on charle's law, the pressure - temperature relation is deduced as, for a given quantity of a gas, at constant volume, the pressure (P) varies directly as its absolute temperature (T)

$P \propto T$	(or)	$\frac{P}{T} = \text{Constant}$
---------------	------	---------------------------------

where T is temperature in kelvin.



### The equation of state for an ideal gas

Gases which obey Boyle's law and Charle's law are known as ideal gases. By combining these two laws, an equation of state of an ideal gas can be derived.

According to Boyle's law at constant temperature,

$$P \propto \frac{1}{V}$$

From Charle's law

$$P \propto T \text{ (at constant volume)}$$

By combining these proportionalities,

$$P \propto \frac{T}{V} \quad (\text{or}) \quad PV \propto T$$

$$\therefore PV = RT$$

where 'R' is a proportionality constant, commonly called as the **gas constant**. Generally, the ideal gas equation is written as

$$PV = n RT$$

where 'n' is the number of moles of the gas.

$$\text{No. of moles} = \frac{\text{Mass of the gas in gram } m}{\text{Molecular mass of the gas in gmol}^{-1} M} = \frac{m}{M} = \text{mol}$$

$$PV = \frac{m}{M} RT$$

m = mass of the gas.

The ideal gas equation can be written for a constant mass of a gas as,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

### Standard temperature and Pressure (S.T.P)

The conditions of a gas system present at standard temperature and standard pressure are its temperature at 273K and its pressure being at normal atmospheric pressure namely  $1.013 \times 10^5 \text{ Nm}^{-2}$  (1 atm). Value of R (Gas constant) depends on the different units of pressure and volume.

### 9.3 Numerical values of gas constant (R)

The numerical value of the gas constant 'R' depends upon the units in which pressure and volume are expressed,

$$R = \frac{PV}{T} \text{ (assuming one mole of gas)}$$

$$\begin{aligned} \therefore R &= \frac{\text{Pressure} \times \text{Volume}}{\text{Temperature}} \\ &= \frac{\text{Force}}{\text{Area}} \times \frac{\text{Volume}}{\text{Temperature}} \end{aligned}$$

Since Volume = Area x length

$$\begin{aligned} \therefore R &= \frac{\text{Force} \times \text{Length}}{\text{Temperature}} \\ &= \frac{\text{Work}}{\text{Temperature}} \end{aligned}$$

The dimensions of R are thus energy per degree per mole.

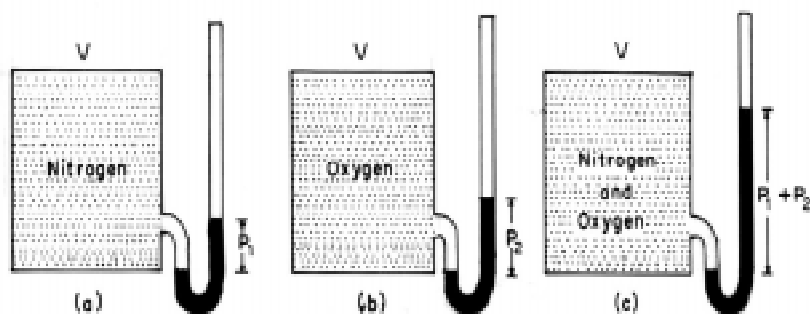
#### a. In litre - atmosphere

One mole of gas at S.T.P occupies a volume of 22.4 litre and thus

At STP

$$P = 1 \text{ atm} \quad R = PV/T \text{ (for 1 mole)}$$

$$V = 22.4 \text{ litre} \quad R = (1 \times 22.4)/273$$



**Fig. 9.1 Total pressure equals the sum of partial pressures of**

$$\begin{aligned} T &= 273 \text{ K} \quad R = 0.0821 \text{ litre atm K}^{-1} \text{ mol}^{-1} \\ &= 0.0821 \text{ dm}^3 \cdot \text{atm K}^{-1} \text{ mol}^{-1} \\ (\because 1 \text{ litre} &= 1 \text{ dm}^3) \end{aligned}$$

**b. In C.G.S. System**

At STP 1 mole of gas has

$$\begin{aligned} P &= 1 \text{ atm} = 1 \times 76 \times 13.6 \times 980 \text{ dyne cm}^{-2} \\ &= 1.013 \times 10^6 \text{ dyne cm}^{-2} \end{aligned}$$

$$V = 22400 \text{ cm}^3; T = 273 \text{ K}$$

$$PV = 1.013 \times 10^6 \times 22400$$

$$\therefore R = \frac{PV}{T} = \frac{1.013 \times 10^6 \times 22400}{273}$$

$$R = 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}$$

**c. In M.K.S. System**

In MKS or SI units, the unit of R is joule

$$\text{Since } 10^7 \text{ erg} = 1 \text{ Joule}$$

$$\therefore R = 8.314 \text{ Joule K}^{-1} \text{ mol}^{-1}$$

$$1 \text{ calorie} = 4.184 \text{ Joule}$$

$$\therefore R = 1.987 \text{ cal deg}^{-1} \text{ mol}^{-1}$$

#### 9.4 Dalton's law of partial Pressures

When two or more gases, which do not react chemically, are mixed together in a vessel, the total pressure of the mixture is given by Dalton's law of partial pressures which states that,

"At constant temperature, the total pressure exerted by the gaseous mixture is equal to the sum of the individual pressures which each gas would exert if it occupies the same volume of mixture fully by itself. Partial pressure is the measure of the pressure of an individual gas in a mixture of same volume and temperature.

Thus, if  $p_1, p_2, p_3 \dots$  are the partial pressures of the various gases present in a mixture, then the total pressure  $P$  of the gaseous mixture is given by

$P = p_1 + p_2 + p_3 \dots$ , provided the volume and temperature of mixture and that of the individual gases are the same.

#### Equation of state of a Gaseous mixture

Let a gaseous mixture consists of  $n_A, n_B$  and  $n_C$  moles of three ideal gases A, B and C respectively, subjected to constant  $T$  and  $V$ , then, according to ideal gas equation.

$$p_A = \frac{n_A RT}{V}; \quad p_B = \frac{n_B RT}{V}$$

and

$$p_C = \frac{n_C RT}{V}$$

where  $p_A, p_B, p_C$  are the partial pressures of A,B,C gases respectively. Hence the total pressure of the mixture is given as

$$P = p_A + p_B + p_C$$

$$P = \frac{n_A RT}{V} + \frac{n_B RT}{V} + \frac{n_C RT}{V}$$

$$\therefore PV = (n_A + n_B + n_C) RT$$

This equation is known as **equation of state of gaseous mixture**.

### Calculation of Partial Pressure

In order to calculate the pressure ( $p_A$ ) of the individual component say A, in a mixture (A and B), which is equal to the partial pressure of A, according to the equation of state of gaseous mixture it is seen that,

$P$  = Total pressure of the mixture

$$P = (n_A + n_B) \frac{RT}{V}$$

$$\text{But } p_A = \frac{n_A}{V} RT \quad \text{and} \quad p_B = \frac{n_B}{V} RT$$

The ratio is given by

$$\begin{aligned} \frac{p_A}{P} &= \frac{n_A}{(n_A + n_B)} \cdot \frac{V}{RT} \cdot \frac{RT}{V} \\ &= x_A = \text{mole fraction of A.} \end{aligned}$$

Or

$$\boxed{p_A = X_A P}$$

i.e:- Partial pressure,  $p_A$  = mole fraction of A x total pressure. Similarly;

$$\boxed{p_B = X_B P}$$

Thus, the partial pressure of the individual component in the mixture can be calculated by the product of its mole fraction and total pressure.

### Problem 1

Calculate the partial pressures  $N_2$  and  $H_2$  in a mixture of two moles of  $N_2$  and two moles of  $H_2$  at STP.

$$p_{N_2} = \frac{\text{number of moles of } N_2}{V} \times RT$$

$$p_{H_2} = \frac{\text{number of moles of } H_2}{V} \times RT$$

$$\begin{aligned} \text{Mole fraction of } N_2 = X_{N_2} &= \frac{2}{2+2} \\ &= \frac{2}{4} = 0.5 \end{aligned}$$

$$\therefore X_{H_2} = 0.5 \quad (X_{N_2} + X_{H_2} = 1.0)$$

$$RT$$

$$\text{But } P = \frac{RT}{V} \text{ . For 1 mole, } V = 22.4 \text{ litres}$$

$$\begin{aligned} \text{For 4 moles } V &= 4 \times 22.4 \text{ litres and} \\ R &= 0.0821 \text{ lit - atm K}^{-1}\text{mol}^{-1} \end{aligned}$$

$$P = \frac{0.0821 \times 273}{4 \times 22.4} = 0.2501 \text{ atm.}$$

$$p_{N_2} = 0.2501 \times 0.5 = 0.1251 \text{ atm}$$

$$p_{H_2} = 0.2501 \times 0.5 = 0.1251 \text{ atm}$$

### Self Test

Calculate the partial pressures of  $O_2$  and  $H_2$  in a mixture of 3 moles of  $O_2$  and 1 mole of  $H_2$  at S.T.P.

[Ans:  $p_{O_2} = 0.1876 \text{ atm}$ ;  $p_{H_2} = 0.0625 \text{ atm}$ ]

## 9.5 Graham's Law of Diffusion

When two gases are placed in contact, they mix spontaneously. This is due to the movement of molecule of one gas into the other gas. This process of mixing of gases by random motion of the molecules is called as **diffusion**.

In 1829, Graham formulated what is now known as Graham's law of diffusion. It states that,

"Under the same conditions of temperature and pressure, the rates of diffusion of different gases are inversely proportional to the square roots of their molecular masses". Mathematically the law can be expressed as

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

where  $r_1$  and  $r_2$  are the rates of diffusion of gases 1 and 2, while  $M_1$  and  $M_2$  are their molecular masses respectively.

When a gas escapes through a pin-hole into a region of low pressure or vacuum, the process is called **Effusion**. The rate of diffusion of a gas also depends on the molecular mass of the gas. Dalton's law when applied to effusion of a gas is called the Dalton's law of Effusion. It may be expressed mathematically as

$$\frac{\text{Effusion rate of Gas 1}}{\text{Effusion rate of Gas 2}} = \sqrt{\frac{M_2}{M_1}}$$

The determination of rate of effusion is much easier compared to the rate of diffusion. Therefore Dalton's law of effusion is often used to find the molecular mass of a given gas.

### Problem 2

If a gas diffuses at the rate of one-half as fast as  $O_2$ , find the molecular mass of the gas.

### Solution

Applying Graham's law of diffusion.

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}; \quad \frac{1/2}{1} = \sqrt{\frac{32}{M_1}}$$

Squaring both sides of the equation

$$\left(\frac{1}{2}\right)^2 = \frac{32}{M_1} \quad (\text{or}) \quad \frac{1}{4} = \frac{32}{M_1}$$

$$M_1 = 128$$

Thus the molecular mass of the unknown gas is 128.

### Self Test

If a gas diffuses at the rate of one quarter as fast as  $N_2$ . Find the molecular mass.

[Ans = 448]

### Problem 3

50ml of gas A effuse through a pin - hole in 146 seconds. The same volume of  $CO_2$  under identical conditions effuse in 115 seconds. Calculate the molecular mass of A.

$$\frac{\text{Effusion rate of } CO_2}{\text{Effusion rate of A}} = \sqrt{\frac{M_A}{M_{CO_2}}}$$

$$\frac{50/115}{50/146} = \sqrt{\frac{M_A}{44}}; \quad (1.27)^2 = \frac{M_A}{44}$$

$M_A = 71$   $\therefore$  Molecular mass of A is 71.

### Self Test

75ml of gas A effuses through a pin hole in 73 seconds. The same volume of  $SO_2$  under identical conditions effuses in 75 seconds. Calculate the molecular mass of A.

(Ans = 60.6)



## 9.6 Causes for deviation of real gas from ideal behaviour

The perfect gas equation of state is given by

$$PV = nRT$$

The gases which obey this equation exactly are referred as ideal gases or perfect gases. Real gases do not obey the perfect gas equation exactly. Real gases show deviation because of intermolecular interaction of the gaseous molecules. Repulsive forces between the molecules cause expansion, and attractive forces cause reduction in volume. Under the conditions of low pressure and high temperature the inter-molecular interactions of the gaseous molecules are lower and tend to behave ideally under these conditions. At other conditions of pressure and volume, deviations are seen.

### Volume deviation

Based on one of the postulates of the kinetic theory of the gases it is assumed that the volume occupied by the gaseous molecules themselves is negligibly small compared to the total volume of the gas. This postulate holds good for ideal gases and only under normal conditions of temperature and pressure for real gases. When temperature is lowered considerably, the total volume of the real gas decreases tremendously and becomes comparable with the actual volume of gaseous molecules. In such cases, the volume occupied by the gaseous molecules cannot be neglected in comparison with total volume of the gas.

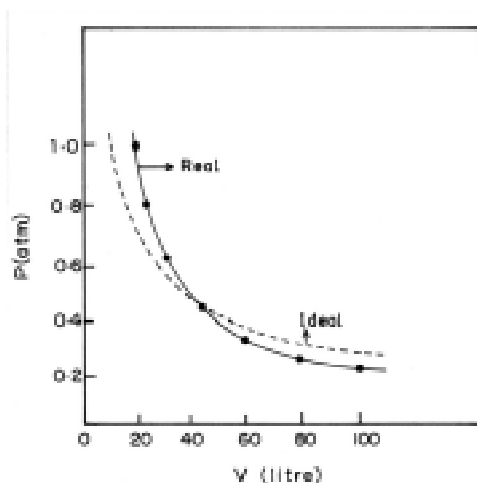


Fig. 9.2 Pressure - volume dependence of ideal and real gases

Thus, the volume deviations created at high pressure and low temperature make the real gas to deviate from the ideal behaviour.

### Pressure deviation

For an ideal gas the forces of attraction between the gaseous molecule are considered to be nil at all temperature and pressure.

For a real gas this assumption is valid only at low pressure or at high temperature. Under these conditions, the volume of the gas is high and the molecules lie far apart from one another. Therefore the intermolecular forces of attraction becomes negligible.

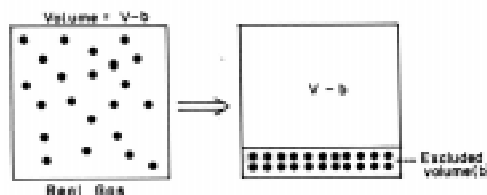
But at high pressure (or) at low temperature, the volume of the gas is small and molecules lie closer to one another. The intermolecular forces of attraction becomes appreciable and cannot be neglected. Therefore it is necessary to apply suitable corrections to the pressure of the real gas in the equation of state.

## 9.7 Vanderwaal's Equation of state

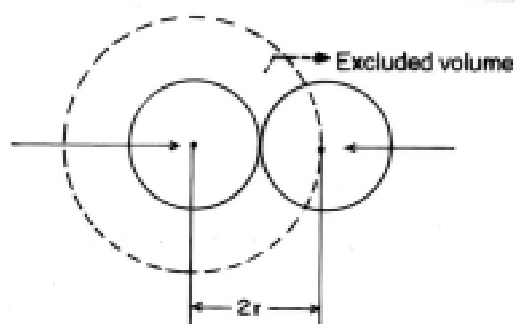
For an ideal gas  $PV = nRT$ , is considered as the equation of state. By including the correction terms in the ideal gas equation to account for (i) volume of the gaseous molecules themselves in  $V$  and (ii) the intermolecular forces of attraction in pressure,  $P$ , the equation of state for the real gas is arrived, J.O Vanderwaal's deduced the equation of state of real gases.

### i) Volume correction of real gas

The volume of a gas is the free space in the container in which molecules move about. Volume  $V$  of an ideal gas is the same as the volume of the container. The volume of a real gas is, therefore, ideal volume minus the volume occupied by the gas molecules themselves. If  $V_m$  is the volume of the single molecule then, the excluded volume which is termed as "b" is determined as follows.



**Fig. 9.3 Free volume and excluded volume of a real gas**



**Fig. 9.4 Collision diameter (2r) and excluded volume of real gas molecules**

Let us consider two colliding molecules with radius 'r'. The space indicated by dotted sphere of radius 2r will not be available for other molecules to freely move about. (i.e) the dotted spherical volume is known as **excluded volume** per pair of the molecules.

Thus,

$$\text{excluded volume for two molecules} = \frac{4}{3} \pi (2r)^3$$

$$= 8 \left( \frac{4}{3} \pi r^3 \right)$$

Excluded volume per molecule

$$V_C = \frac{1}{2} \times 8 \frac{4}{3} \pi r^3$$

$$= 4 V_m$$

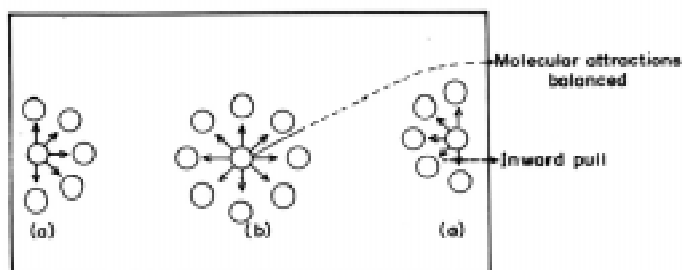
where  $V_m$  is the actual volume of a single molecule.

∴ The excluded volume for n molecules, 'b' = 4n  $V_m$ , where 4  $V_m$  is the excluded volume of a molecule.

∴ The corrected volume of the real gas is  $= (V-b)$  = free space for molecular movement.

## ii) Pressure Correction

In a real gas the pressure deviation is caused by the intermolecular forces of attraction. According to kinetic theory, the pressure of the gas is directly proportional to forces of bombardment of the molecules on the walls of the container. Consider a molecule placed in the interior of the container. It is surrounded equally by other gas molecules in all directions such that the forces of attraction in any direction is cancelled (or) nullified by similar force operating in the opposite direction. However a molecule near the wall of the container which is about to strike is surrounded unequally by other gaseous molecules as shown in Fig 9.5.



**Fig. 9.5 Intermolecular forces of attraction and pressure deviation in real gas molecules**

The molecule near the wall experiences attractive forces only such that it will strike the wall with a lower force which will exert a lower pressure than if such attractive forces are not operating on it. Therefore it is necessary to add the pressure correction term to the pressure of the gas to get the ideal pressure. The corrected pressure should be  $P + p'$  where  $p'$  is the pressure correction factor.

The force of attraction experienced by a molecule near the wall depends upon the number of molecules per unit volume of the bulk of the gas. It is found experimentally that,  $p'$  is directly proportional to the square of the density of the gas ( $\rho$ ) which is a measure of the intermolecular attraction of the molecules.

$$(i.e) \quad P' \propto \rho^2 \quad \left( \text{where } \rho = \frac{n}{V} \right)$$

Density is inversely related to the volume 'V' which is the volume occupied by one mole of the gas. Therefore P' of one mole of the gas is given by

$$P' \propto \frac{1}{V^2} ; \quad (or) \quad \left( P' = \frac{a}{V^2} \right)$$

where 'a' is a proportionality constant that depends upon the nature of the gas.

$$\begin{aligned} \therefore \text{corrected pressure} &= P + P' \\ &= \left( P + \frac{a}{V^2} \right) \end{aligned}$$

Replacing the term for corrected volume and the corrected pressure in the ideal gas equation for one mole, the equation of state of the real gas is

$$\left( P + \frac{a}{V^2} \right) (V-b) = RT$$

where 'a' and 'b' are known as vanderwaal's constants.

This equation is also known as Vanderwaal's equation of state.

If there are 'n' moles of the real gas then the vanderwall's equation becomes

$$\boxed{\left( P + \frac{n^2 a}{V^2} \right) (V-nb) = nRT}$$

### Units for vanderwaal's constant

The dimensions of the vanderwaal's constant a and b depend upon the units of P and V respectively.

$$a = \frac{\text{Pressure} \cdot (\text{Volume})^2}{\text{mole}^2}$$

$$a = \text{atm} \cdot \text{dm}^6 \text{mol}^{-2} \quad (\text{1 litre} = 1 \text{ dm}^3)$$

Thus a is expressed as  $\text{atm} \cdot \text{dm}^6 \text{mol}^{-2}$  units. If volume is expressed in  $\text{dm}^3$  then b is expressed as

$$\frac{\text{Vol}}{n} = \frac{\text{dm}^3}{\text{mol}}$$

$$\frac{V}{n} = \text{dm}^3 \text{mol}^{-1}$$

$$\text{Unit of b} = \text{dm}^3 \text{mol}^{-1}$$

### Significance of Vanderwaal's constant (a) and (b)

1. The term  $a/V^2$  is the measure of the attractive forces of the molecules. It is also called as the cohesion pressure (or) internal pressure.
2. The inversion temperature of a gas can be expressed in terms of 'a' and 'b'

$$T_i = \frac{2a}{Rb}$$

3. The vanderwaal constants 'a' and 'b' enable the calculation of critical constants of a gas.

### Problem 4

One mole of carbon-dioxide was found to occupy a volume of 1.32 litre at  $48^\circ\text{C}$  and at a pressure of 16.4 atm. Calculate the pressure of the gas that would have been expected to behave ideally and non-ideally.

$$\begin{aligned}
 [a &= 3.59 \text{ atm dm}^6 \text{ mol}^{-2}]; \\
 [b &= 4.27 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ and} \\
 R &= 0.082 \text{ dm}^3 \text{ atm deg}^{-1} \cdot \text{mol}^{-1}] \\
 V &= 1.32 \text{ lit} \\
 T &= 48 + 273 = 321 \text{ K} \\
 R &= 0.082 \text{ dm}^3 \cdot \text{atm K}^{-1} \cdot \text{mol}^{-1}
 \end{aligned}$$

$$(n = 1 \text{ mole})$$

For ideal behaviour,

$$\begin{aligned}
 PV &= RT \\
 P &= \frac{RT}{V} = \frac{0.082 \times 321}{1.32} \\
 P_{\text{ideal}} &= 19.94 \text{ atm}
 \end{aligned}$$

For real behaviour,

$$\begin{aligned}
 P &= \frac{RT}{V-b} - \frac{a}{V^2} \quad (n = 1 \text{ mole}) \\
 P &= \left( \frac{0.082 \times 321}{1.32 - 0.0427} \right) - \left( \frac{3.59}{(1.32)^2} \right) \\
 &= 20.6 - 2.06 \\
 P_{\text{real}} &= 18.54 \text{ atm}
 \end{aligned}$$

### Limitations of Vanderwaal's equation

1. It could not explain the quantitative aspect of deviation satisfactorily as it could explain the qualitative aspects of P and V deviations.
2. The values of 'a' and 'b' are also found to vary with P and T, and such variations are not considered in the derivation of Vanderwaal equation.
3. Critical constants calculated from Vanderwaal's equation deviate from the original values determined by other experiments.

## 9.8 Critical phenomena

The essential condition for the liquefaction of the gas is described by the study of critical temperature, critical pressure and critical volume and their inter relationships.

When a gaseous system is transformed to its liquid state, there is a tremendous decrease in the volume. This decrease in volume can be effectively brought about by lowering of temperature, or by increasing pressure (or) by both. In both these effects the gaseous molecules come closer to each other and experience an increase in force of attraction which results in liquefaction of gases. At any constant temperature when pressure is increased volume is decreased and vice versa. Such P-V curves at constant temperature are known as isotherms. A typical isotherm can be considered similar to Fig.9.2.

The figure 9.2 shows the continuous decrease in pressure with increase in volume for both ideal and real gases. There is a definite deviation exhibited by the real gas from ideal gas behaviour at high pressure and low volumes.

### Critical temperature ( $T_c$ )

It is defined as the characteristic temperature of a gas at which increase in pressure brings in liquefaction of gas above which no liquefaction occurs although the pressure may be increased many fold. For instance  $T_c$  of  $\text{CO}_2$  is  $31.1^\circ\text{C}$ . This means that it is not possible to liquefy  $\text{CO}_2$  by applying pressure when its temperature is above  $31.1^\circ\text{C}$ .

### Critical pressure ( $P_c$ )

It is defined as the minimum pressure required to liquefy 1 mole of a gas present at its critical temperature.

### Critical volume ( $V_c$ )

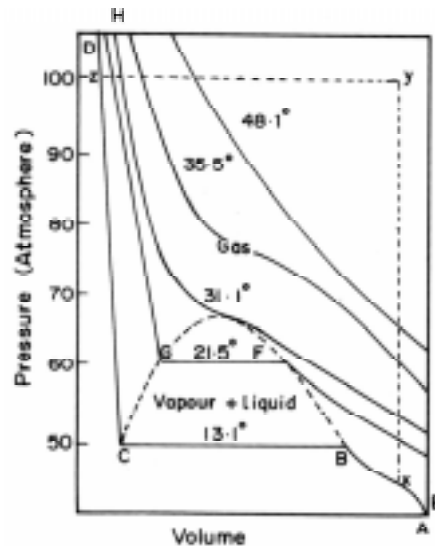
The volume occupied by 1 mole of a gas at its critical pressure and at critical temperature is the critical volume ( $V_c$ ) of the gas.

A gas is said to be at its **critical state** when its pressure, volume and temperature are  $P_c$ ,  $V_c$  and  $T_c$ .



### 9.8.1 Andrews isotherms of carbondioxide

The importance of critical temperature of a gas was first discovered by Andrews in his experiments on pressure - volume isotherms of carbon dioxide gas at a series of temperature. The isotherm of carbondioxide determined by him at different temperatures are shown in Fig.9.6.



**Fig. 9.6 Andrews isotherms of carbondioxide**

Consider first the isotherm at the temperature 13.1°C. The point A represents carbondioxide in the gaseous state occupying a certain volume under a certain pressure. On increasing the pressure its volume diminishes as is indicated by the curve AB. At B, liquefaction of gas commences and thereafter a rapid decrease in the volume takes place at the same pressure, since more and more of the gas is converted into the liquid state. At C, the gas becomes completely liquefied. After 'C' the increase of pressure produces only a very small decrease in volume. This is shown by a steep line CD which is almost vertical. Thus, along the curve AB, carbon dioxide exist as gas. Along BC, it exists in equilibrium between gaseous and liquid state. Along CD it exists entirely as a liquid. The isotherm at 21.5°C shows that the decrease in volume becomes smaller because higher the temperature greater is the volume. Therefore more pressure is applied to

decrease the volume. This effect makes liquefaction to commence at higher pressure compared to the previous isotherm at 13.1°C.

At still higher temperature, the horizontal portion of the curve becomes shorter and shorter until at 31.1°C it reduces to a point. The temperature 31.1°C is regarded as the critical temperature of CO<sub>2</sub>. At this temperature, the gas passes into liquid imperceptibly. Above 31.1°C the isotherm is continuous. CO<sub>2</sub> cannot be liquefied above 31.1°C no matter how high the pressure may be. The portion of area covered by curve H with zyx portion always represents the gaseous state of CO<sub>2</sub>.

## 9.8.2 Continuity of state

### Thomson's experiment

Thomson (1871) studied the isotherm of CO<sub>2</sub> drawn by Andrews. He suggested that there should be no sharp points in the isotherms below the critical temperature. These isotherms should really exhibit a complete continuity of state from gas to liquid. This, he showed as a theoretical wavy curve. The curve MLB in Fig.9.7 represents a gas compressed in a way that it would remain stable. The curve MNC represents a superheated liquid because compression above T<sub>c</sub>, leads to heating effects. This type of continuity of state is predicted by Vanderwaal's equation of state which is algebraically a cubic equation. The Vanderwaal's equation may be written as

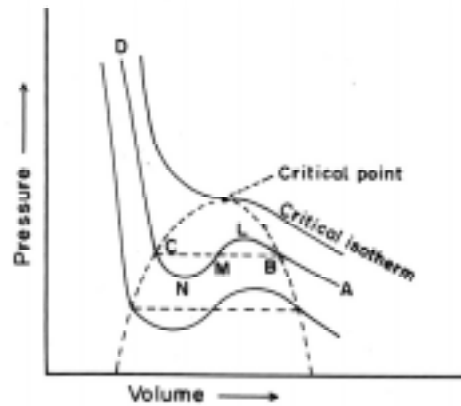
$$\left( P + \frac{a}{V^2} \right) (V-b) = RT$$

expanding the expression,

$$PV - Pb + \frac{a}{V} - \frac{ab}{V^2} - RT = 0$$

Multiplying by V<sup>2</sup>

$$PV^3 - (RT + Pb) V^2 + aV - ab = 0$$



**Fig. 9.7 Thomson's isotherms of CO<sub>2</sub>**

Thus, for any given values of  $P$  and  $T$  there should be three values of  $V$ . These values are indicated by points B, M and C of the wavy curve. The three values of  $V$  become closer as the horizontal part of the isotherm rises. At the critical point the three roots of Vanderwaal 'V' become identical and there is no longer any distinction between the gas and liquid states. Here, the gas is said to be in critical state. This effect enables the calculation of  $T_c$ ,  $P_c$  and  $V_c$  in terms of Vanderwaal's constants.

### 9.8.3 Derivation of critical constants from Vanderwaal's constants

Let us derive the values of critical constants  $T_c$  (critical temperature),  $V_c$  (critical volume) and  $P_c$  (critical pressure) in terms of the Vanderwaal's constants 'a' and 'b'. The Vanderwaal's equation is given by

$$\left( P + \frac{a}{V^2} \right) (V-b) = RT \quad (1)$$

Expanding this equation

$$PV + \frac{a}{V} - Pb - \frac{ab}{V^2} - RT = 0 \quad (2)$$

$$\begin{aligned}
 & \text{Multiplying by } \frac{V^2}{P} \\
 & \frac{V^2}{P} \left( PV + \frac{a}{V} - Pb - \frac{ab}{V^2} - RT \right) = 0 \\
 & \therefore V^3 + \frac{aV}{P} - bV^2 - \frac{ab}{P} - \frac{RTV^2}{P} = 0 \quad (3)
 \end{aligned}$$

Rearranging this equation in the powers of V

$$V^3 - \left( \frac{RT}{P} + b \right) V^2 + \frac{aV}{P} - \frac{ab}{P} = 0 \quad (4)$$

For this cubic equation of V, three roots (values of V) are possible. At the critical point, the three values of V become identical and is equal to the critical volume ( $V_c$ ).

Therefore  $V = V_c$  at  $T_c$

$$\therefore (V - V_c) = 0 \quad (5)$$

$$\therefore (V - V_c)^3 = 0 \quad (6)$$

upon expanding this equation

$$V^3 - 3V_c V^2 + 3V_c^2 V - V_c^3 = 0 \quad (7)$$

This equation is identical with the cubic equation derived from Vanderwaal's equation if we substitute T by  $T_c$  and P by  $P_c$ .

$$V^3 - \left( \frac{RT_c}{P_c} + b \right) V^2 + \frac{aV}{P_c} - \frac{ab}{P_c} = 0 \quad (8)$$

Equating the powers of V from equation

$$-3 V_c V^2 = - \left( \frac{RT_c}{P_c} + b \right) V^2$$

$$3 V_c = b + \frac{RT_c}{P_c} \quad (9)$$

$$3 V_c^2 = \frac{a}{P_c} \quad (10)$$

$$V_c^3 = \frac{ab}{P_c} \quad (11)$$

$$\frac{V_c^3}{3V_c^2} = \frac{ab}{P_c} \cdot \frac{P_c}{a}$$

$$\frac{V_c}{3} = b$$

$$\text{or } \boxed{V_c = 3b} \quad (12)$$

substituting  $V_c = 3b$  in equation (11)

$$(3b)^3 = \frac{ab}{P_c}$$

$$27b^3 = \frac{ab}{P_c}$$

$$\boxed{P_c = \frac{a}{27b^2}} \quad (13)$$

substituting the value of  $V_c$  and  $P_c$  in equation (9)

$$\begin{aligned}
 3 \times 3b &= b + \frac{RT_c}{a} \times 27b^2 \\
 9b - b &= \frac{RT_c}{a} 27b^2 \\
 8b &= \frac{RT_c 27b^2}{a} \\
 \boxed{T_c = \frac{8a}{27Rb}} & \quad (14)
 \end{aligned}$$

Hence the critical constants can be calculated using the values of Vanderwaal's constants of a gas and vice versa. Since  $P_c$  and  $T_c$  can often be determined experimentally, these values may be employed to calculate the constants  $a$  and  $b$ .

$$\begin{aligned}
 a &= 3V_c^2 P_c \\
 b &= \frac{V_c}{3}
 \end{aligned}$$

Based on the critical temperature values, gases are categorised as "permanent" and "temporary" gases.  $H_2$ ,  $N_2$ ,  $He$ , .... gases having very low critical temperature belong to the permanent type. Gases like  $NH_3$ ,  $CO_2$ ,  $SO_2$ ,  $HCl$  etc. having critical temperature in the ordinary range of temperatures belong to the temporary gases type.

### Problem 5

Vanderwaal's constants for hydrogen chloride gas are  $a = 3.67 \text{ atm lit}^{-2}$  and  $b = 40.8 \text{ ml mol}^{-1}$ . Find the critical temperature and critical pressure of the gas.

**Solution**

$$\begin{aligned}
 T_c &= \frac{8a}{27Rb} \\
 &= \frac{8 \times 3.67}{27 \times 0.0821 \times 0.0408} = 324.7 \text{ K} \\
 &= 51.7^\circ\text{C} \\
 P_c &= \frac{a}{27b^2} = \frac{3.67}{27 \times (0.0408)^2} \\
 &= 81.6 \text{ atm}
 \end{aligned}$$

**Problem 6**

The critical temperature of hydrogen gas is  $33.2^\circ\text{C}$  and its critical pressure is 12.4 atm. Find out the values of 'a' and 'b' for the gas.

**Solution :** We know

$$T_c = \frac{8a}{27Rb} \quad \dots (i); \quad P_c = \frac{a}{27b^2} \quad \dots (ii)$$

Dividing (i) by (ii) we get

$$\frac{T_c}{P_c} = \frac{8a}{27Rb} \times \frac{27b^2}{a} = \frac{8b}{R} \quad \dots (iii)$$

Given  $T_c = 33.2^\circ\text{C} = 33.2 + 273 = 306.2\text{K}$  and  $P_c = 12.4 \text{ atm}$ ;  $R = 0.082 \text{ atm. litre K}^{-1} \text{ mol}^{-1}$ . Substituting the values in equation (iii), we get

$$\frac{306.2}{12.4} = \frac{8 \times b}{0.082}$$

$$b = \frac{306.2 \times 0.082}{12.4 \times 8}$$

$$= 0.253 \text{ litre mol}^{-1}.$$

Now, substituting the value of 'b' in equation (i) we have

$$T_c = \frac{8a}{27Rb} \quad (\text{or}) \quad 306.2 = \frac{8 \times a}{27 \times 0.082 \times 0.253}$$

$$(\text{or}) a = 21.439 \text{ atm litre}^2 \text{ mol}^{-1}$$

### 9.9 Joule-Thomson Effect

Joule-Thomson showed that when a compressed gas is forced through a porous plug into a region of low pressure, there is appreciable cooling.

The phenomenon of producing lowering of temperature when a gas is made to expand adiabatically from a region of high pressure into a region of low pressure, is known as Joule - Thomson effect.

When the gas is allowed to escape into a region of low pressure the molecules move apart rapidly against the intermolecular attractive forces. In this case work is done by the gas molecules at the expense of internal energy of the gas. Therefore cooling occurs as the gas expands. This reduction in the temperature is generally referred as Joule-Thomson effect and is used in the liquefaction of gases.

### 9.10 Inversion temperature (Ti)

The Joule-Thomson effect is obeyed by a gaseous system only when its temperature is below a characteristic value. The characteristic temperature below which a gas expands adiabatically into a region of low pressure through a porous plug with a fall in temperature is called as inversion temperature (Ti).

Ti is characteristic of a gas and it is related to the Vanderwaal's constant 'a' and 'b',

$T_i = \frac{2a}{Rb}$
-----------------------



At the inversion temperature there is no Joule Thomson effect (ie) there is neither fall nor rise in temperature. Only when the temperature of the gas is below the inversion temperature there is a fall in temperature during adiabatic expansion. If the temperature of the gas is above  $T_i$  there is a small rise in temperature. For gases like  $H_2$  and He whose  $T_i$  values are very low  $-80^\circ\text{C}$  and  $-240^\circ\text{C}$  respectively, these gases get warmed up instead of getting cooled during the Joule-Thomson experiment. These gases will obey Joule-Thomson effect only when they are cooled to a temperature below these  $T_i$  values.

### **9.11 Conditions of liquefaction of gases**

Many industrial processes require large quantities of liquid air, liquid ammonia, liquid carbondioxide etc. The production of liquids from various gases is therefore an important commercial operation.

There are different methods of liquefaction of gases, such as (i) based on the concept of critical temperature followed by the compression (ii) based on Joule-Thomson effect (iii) Adiabatic demagnetisation.

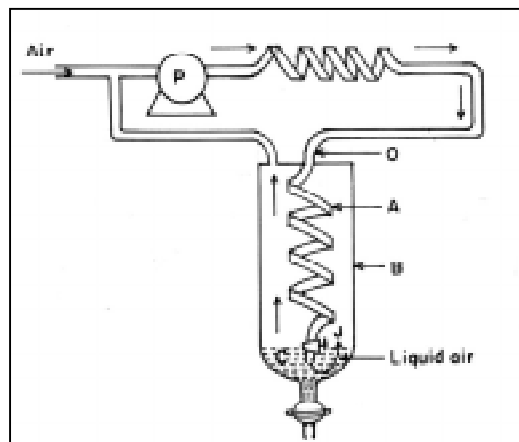
In the case of gases like  $NH_3$ ,  $Cl_2$ ,  $SO_2$  and  $CO_2$  whose  $T_c$  values are near and below the ordinary temperatures, they can be liquefied easily by increasing the pressure alone at their respective  $T_c$  values.

Gases like  $H_2$ ,  $O_2$ ,  $N_2$  and He have very low  $T_c$  values and hence Joule Thomson effect may be applied to bring in effective cooling.

Helium is cooled by Joule-Thomson effect to a lower temperature and further cooling for its liquefaction, is carried out by the method of adiabatic demagnetisation.

#### **Linde's Method**

This method makes use of Joule Thomson effect and is used to liquify air or any other gas. Pure air or any gas is first compressed to about 200 atmospheres and is allowed to enter the innertube of the concentric pipes as shown in Fig.10.8. The valve v of jet J is then opened and the gas is allowed to expand suddenly into the wider chamber C.



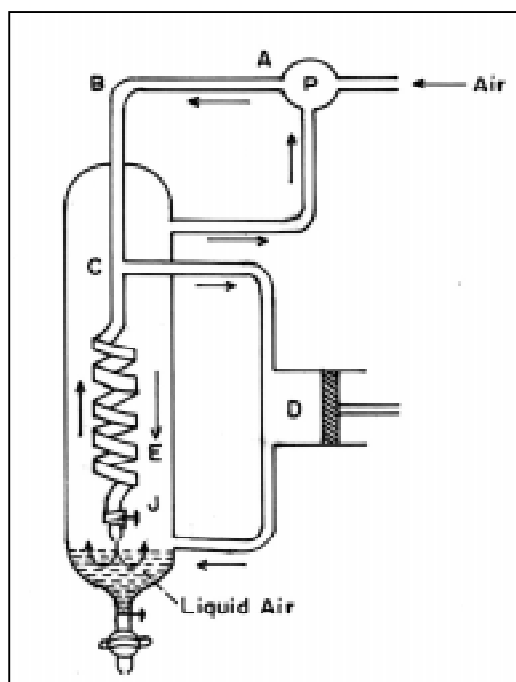
**Fig. 9.8 Linde's apparatus for liquefaction of gas**

The gas gets cooled due to expansion and its pressure is reduced to about 50 atm. The gas is now allowed to pass through the outer tube 'O'. At this stage the incoming gas is initially cooled by the outgoing gas. Further cooling of the incoming gas occurs during expansion in the chamber C. The cooled gas is again compressed and is circulated in. By repeating the process of cooling and compression followed by expansion, the gas is liquefied and finally the liquid air drops out from the jet into the bottom of chamber C.

### **Claude's process**

In this method compressed air is allowed to do mechanical work of expansion. This work is done at the expense of the kinetic energy of the gas and hence a fall of temperature is noted. This principle is combined with Joule-Thomson effect and utilised in Claude's process of liquefaction of air. Air is compressed to about 200 atmospheres and is passed through the pipe ABC (Fig.9.9). At C, a part of the air goes down the spiral towards the jet nozzle J and a part of the air is led into the cylinder D provided with an air tight piston. Here the air moves the piston outwards and expands in volume as a result of which considerable cooling is produced. The cooled air passes up the liquefying chamber during which process it cools the portion of the incoming compressed air. The precooled incoming compressed air then experiences Joule-Thomson expansion when passed through Jet nozzle J

and gets cooled further. The above process takes place repeatedly till the air is liquefied.



**Fig. 9.9 Claude's apparatus for liquefaction of air**

#### **Adiabatic demagnetisation**

Generally, the method used to reach the very low temperature of about  $10^{-4}$  K is adiabatic demagnetisation. In this method the paramagnetic samples such as Gadolinium sulphate is placed surrounding the gas sample and cooled to about 1K along with the gas in any one of the cooling methods. The paramagnetic sample used in this method is suddenly magnetised by the application of strong magnetic field. This magnetisation (ordering of molecular magnets) occurs while the sample surrounds the cooled gas and has thermal contact with the walls of the container. When the magnetic field is suddenly removed, demagnetisation occurs which brings in a disordered state of the molecular magnets. To reach this state

thermal energy is taken away from the cooled air such that its temperature gets further lowered. By this technique, as low as zero kelvin can be reached.

### Questions

#### A. Choose the correct answer :

- A curve drawn at constant temperature is called an isotherm. This shows relationship between  
 (a)  $P$  and  $\frac{1}{V}$  (b)  $PV$  and  $V$   
 (c)  $P$  and  $V$  (d)  $V$  and  $\frac{1}{P}$
- The critical temperature of a gas is that temperature  
 (a) Above which it can no longer remain in the gaseous state  
 (b) Above which it can not be liquified by pressure  
 (c) At which it solidifies  
 (d) At which volume of gas becomes zero.
- If a gas expands at constant temperature.  
 (a) Number of molecules of the gas decreases  
 (b) The kinetic energy of the molecules decreases  
 (c) The kinetic energy of the molecules decreases  
 (d) The kinetic energy of the molecules increases
- The molecules of a gas A travel four times faster than the molecules of gas B at the same temperature. The ratio of molecular weight ( $M_A/M_B$ ) will be  
 (a)  $\frac{1}{16}$  (b) 4 (c)  $\frac{1}{4}$  (d) 16

#### B. Fill in the blanks

- The correction term for pressure deviation is .....in the Vanderwaal equation of state.
- The relation between inversion temperature and Vanderwaal's constants 'a' and 'b' is \_\_\_\_
- To liquefy Helium \_\_\_\_\_ method is exclusively used.
- The adiabatic expansion of a real gas results in \_\_\_\_\_

10. The rate of diffusion of gas is \_\_\_\_\_ to square root of both \_\_\_\_\_ and molecular mass.

**C. Match the following**

A	B
11. Ideal gas behaviour	(a) Critical temperature
12. Adiabatic demagnetization	(b) Liquid oxygen
13. CO <sub>2</sub> at 31.1°C	(c) Mole fraction of the gas
14. Joule Thomson Experiment	(d) Number of moles of the gas
15. Ratio of the partial pressure to the total pressure	(e) Low pressure and high temperature
	(f) Liquid Helium

**D. Write in one or two sentence**

16. Write the mathematical expression for Boyle's law.
17. Compare the partial pressures of gases A and B when 3 moles of A and 5 moles of B mixed in constant volume, and 25°C and 1 atm pressure.
18. Give the correction factors for the volume and pressure deviation for a Vanderwaal's gas.
19. A sample of an ideal gas escapes into an evacuated container, there is no change in the kinetic energy of the gas. Why?
20. What is the change in temperature when a compressed real gas is allowed to expand adiabatically through a porous plug.
21. Define Boyle's law and Charle's law.
22. What are measurable properties of gases?
23. What is the molar volume of nitrogen at 500K and 600 atm according to ideal gas law?
24. Define Graham's law of diffusion.
25. Give the values of R-gas constant in calories and Joules.
26. What are the units of Vanderwaals constants 'a' and 'b' ?
27. Write the significance of Vanderwaal's constants.
28. Write the limitations of vanderwaal equation of state.
29. Define Joule-Thomson effect.
30. What is meant by inversion temperature ?

**E. Explain briefly on the following**

- 31 At 27°C, H<sub>2</sub> is leaked through a tiny hole into a vessel for 20 minutes.

Another unknown gas at the same T and P as that of H<sub>2</sub> is leaked through the same hole for 20 minutes. After effusion of the gas, the mixture exerts a pressure of 6 atm. The H<sub>2</sub> content of the mixture is 0.7 moles. If volume of the container is 3 litres what is the molecular weight of unknown gas ?

32. Calculate the pressure exerted by 5 moles of CO<sub>2</sub> in one litre vessel at 47°C using Vanderwaal's equation. Also report the pressure of gas if it behaves ideally in nature. Given that  $a=3.592 \text{ atm lit}^2 \text{ mol}^{-2}$ .  $b = 0.0427 \text{ lit mol}^{-1}$

$$\left( \begin{array}{lcl} \text{Ans.: } P_{\text{real}} & = & 77.2 \text{ atm} \\ P_{\text{ideal}} & = & 131.36 \text{ atm} \end{array} \right)$$

33. Calculate the total pressure in a 10 L cylinder which contains 0.4 g of helium, 1.6 g of oxygen and 1.4 g of nitrogen at 27°C. Also calculate the partial pressures of He gas in the cylinder. Assume Ideal behaviour for gases.  
 $R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$

$$\left( \begin{array}{lcl} \text{Ans. } P_{\text{total}} & = & 0.4926 \text{ atm} \\ p_{\text{He}} & = & 0.2463 \text{ atm.} \\ P_{\text{O}_2} & = & 0.1231 \text{ atm,} \\ p_{\text{N}_2} & = & 0.123 \text{ atm} \end{array} \right)$$

34. The critical constants for water are 374°C, 218 atm and 0.0566 litre mol<sup>-1</sup>. Calculate 'a' and 'b' of water.

$$\left( \begin{array}{lcl} \text{Ans. } a & = & 2.095 \text{ lit}^2 \text{ atm mol}^{-1} \\ b & = & 0.0189 \text{ lit mol}^{-1} \end{array} \right)$$

35. Vanderwaal's constant in litre atmosphere per mole for carbon dioxide are  $a = 3.6$  and  $b = 4.28 \times 10^{-2}$ . Calculate the critical temperature and critical volume of the gas.  $R = 0.0820 \text{ lit atm K}^{-1} \text{ mol}^{-1}$
36. Explain the causes for deviation for real gases from ideal behaviour.
36. Deduce the relationship between critical constants and Vanderwaal's constants.
38. Describe Linde's process of liquefaction of gases with neat diagram.
39. Describe Claude's process of liquefaction of gases with neat diagram.
40. What is meant by adiabatic demagnetisation? Explain its use in liquefaction of gases.

## SUMMARY

- P,V,T and mass are the measurable properties of gas. They obey Boyle's and Charle's law. The equation of state for an ideal gas in  $PV = nRT$ .

- For constant mass of a gas,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

- Different units of R :0.0821 it atm K<sup>-1</sup>mol<sup>-1</sup>;

$$8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1};$$

$$8.314 \text{ joule K}^{-1} \text{ mol}^{-1};$$

$$1.987 \text{ cal K}^{-1} \text{ mol}^{-1}.$$

- Equation of state of gaseous mixture is  $PV = (n_A + n_B + n_C) RT$ .
- By Graham's law,  $(\text{diffusion rate}_1 / \text{diffusion rate}_2) = (M_2 / M_1)^{1/2}$  (or)  $(\text{effusion rate}_1 / \text{effusion rate}_2) = (M_2 / M_1)^{1/2}$
- Real gases deviate from  $V_{\text{ideal}}$  and  $P_{\text{ideal}}$ . The equation of state of real gas = Vanderwaal equation.

$$\left[ P + \frac{a}{V^2} \right] (V-b) = RT \text{ for } n = 1.$$

- Critical temperature, critical pressure, critical volume represent the critical state of the gas. Andrew's isotherm describes critical temperature of carbondioxide. Thomson's experiment describes continuity of state.

$P_c, V_c, T_c$  are related to Vanderwaal's constants a and b as  $V_c = 3b$ ;

$$P_c = \frac{a}{27b^2}; \quad T_c = \frac{8a}{27Rb}$$

- Joule Thomson effect predicts adiabatic expansion of a compressed gas through an orifice to cause a fall in temperature. Inversion temperature  $= 2a/Rb$  is the temperature below which Joule Thomson effect is obeyed.
- Liquefaction of gases is carried out by Linde's and Claude's processes adopting Joule-Thomson effect. Liquefaction of Helium and zero kelvin are achieved by adopting adiabatic demagnetisation.

**REFERENCES :**

Text book of physical chemistry, Lewis and Glasstone.

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## 10. CHEMICAL BONDING

### OBJECTIVES

- *To know about bonding as binding forces between atoms to form molecules.*
- *To learn about Kossel-Lewis approach to chemical bonding, the octet rule, its limitations and Lewis representations of simple molecules.*
- *To know about ionic bond, lattice energy and Born-Haber cycle.*
- *To understand covalent bond, directional character.*
- *To learn about VSEPR model and predict the geometry of simple molecules.*
- *To understand the concepts of hybridisation,  $\sigma$  and  $\pi$  bonds, resonance and coordinate covalent bonds.*

### 10.1 Elementary theories on Chemical Bonding

The study on the "nature of forces that hold or bind atoms together to form a molecule" is required to gain knowledge of the following-

- i) to know about how atoms of same element form different compounds combining with different elements.
- ii) to know why particular shapes are adopted by molecules.
- iii) to understand the specific properties of molecules or ions and the relation between the specific type of bonding in the molecules.

### Chemical bond

Existence of a strong force of binding between two or many atoms is referred to as a **Chemical Bond** and it results in the formation of a stable compound with properties of its own. The bonding is permanent until it is acted upon by external factors like chemicals, temperature, energy etc. It is known that, a molecule is made up of two or many atoms having its own characteristic properties which depend on the types of bonding present.

## Classification of molecules

Molecules having two identical atoms like  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{Cl}_2$ ,  $\text{N}_2$  etc. are called as **homonuclear diatomic molecules**. Molecules containing two different atoms like  $\text{CO}$ ,  $\text{HCl}$ ,  $\text{NO}$ ,  $\text{HBr}$  etc., are called as **heteronuclear diatomic molecules**. Molecules containing identical but many atoms bonded together such as  $\text{P}_4$ ,  $\text{S}_8$  etc., are called as **homonuclear polyatomics**. In most of the molecules, more than two atoms of different kinds are bonded such as in molecules like  $\text{NH}_3$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{SO}_2$ ,  $\text{HCHO}$  and they are called as **heteronuclear polyatomics**.

**Chemical bonds** are basically classified into three types consisting of (i) ionic or electrovalent bond (ii) covalent bond and (iii) coordinate-covalent bond. Mostly, valence electrons in the outer energy level of an atom take part in the chemical bonding.

In 1916, W.Kossel and G.N.Lewis, separately developed theories of chemical bonding in order to understand why atoms combined to form molecules. According to the electronic theory of valence, a chemical bond is said to be formed when atoms interact by losing, gaining or sharing of valence electrons and in doing so, a stable noble gas electronic configuration is achieved by the atoms.

Except Helium, each noble gas has a stable valence shell of eight electrons. The tendency for atoms to have eight electrons in their outershell by interacting with other atoms through electron sharing or electron-transfer is known as the **octet rule** of chemical bonding.

### 10.1.1 Kossel-Lewis approach to Chemical Bonding

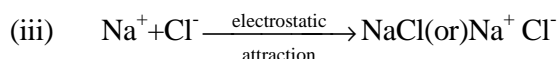
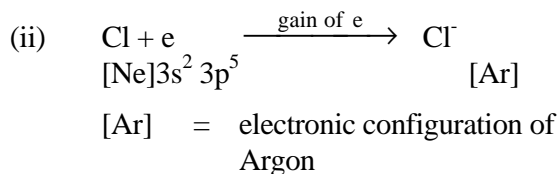
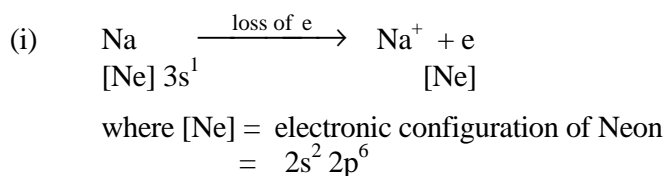
W.Kossel laid down the following postulates to the understanding of ionic bonding:

- In the periodic table, the highly electronegative halogens and the highly electropositive alkali metals are separated by the noble gases. Therefore one or small number of electrons are easily gained and transferred to attain the stable noble gas configuration.
- The formation of a negative ion from a halogen atom and a positive ion from an alkali metal atom is associated with the gain and loss of an electron by the respective atoms.

- The negative and positive ions so formed attain stable noble gas electronic configurations. The noble gases (with the exception of helium which has two electrons in the outermost shell) have filled outer shell electronic configuration of eight electrons (octet of electrons) with a general representation  $ns^2 np^6$ .
- The negative and positive ions are bonded and stabilised by force of electrostatic attraction.

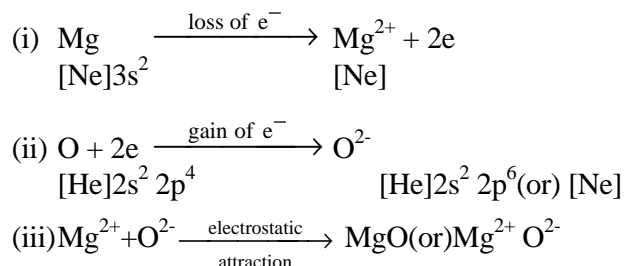
Kossel's postulates provide the basis for the modern concepts on electron transfer between atoms which results in ionic or electrovalent bonding.

For example, formation of NaCl molecule from sodium and chlorine atoms can be considered to take place according to Kossel's theory by an electron transfer as:



NaCl is an electrovalent or ionic compound made up of sodium ions and chloride ions. The bonding in NaCl is termed as electrovalent or ionic bonding. Sodium atom loses an electron to attain Neon configuration and also attains a positive charge. Chlorine atom receives the electron to attain the Argon configuration and also becomes a negatively charged ion. The coulombic or electrostatic attraction between  $\text{Na}^+$  and  $\text{Cl}^-$  ions result in NaCl formation.

Similarly formation of MgO may be shown to occur by the transfer of two electrons as:



The bonding in MgO is also electrovalent or ionic and the electrostatic forces of attraction binds  $\text{Mg}^{2+}$  ions with  $\text{O}^{2-}$  ions. Thus, "the binding forces existing as a result of electrostatic attraction between the positive and negative ions", is termed as **electrovalent** or **ionic** bond. The electrovalency is considered as equal to the number of charges on an ion. Thus magnesium has positive electrovalency of two while chlorine has negative electrovalency of one.

The valence electron transfer theory could not explain the bonding in molecules like  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{Cl}_2$  etc., and in other organic molecules that have ions.

G.N.Lewis, proposed the octet rule to explain the valence electron sharing between atoms that resulted in a bonding type with the atoms attaining noble gas electronic configuration. The statement is : "a bond is formed between two atoms by mutual sharing of pairs of electrons to attain a stable outer-octet of electrons for each atom involved in bonding". This type of valence electron sharing between atoms is termed as **covalent bonding**. Generally homonuclear diatomics possess covalent bonds.

It is assumed that the atom consists of a 'Kernel' which is made up of a nucleus plus the inner shell electrons. The Kernel is enveloped by the outer shells that could accommodate a maximum of eight electrons. The eight outershell electrons are termed as octet of electrons and represents a stable electronic configuration. Atoms achieve the stable outer octet when they are involved in chemical bonding.

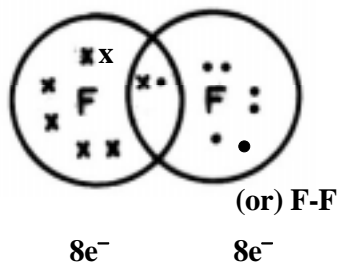
In case of molecules like  $\text{F}_2$ ,  $\text{Cl}_2$ ,  $\text{H}_2$  etc., the bond is formed by the sharing of a pair of electrons between the atoms. For example, consider the formation of a fluorine molecule ( $\text{F}_2$ ). The atom has electronic configuration.  $[\text{He}]2s^2 3s^2 3p^5$  which is having one electron less than the electronic configuration of Neon. In the fluorine molecule, each atom

contributes one electron to the shared pair of the bond of the  $F_2$  molecule. In this process, both the fluorine atoms attain the outershell octet of a noble gas (Argon) (Fig. 10.1(a)). Dots (•) represent electrons. Such structures are called as Lewis dot structures.

Lewis dot structures can be written for combining of like or different atoms following the conditions mentioned below :

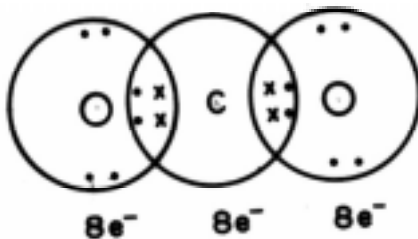
- Each bond is the result of sharing of an electron pair between the atoms comprising the bond.
- Each combining atom contributes one electron to the shared pair.
- The combining atoms attain the outer filled shells of the noble gas configuration.

If the two atoms share a pair of electrons, a single bond is said to be formed and if two pairs of electrons are shared a double bond is said to be formed etc. All the bonds formed from sharing of electrons are called as covalent bonds.



**Fig. 10.1(a)  $F_2$  molecule**

In carbon dioxide ( $CO_2$ ) two double bonds are seen at the centre carbon atom which is linked to each oxygen atom by a double bond. The carbon and the two oxygen atoms attain the Neon electronic configuration.



**Fig. 10.1 (b)  $CO_2$  molecule**

When the two combining atoms share three electron pairs as in  $N_2$  molecule, a triple bond is said to be formed. Each of the Nitrogen atom shares 3 pairs of electrons to attain neon gas electronic configuration.

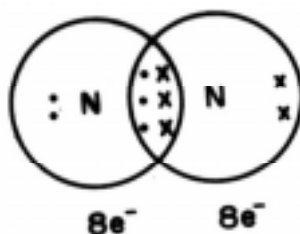


Fig. 10.1 (c)  $N_2$  molecule

## 10.2 Types of Bond

There are more than one type of chemical bonding possible between atoms which makes the molecules to show different characteristic properties. The different types of chemical bonding that are considered to exist in molecules are (i) **ionic or electrovalent bond** which is formed as a result of complete electron transfer from one atom to the other that constitutes the bond; (ii) **covalent bond** which is formed as a result of mutual electron pair sharing with an electron being contributed by each atom of the bond and (iii) **coordinate - covalent bond** which is formed as a result of electron pair sharing with the pair of electrons being donated by only one atom of the bond. The formation and properties of these types of bonds are discussed in detail in the following sections.

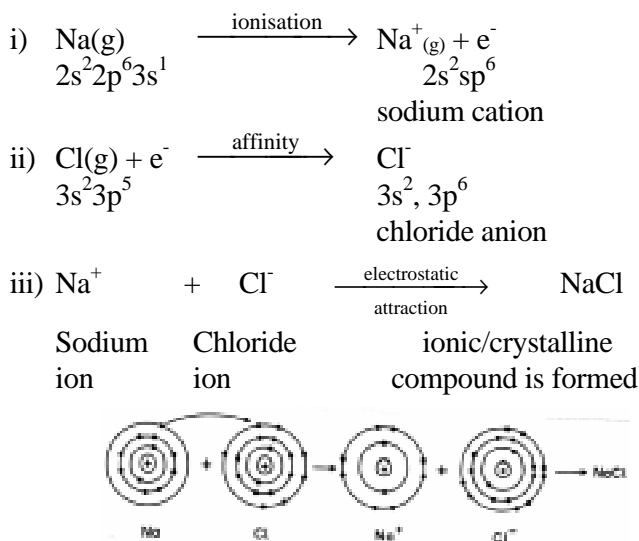
## 10.3 Ionic (or) Electrovalent bond

The electrostatic attraction force existing between the cation and the anion produced by the electron transfer from one atom to the other is known as the ionic (or) electrovalent bond. The compounds containing such a bond are referred to as ionic (or) electrovalent compounds.

Ionic bond is non directional and extends in all directions. Therefore, in solid state single ionic molecules do not exist as such. Only a network of cations and anions which are tightly held together by electro-static forces exist in the ionic solids. To form a stable ionic compound there must be a net lowering of energy. That is, energy is released as a result of electrovalent bond formation between positive and negative ions.

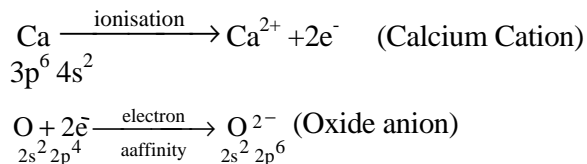
When the electronegativity difference between the interacting atoms are greatly different they will form an ionic bond. In fact, a difference of 2 or more is necessary for the formation of an ionic bond. Na has electronegativity 0.9 while Cl has 3.0, thus Na and Cl atoms when brought together will form an ionic bond.

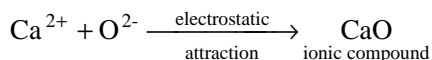
For example, NaCl is formed by the electron ionisation of sodium atom to  $\text{Na}^+$  ion due to its low ionisation potential value and chlorine atom to chloride ion by capturing the odd electron due to high electron affinity. Thus, NaCl (ionic compound) is formed. In NaCl, both the atoms possess unit charges.



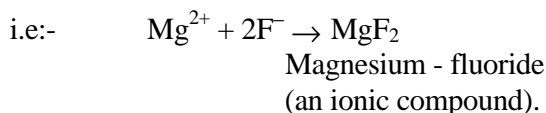
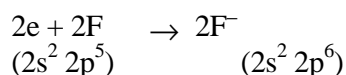
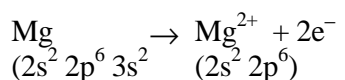
**Fig. 10.2 Electron transfer between Na and Cl atoms during ionic bond formation in NaCl**

In CaO, which is an ionic compound, the formation of the ionic bond involves two electron transfers from Ca to O atoms. Thus, doubly charged positive and negative ions are formed.

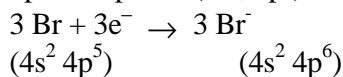
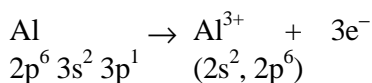




Ionic bond may be also formed between a doubly charged positive ion with single negatively charged ion and vice versa. The molecule as a whole remains electrically neutral. For example in  $\text{MgF}_2$ , Mg has two positive charges and each fluorine atom has a single negative charge. Hence,  $\text{Mg}^{2+}$  binds with two fluoride ( $\text{F}^-$ ) ions to form  $\text{MgF}_2$  which is electrically neutral.



Similarly in Aluminium bromide ( $\text{AlBr}_3$ ), Aluminium ion has three positive charges and therefore it bonds with three Bromide ions to form  $\text{AlBr}_3$  which is a neutral ionic molecule.



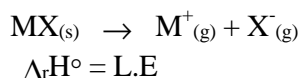
### 10.3.1 Lattice energy and Born - Haber's cycle

Ionic compounds in the crystalline state exist as three dimensionally ordered arrangement of cations and anions which are held together by columbic interaction energies. The three dimensional network of points that represents the basic repetitive arrangement of atoms in a crystal is known as lattice or a space lattice. Thus a qualitative measure of the stability of an ionic compound is provided by its enthalpy of lattice formation.

Lattice enthalpy of an ionic solid is defined as the energy required to completely separate one mole of a solid ionic compound into gaseous constituent ions. That is, the enthalpy change of dissociation of MX ionic



solid into its respective ions at infinity separation is taken the lattice enthalpy.



Lattice enthalpy is a positive value.

For example, the lattice enthalpy of NaCl is  $788 \text{ kJ.mol}^{-1}$ . This means that 788 kJ of energy is required to separate 1 mole of solid NaCl into 1 mole of  $\text{Na}^+_{(g)}$  and 1 mole of  $\text{Cl}^-_{(g)}$  to an infinite distance.

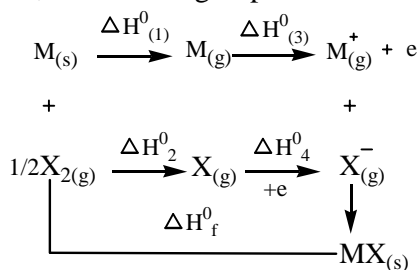
In ionic solids, the sum of the electron gain enthalpy and the ionisation enthalpy may be positive but due to the high energy released in the formation of crystal lattice, the crystal structure gets stabilised.

### Born Haber's Cycle

#### Determination of Lattice enthalpy

It is not possible to calculate the lattice enthalpy directly from the forces of attraction and repulsion between ions but factors associated with crystal geometry must also be included. The solid crystal is a three-dimensional entity. The lattice enthalpy is indirectly determined by the use of Born - Haber Cycle. The procedure is based on Hess's law, which states that the enthalpy change of a reaction is the same at constant volume and pressure whether it takes place in a single or multiple steps long as the initial reactants and the final products remain the same. Also it is assumed that the formation of an ionic compound may occur either by direct combination of elements (or) by a step wise process involving vaporisation of elements, conversion of gaseous atoms into ions and the combination of the gaseous ions to form the ionic solid.

For example consider the formation of a simple ionic solid such as an alkali metal halide MX, the following steps are considered.



$\Delta H^0_1$  = enthalpy change for sublimation of  $\text{M}_{(s)}$  to  $\text{M}_{(g)}$

- $\Delta H_2^0$  = enthalpy change for dissociation of  $1/2 X_{2(g)}$  to  $X_{(g)}$   
 $\Delta H_3^0$  = ionization energy of  $M_{(g)}$  to  $M^+_{(g)}$   
 $\Delta H_4^0$  = electronic affinity or electron gain energy for conversion of  $X_{(g)}$  to  $X^-_{(g)}$   
 $\Delta H_5^0$  = the lattice enthalpy for formation of solid MX (1 mole).  
 $\Delta_f H^0$  = enthalpy change for formation of MX solid directly from the respective elements such as 1 mole of solid M and 0.5 moles of  $X_{2(g)}$ .

According to Hess's law,

$$\Delta H_f^0 = \Delta H_1^0 + \Delta H_2^0 + \Delta H_3^0 + \Delta H_4^0 + \Delta H_5^{0*}$$

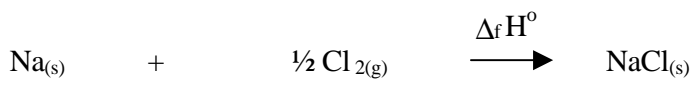
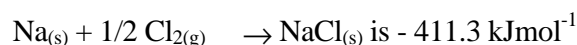
**Some important features of lattice enthalpy are:**

- The greater the lattice enthalpy the more stabler the ionic bond formed.
- The lattice enthalpy is greater for ions of higher charge and smaller radii.
- The lattice enthalpies affect the solubilities of ionic compounds.

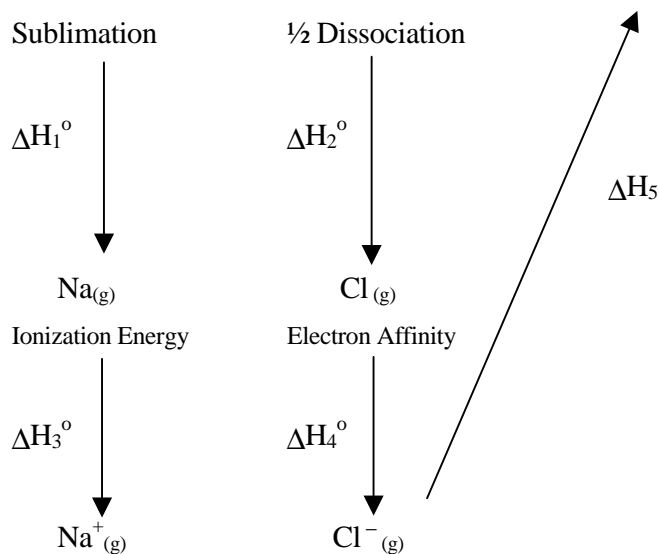
### Calculation of lattice enthalpy of NaCl

Let us use the Born - Haber cycle for determining the lattice enthalpy of NaCl as follows :

The standard enthalpy change,  $\Delta_f H^0$  overall for the reaction,



\* The value of  $\Delta H_5^0$  calculated using the equation of Born - Haber cycle should be reversed in sign



**Fig. 10.3 Born-Haber cycle for Lattice enthalpy determination involving various stepwise enthalpic processes for NaCl solid formation**

Since the reaction is carried out with reactants in elemental forms and products in their standard states, at 1 bar, the overall enthalpy change of the reaction is also the enthalpy of formation for NaCl. Also, the formation of NaCl can be considered in 5 steps. The sum of the enthalpy changes of these steps is considered equal to the enthalpy change for the overall reaction from which the lattice enthalpy of NaCl is calculated.

Atomisation :

$$\Delta H^\circ_1 \text{ for } \text{Na(s)} \rightarrow \text{Na(g)} \text{ is } +108.70 \text{ (kJ mol}^{-1}\text{)}$$

Dissociation:

$$\Delta H^\circ_2 \text{ for } \frac{1}{2} \text{Cl}_2(\text{g}) \rightarrow \text{Cl(g)} \text{ is } +122.0$$

Ionisation :

$$\Delta H^\circ_3 \text{ for } \text{Na(g)} \rightarrow \text{Na}^+(\text{g}) + \text{e} \text{ is } +495.0$$

Electron affinity :

$$\Delta H^\circ_4 \text{ for } \text{e} + \text{Cl(g)} \rightarrow \text{Cl}^-(\text{g}) \text{ is } -349.0$$

Lattice enthalpy :

$$\Delta H^\circ_5 \text{ for } \text{Na}^+(\text{g}) + \text{Cl}^-(\text{g}) \rightarrow \text{NaCl(g)} \text{ is ?}$$

$$\Delta_f H^\circ = \Delta H^\circ_1 + \Delta H^\circ_2 + \Delta H^\circ_3 + \Delta H^\circ_4 + \Delta H^\circ_5$$

$$-411.3 = 108.70 + 122.0 + 495 - 349.0 + \Delta H^\circ_5$$

$$\therefore \Delta H^\circ_5 = -788.0 \text{ kJ mol}^{-1}$$

But the lattice enthalpy of NaCl is defined by the reaction  $\text{NaCl(g)} \rightarrow \text{Na}^+(\text{g}) + \text{Cl}^-(\text{g})$  only.

$\therefore$  Lattice enthalpy value from  $\Delta H^\circ_5$  is written with a reversed sign.

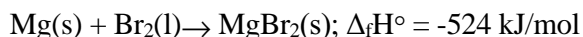
$\therefore$  Lattice enthalpy of NaCl = +788.0 kJ mol<sup>-1</sup>.

### Problem 1

Calculation of lattice enthalpy of MgBr<sub>2</sub> from the given data.

### Solution

The enthalpy of formation of MgBr<sub>2</sub> according to the reaction



$$\Delta H^\circ_1 \text{ for } \text{Mg(s)} \rightarrow \text{Mg(g)} = +148 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ_2 \text{ for } \text{Mg(g)} \rightarrow \text{Mg}^{2+}(\text{g}) + 2\text{e}^- = +2187 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ_3 \text{ for } \text{Br}_2(\text{l}) \rightarrow \text{Br}_2(\text{g}) = 31 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ_4 \text{ for } \text{Br}_2(\text{g}) \rightarrow 2\text{Br(g)} = 193 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ_5 \text{ for } \text{Br(g)} + \text{e}^-(\text{g}) \rightarrow \text{Br}^- = -331 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ_6 \text{ for } \text{Mg}^{2+}(\text{g}) + 2\text{Br}^-(\text{g}) \rightarrow \text{Mg Br}_2(\text{s}) = ?$$

$$\Delta_f H^\circ = \Delta H^\circ_1 + \Delta H^\circ_2 + \Delta H^\circ_3 + \Delta H^\circ_4 + \Delta H^\circ_5 + \Delta H^\circ_6$$

$$\begin{aligned} -524 \text{ kJ mol}^{-1} &= (+148 + 2187 + 31 \\ &\quad + 193 - 2(331) + \Delta H^\circ_6) \text{ kJ mol}^{-1} \\ &= -2421 \text{ kJ mol}^{-1} = \Delta H^\circ_6 \end{aligned}$$

Hence, lattice enthalpy of Mg Br<sub>2</sub> =  $\Delta H^\circ_6 = 2421 \text{ kJ mol}^{-1}$

### 10.3.2 Properties of electrovalent (or) ionic compounds

Ionic compounds possess characteristic properties of their own like physical state, solubility, melting point, boiling point and conductivity. The nature of these properties are discussed as follows.

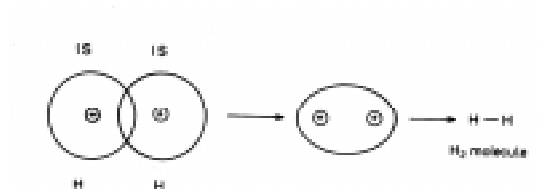
- i. Due to strong coulombic forces of attraction between the oppositely charged ions, electrovalent compounds exist mostly as hard

crystalline solids. Due to the hardness and high lattice enthalpy, low volatility, high melting and boiling points are seen.

- ii. Because of the strong electrostatic forces, the ions in the solid are not free to move and act as poor conductor of electricity in the solid state. However, in the molten state, or in solution, due to the mobility of the ions electrovalent compounds become good conductor of electricity.
- iii. Ionic compounds possess characteristic lattice enthalpies since they exist only as ions packed in a definite three dimensional manner. They do not exist as single neutral molecule or ion.
- iv. Ionic compounds are considered as polar and are therefore, soluble in high dielectric constant solvents like water. In solution, due to solvation of ions by the solvent molecules, the strong interionic attractions are weakened and exist as separated ions.
- v. Electrovalent compounds having the same electronic configuration exhibit isomorphism.

#### **10.4 Covalent bond**

A covalent bond is a chemical bond formed when two atoms mutually share a pair of electron. By doing so, the atoms attain stable octet electronic configuration. In covalent bonding, overlapping of the atomic orbitals having an electron from each of the two atoms of the bond takes place resulting in equal sharing of the pair of electrons. Also the interatomic bond thus formed due to the overlap of atomic orbitals of electrons is known as a covalent bond. Generally the orbitals of the electrons in the valency shell of the atoms are used for electron sharing. The shared pair of electrons lie in the middle of the covalent bond. Including the shared pair of electrons the atoms of the covalent bond attain the stable octet configuration. Thus in hydrogen molecule ( $H_2$ ) a covalent bond results by the overlap of the two s orbitals each containing an electron from each of the two H atoms of the molecule. Each H atom attains ' $1s^2$ ' filled K shell.



### **H<sub>2</sub> molecule**

A covalent bond can be formed by sharing of s,p,d,f electrons also. Consider Cl<sub>2</sub> molecule. The outer shell electronic configuration of atom is  $3s^2 2p_x^2 2p_y^2 2p_z^1$ . When each chlorine atom mutually share the  $2p_z$  unpaired electron contributed from each Cl atom of the molecule, a covalent bond is formed. By doing so, each chlorine atom attains argon electron configuration.

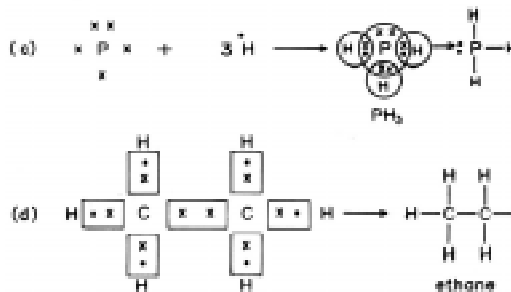
#### **The Lewis dot structure will be :**

More than one  $e^-$  can also be mutually shared to result in two covalent bonds between the atoms of a bond. Example in O<sub>2</sub> molecule (O=O) 2 covalent bonds exist.

The two unpaired electrons in  $2p_y$  and  $2p_z$  orbitals of each of O atom is mutually shared so that after the double bond formation stable octet electronic configuration is attained by each oxygen atom of the molecule.

In the phosphine PH<sub>3</sub> molecule, three hydrogen atoms combine with one phosphorous atom. Each hydrogen atom shares its 1s electron with phosphorous. So that three covalent bonds are formed in PH<sub>3</sub>. The lewis dot structure is in Fig. 10.4.

In case of ethane molecule, the six C-H bonds and a C-C bond are covalent in nature. They are formed by mutual sharing of a pair of electrons between the two atoms of a bond. Each carbon atom completes its stable octet and each H atom has completed K shell.



## Double bond formation

### 10.4.1 Characteristics of covalent compounds

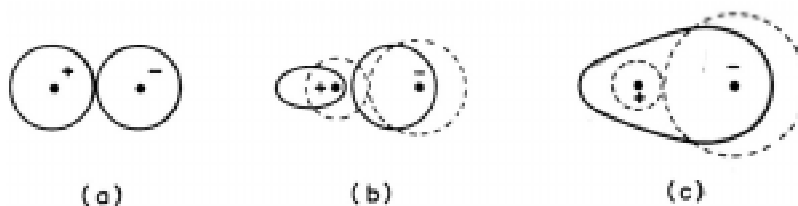
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in fused or molten or dissolved state.

2. They possess low melting and boiling points. This is because of the weak intermolecular forces existing between the covalent molecules. Since, no strong coulombic forces are seen, some of covalent molecules are volatile in nature. Mostly covalent compounds possess low melting and boiling points.
3. Covalent bonds are rigid and directional therefore different shapes of covalent molecules are seen.
4. Most of the covalent molecules are non polar and are soluble in nonpolar (low dielectric constant) solvents like benzene, ether etc and insoluble in polar solvents like water. Carbon tetrachloride ( $\text{CCl}_4$ ) is a covalent nonpolar molecule and is soluble in benzene.

#### 10.4.2 Fajan's rules

##### Covalent character of ionic bonds



**Fig. 10.5 Polarization effects : (a) idealized ion pair with no polarization, (b) mutually polarized ion pair (c) polarization sufficient to form covalent bond. Dashed lines represent hypothetical unpolarized ions**

When cations and anions approach each other, the valence shell of anions are pulled towards cation nucleus due to the coulombic attraction and thus shape of the anion is deformed. This phenomenon of deformation of anion by a cation is known as **polarization** and the ability of cation to polarize a nearby anion is called as polarizing power of cation.

Fajan points out that greater is the polarization of anion in a molecule, more is covalent character in it. This is **Fajan's rule**.

Fajan also pointed out the influence of various factors on cations for polarization of anion.



- (i) When the size of a cation is smaller than a cation with the same charge, then the smaller sized cation causes a greater extent of polarization on the anion than the larger sized cation.
- (ii) The polarizing capacity of a cation is related to its ionic potential (which is  $Z^+/r$ ) which is inversely related to the ionic radius. Therefore comparing  $\text{Li}^+$  and  $\text{Na}^+$  or  $\text{K}^+$  ions, although these cations have single positive charge,  $\text{Li}^+$  ion polarizes an anion more than  $\text{Na}^+$  or  $\text{K}^+$  ions can do on the same anion. This is because of the smaller size of  $\text{Li}^+$  than  $\text{Na}^+$  or  $\text{K}^+$  ions.
- (iii) Greater the polarization effects greater will be the covalent character imparted into the ionic bond.

The general trend in the polarizing power of cations:  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$

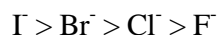
∴ covalent character:



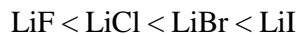
#### a) Size of the anion

When the size of anion is larger, valence electrons are less tightly held by its nucleus. Therefore more effectively the cation pulls the valence electrons towards its nucleus. This results in more polarization effect. That is, for the same charge of the anion, larger sized anion is more polarized than a smaller sized anion.

The trend in the polarization of anions:



∴ covalent character :



#### b) Charge on cation

If the oxidation state of the cation is higher the polarization of anion will be more. Thus more will be covalent nature in the bonding of the molecule.

Thus polarizing power:  $\text{Fe}^{+2} < \text{Fe}^{+3}$

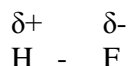
∴ Covalent character :  $\text{FeCl}_2 < \text{FeCl}_3$ .

### c) Presence of polar medium

Presence of a polar medium keeps away the cations and anions from each other due to solvation. This prevents polarization of anion by the cation. Therefore  $\text{AlCl}_3$  behaves as an ionic molecule in water, while it is a covalent molecule in the free state.

#### 10.4.3 Polarity of Covalent Bonds

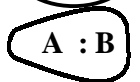
The existence of a purely ionic or covalent bond represents an ideal situation. In the covalently bonded molecules like  $\text{H}_2$ ,  $\text{Cl}_2$ ,  $\text{F}_2$  (homonuclear diatomics), the bond is a pure covalent bond. In case of heteronuclear molecules like,  $\text{HF}$ ,  $\text{HCl}$ ,  $\text{CO}$ ,  $\text{NO}$  etc, the shared electron pair gets displaced more towards the atom possessing higher electronegativity value than the other one. In  $\text{HF}$ , the shared electron pair is displaced more towards fluorine because the electronegativity of Fluorine is far greater than that of Hydrogen. This results in partial ionic character induced in the covalent bond and is represented as:



However, no specific charges are being found on H or F and the molecule as a whole is neutral. Thus the extent of ionic character in a covalent bond will depend on the relative attraction of electrons of the bonded atoms which depends on the electronegativity differences between the two atoms constituting the covalent bond.



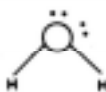
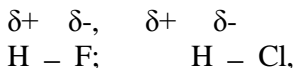
a pure covalent bond



a polarised covalent bond.

Polarisation of a covalent bond causes fractional charges ( $\delta+$  or  $\delta-$ ) on the atoms which are separated by the bond distance. This causes a dipolar molecule formation.

Some dipolar molecules are



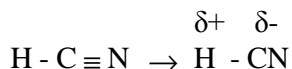


As a result of polarisation, the molecule possessed a dipole moment. In a triatomic molecule like water two covalent bonds exist between the oxygen atom and the two H atoms. Oxygen with higher electronegativity attracts the shared pair of electrons to itself and thus oxygen becomes the negative end of the dipole while the two hydrogen atoms form the positive end. Thus the two covalent bonds in the water molecule possess partial ionic character.

Generally larger the electronegativity difference between the atoms consisting the bond, greater will be the ionic character. For H atom electronegativity is 2.1 and for Cl atom it is 3.0. Thus H-Cl covalent bond is polarised and it has more ionic character.



Consider the molecule like hydrogen cyanide HCN, the bond between hydrogen atoms and the cyanide anion is of covalent type.  $\text{CN}^-$  ion has more capacity to pull the shared pair of electrons in the H-CN bond that, partially  $\text{H}^+ \text{CN}^-$  are created. Thus in water medium this compound is ionised into  $\text{H}^+$  and  $\text{CN}^-$  ions.



### 10.5 Valence Shell Electron Pair Repulsion Theory (VSEPR) Theory

Molecules exist in different shapes. Many of the physical and chemical properties of molecules arise due to different shapes of the molecules.

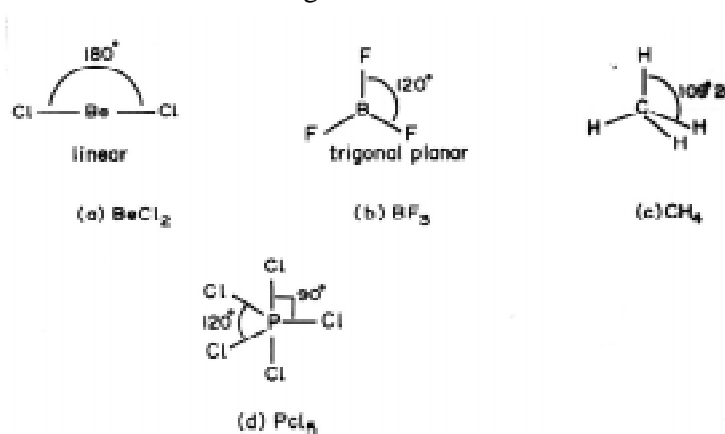
Some of the common geometrical shapes found among the molecules are: linear, trigonal, planar, tetrahedral, square planar, trigonal bipyramidal, square pyramidal, octahedral, pentagonal-bipyramidal etc. The VSEPR theory provides a simple treatment for predicting the shapes of polyatomic molecules. The theory was originally proposed by Sigdwick and Powell in 1940. It was further developed and modified by Nyholm and Gillespie (1957).

The basic assumptions of the VSEPR theory are that:

- i) Pairs of electrons in the valence shell of a central atom repel each other.
- ii) These pairs of electrons tend to occupy positions in space that minimize repulsions and maximise the distance of separation between them.
- iii) The valence shell is taken as a sphere with electron pairs localising on the spherical surface at maximum distance from one another.
- iv) A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair.
- v) Where two or more resonance structures can depict a molecule the VSEPR model is applicable to any such structure.



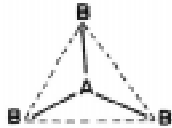

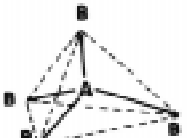

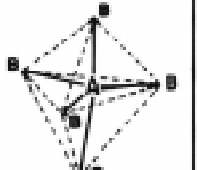
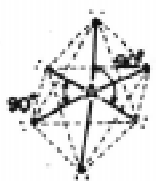
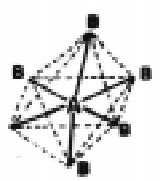
It is convenient to divide molecule into two categories (i) molecules in which the central atom has no lone pairs of electrons and (i) molecules in which the central atom has one or more lone pairs.

Table 10.1 shows the different geometries of molecules or ions with central atom having no lone pair of electrons and represented by general type  $AB_x$ . In compounds of  $AB_2$ ,  $AB_3$ ,  $AB_4$ ,  $AB_5$ ,  $AB_6$ , types the arrangement of electron pairs (bonded pairs) as well as the B atoms around the central atom A are, linear, trigonal planar, tetrahedral, trigonal-bipyramidal and octahedral respectively. Such arrangements are present in  $BeCl_2$  ( $AB_2$ );  $BF_3$  ( $AB_3$ );  $CH_4$  ( $AB_4$ ) and  $PCl_5$  ( $AB_5$ ) molecules with geometries as shown below in Fig.10.6.



**Fig. 10.6 Geometrical structures of some molecules (a)  $BeCl_2$  (b)  $BF_3$  (c)  $CH_4$  and (d)  $PCl_5$**

**Table 10.1**  
**Geometry of molecules in which the central atom has no lone pair of electrons**

Number of electron pairs	Arrangement of electron pairs	Molecular geometry	Examples
2	 Linear	$B-A-B$ Linear	$BeCl_2, HgCl_2$
3	 Trigonal planar	 Trigonal planar	$BF_3$
4	 Tetrahedral	 Tetrahedral	$CH_4, NH_4^+$
5	 Trigonal bipyramidal	 Trigonal bipyramidal	$PCl_5$
6	 Octahedral	 Octahedral	$SF_6$
The dotted lines are used only to show the overall shapes; they do not represent bonds			

In case of molecules with the central atom having one or more lone pairs VSEPR treatment is as follows: In these type of molecules, both lone

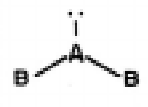
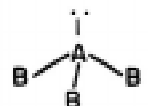
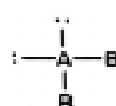
pairs and bond pairs of electrons are present. The lone pairs are localised on the central atom, and bonded pairs are shared between two atoms. Consequently, the lone pair electrons in a molecule occupy more space as compared to the bonding pair electrons. This causes greater repulsions between lone pairs of electrons as compared to the lone pairs of electrons to the lone pair (lp) - bonding pair and bonding pair - bonding pair repulsions (bp).

The descending order of repulsion interaction is

$$\text{lp} - \text{lp} > \text{lp} - \text{bp} > \text{bp} - \text{bp}$$

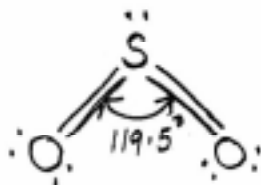
These repulsion effects cause deviations from idealised shapes and alterations in the predicted bond angles in molecules.

**Table 10.2**

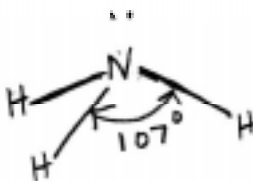
Molecule Type	No of Bonding Pairs	No. of lone pairs	Arrangement of electron pairs	Shape (Geometry)	Examples
$\text{AB}_3\text{E}$	2	1	 Trigonal planar	Bent	$\text{SO}_2, \text{O}_3$
$\text{AB}_3\text{E}$	3	1	 Tetrahedral	Trigonal pyramidal	$\text{NH}_3$
$\text{AB}_2\text{E}_2$	2	2		Bent	$\text{H}_2\text{O}$

Examples : In sulphur dioxide molecule there are three electron pairs on the S atom. The overall arrangement is trigonal planar. However, because one of the three electron pairs is a lone pair, the  $\text{SO}_2$  molecule has a 'bent' shape and due to the lp - lp repulsive interactions the bond angle is reduced

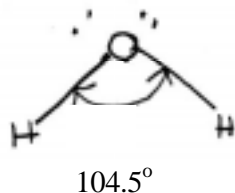
to  $119.5^\circ$  from the value of  $120^\circ$ .



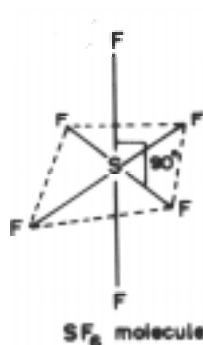
In the ammonia ( $\text{NH}_3$ ) molecule, there are three bonding pairs and one lone pair of electrons. The overall arrangement of four electron pairs is tetrahedral. In  $\text{NH}_3$ , one of the electron pairs, on nitrogen atom is a lone pair, so the geometry of  $\text{NH}_3$  is pyramidal (with the N atom at the apex of the pyramid). The three N-H bonding pairs are pushed closer because of the lp-bp repulsion and the HNH angle gets reduced from  $109^\circ 28'$  (which is the tetrahedral angle) to  $107^\circ$ .



The water  $\text{H}_2\text{O}$  molecule, oxygen atom contains two bonding pairs and two lone pairs of electrons. The overall arrangement for four electron pairs is tetrahedral, but the lp - lp repulsions being greater than lp-bp repulsions in  $\text{H}_2\text{O}$ . The HOH angle is reduced to  $104.5^\circ$  than  $109^\circ 28'$ . The molecule has a bent shape.



The molecule  $\text{SF}_6$  belongs to  $\text{AB}_6$  type consisting of 6 bp of electrons around the central sulphur atom. The geometrical arrangement will be a regular octahedral.



### 10.6 Directional Properties of Covalent Bonds

When the overlapping of orbitals occur along the internuclear axis (Line joining the two nuclei) then the electron orbitals merge to form cylindrically symmetrical region and the bond is called as ' $\sigma$ ' bond. In a  $\sigma$  bond, maximum extent overlap of orbitals are possible and the bond formed is also stronger.

For e.g : H-H bond is a  $\sigma$  bond.

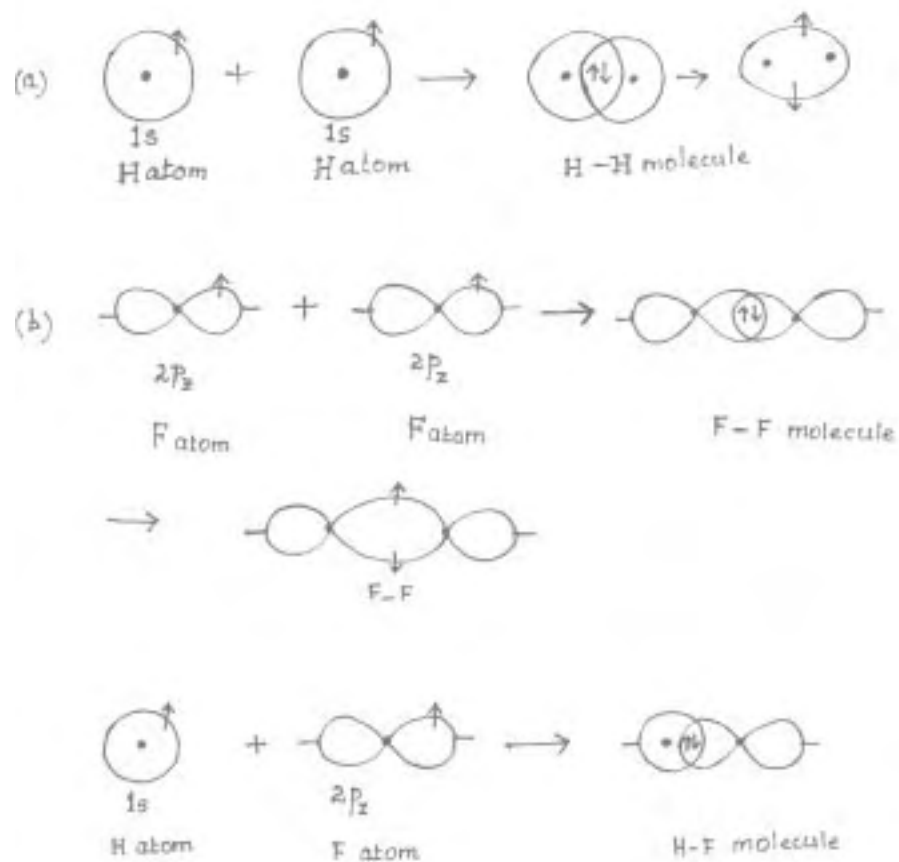
Consider the valence bond description of  $O_2$  molecule : the valence shell electron configuration of each O atom is  $2s^2 2p_x^2 2p_y^1 2p_z^1$ . It is conventional to take z axis as the inter nuclear axis or molecular axis. Along the molecular axis, overlap of  $2p_z$  orbital of two O atoms occur with cylindrical symmetry thus forming a  **$\sigma$  bond**.

The remaining two  $2p_y$  orbitals of two O atoms cannot overlap to the full extent like a  $\sigma$  bond as they do not have cylindrical symmetry around the internuclear axis. Instead,  $2p_y$  orbitals overlap laterally (sideways) above and below the axis and share the pair of electrons. The bond formed by lateral overlap of p orbitals above and below the axis together is called a  **$\pi$  (Pi) bond**. Since  $2p_y$  orbitals are perpendicular to  $2p_z$  orbitals,  $\pi$  bond formed is perpendicular to the  $\sigma$  bond. Thus bonding in oxygen molecule is represented as in fig. 10.8(a).

There are two bonds in  $O_2$  molecule. One of which is a  $\sigma$  bond and another is  $\pi$  bond.

Similarly, in  $N_2$  molecule, 3 bonds are present between 2N atoms. The nature of orbital overlaps in the 3 bonds can be considered as in fig. 10.8(b).





**Fig.10.7**

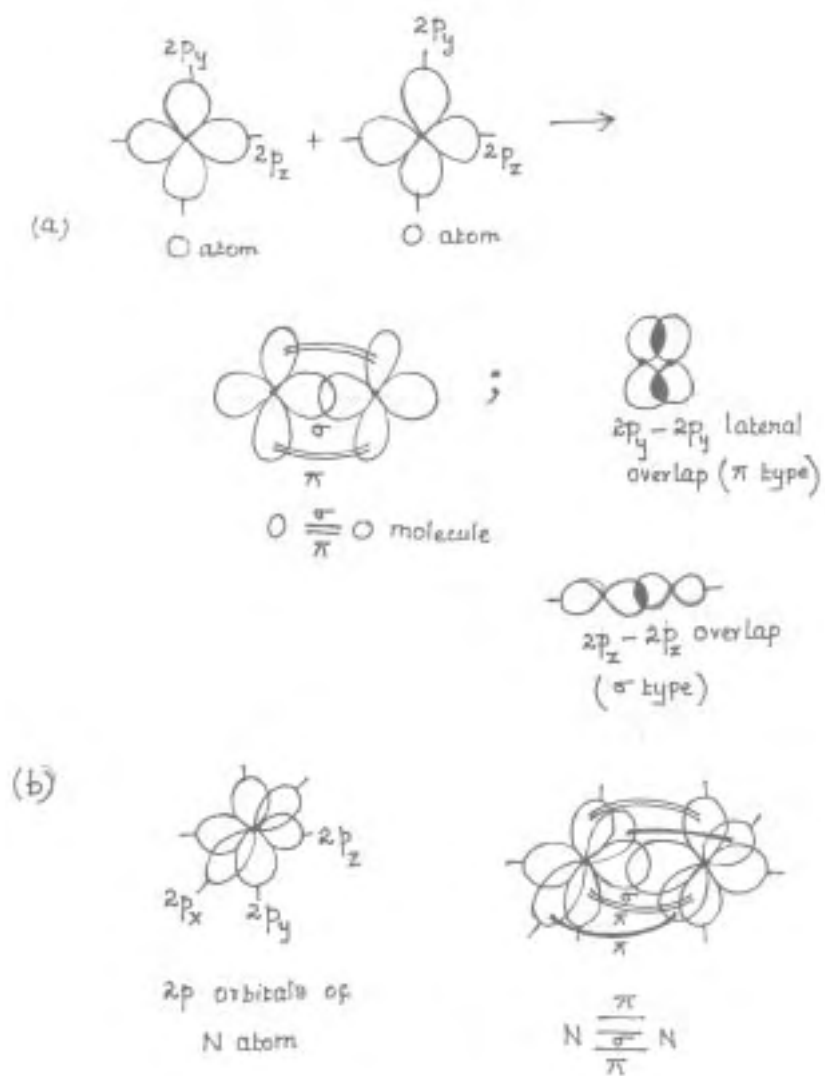


Fig.10.8

to the  $\sigma$  bond. Thus bonding in oxygen molecule is represented as in Fig. 10.8(a).

There are two bonds in  $O_2$  molecule. One of which is a  $\sigma$  bond and another is  $\pi$  bond.

Similarly, in  $N_2$  molecule, 3 bonds are present between 2N atoms. The nature of orbital overlaps in the 3 bonds can be considered as in Fig. 10.10.

The valence electronic configuration of nitrogen atom is  $2s^2 2p_x^1 2p_y^1 2p_z^1$ .

Cylindrically symmetrical overlap of two  $2p_z$  orbitals give a  $\sigma$  bond and lateral overlap of two  $2p_y$  orbitals give a  $\pi$  bond perpendicular to  $\sigma$  bond. Similarly, two  $2p_z$  orbitals laterally overlap to give another  $\pi$  bond which is perpendicular to both  $\sigma$ ,  $\pi$  bonds.

Based on the valence bond orbital overlap theory, the  $H_2O$  molecule is viewed to be formed by the overlap 1s orbital of a H atom with  $2p_y$  orbital of O atom containing one electron each forming a  $\sigma$  bond. Another  $\sigma$  bond is also formed by the overlap of 1s orbital of another H atom with  $2p_x$  orbital of O atom each containing an unpaired electron. The bond angle is therefore  $90^\circ$  (i.e. : HOH bond angle is  $90^\circ$ ), since  $2p_x$  and  $2p_y$  orbitals are mutually perpendicular to each other. However the actual bond angle value is found to be  $104^\circ$ . Therefore based on VB theory, pure orbital overlaps does not explain the geometry in  $H_2O$  molecule.

Similarly, in  $NH_3$ , according to VB theory each of N-H bonds are formed by the overlap of a 2p orbital of N and 1s orbital of H atoms respectively. Here again the bond angle of HNH bond is predicted as  $90^\circ$ . Since  $2p_x$ ,  $2p_y$  and  $2p_z$  orbitals of N are mutually perpendicular. However the experimental bond angle of HNH bond value is found to be  $107^\circ$ .

#### 10.6.1 Theory of Hybridisation

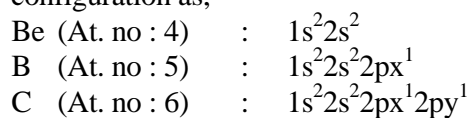
The failures of VB theory based on pure orbital overlaps are explained agreeably based on the concept of hybridisation of orbitals or mixing up of orbitals. There are three major processes that are considered to occur in hybridisation of orbitals. These are:

- i) Promotion of electrons to higher or similar energy levels
- ii) Mixing up of various s,p,d,f orbitals to form the same number of new orbitals and

iii) Stabilisation of the molecule through bond formations involving hybrid orbitals by release of certain amount of energy which compensates the energy requirement in the electron promotion process.

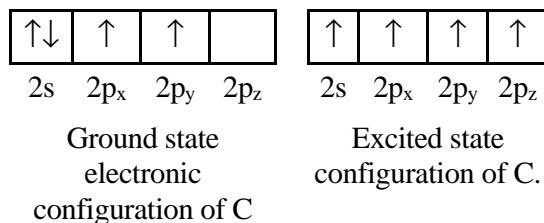
**i) Promotion (Excitation) of Electrons**

Atoms of elements like Beryllium, Boron and Carbon have electronic configuration as,



According to VB theory, Beryllium is expected to behave like a noble gas due to its filled shells, which in practice forms a number of compounds like  $\text{BeF}_2$  and  $\text{BeH}_2$  proving its bivalency. In case of Boron VB theory predicts univalency due to the presence of one unpaired electron but in practice Boron is trivalent since compounds as  $\text{BCl}_3$ ,  $\text{BH}_3$  etc. are found.

The stable state (Ground State) electronic configuration of C is  $(2s^2 2p_x^1 2p_y^1)$ . Electronic configuration of C suggests only bivalency. But carbon forms over a million compounds in all of which carbon is tetravalent. This suggests only tetravalency. This deficiency is overcome by allowing for **promotion** (or) **the excitation** of an electron to an orbital of higher energy. Although for electron promotion energy is needed, if that energy is recovered back during a covalent bond formation, or by a bond with a greater strength or by many number of bonds formation, then the electron promotion becomes energetically allowed and assumed to take place initially. In carbon, promotion of an electron to an orbital which is close to itself with an empty orbital of only slightly higher energy which is the  $2p_z$  orbital can take place. Then the electron pair is unpaired itself by absorbing the required energy available by the atom from its surrounding and one of the electrons in the original orbital  $2s$  or  $2p$  shifts to the empty higher energy orbital.



Thus promotion of an electron leads to four unpaired electron in the excited state electronic configuration of carbon atom. Each electron can now be utilised to form a covalent bond by sharing an electron coming from the combining atom. Thus four  $\sigma$  covalent bonds are possible, each with equivalent strength and overlapping tendency. Further, chemical and physical evidences reveal the four bonds of carbon to be equivalent and that they are tetrahedrally oriented. The promotion of an electron from 2s to 2p orbital leads to four half filled orbitals which can form four bonds leading to greater energy lowering. This energy is more than the initial energy required for the promotion of 2s electron to 2p orbital.

### **Hybridisation (mixing of orbitals)**

After an electron promotion the 4 electrons are not equivalent, since one of them involves with an s orbital while the other three involve with p orbitals. To explain the equivalence of the four bonds, the concept of hybridisation is introduced.

Dissimilar orbitals like s,p,d with one or many numbers, with nearly the same energy on the same atom may combine or mix completely to form an equal number of equivalent energy new orbitals with properties of their own. This is called **as hybridisation** of orbitals. The new orbitals formed are known as hybrid orbitals and these orbitals possess the properties of the pure orbitals that are mixed to form them. The hybrid orbitals of an atom are symmetrically distributed around it in space. Essentially, mixing up of orbitals to form new orbitals explains the different geometries of many compounds like  $\text{CH}_4$ ,  $\text{SF}_6$  etc.

## **10.7 Concept of Resonance**

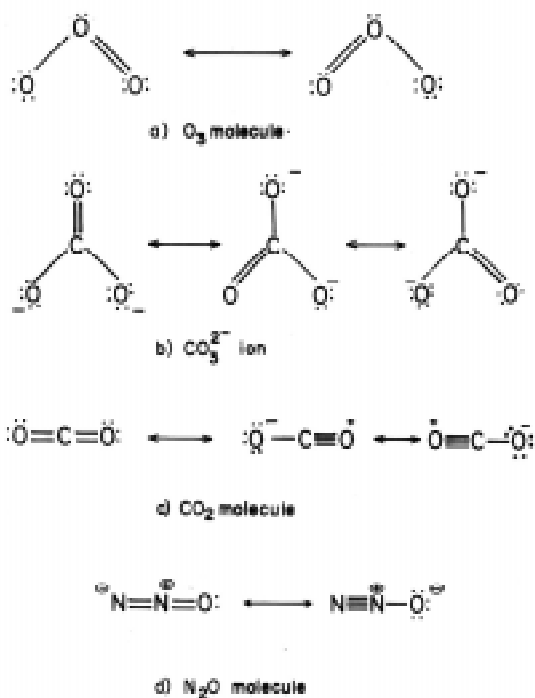
According to the concept of resonance whenever a single Lewis structure cannot describe a molecular structure accurately, a number of structures with similar energy, positions of nuclei, bonding and non bonding pairs of electrons are considered to represent the structure. Each such structure is called as canonical structure. A resonance hybrid consists of many canonical structures. All the canonical structures are equally possible to represent the structure of the molecule.

For example, in ozone ( $\text{O}_3$ ) molecule, the two canonical structures as shown below and their hybrid represents the structure of  $\text{O}_3$  more

accurately. Resonance is represented by a double headed arrow placed between the canonical structures. There are two canonical forms of  $O_3$ .

The resonance structures are possible for molecular ions also. For example, consider resonance in  $CO_3^{2-}$  ion:-

The single Lewis structure based on the presence of two single bonds and one double bond between each carbon and oxygen atoms is inadequate to represent the molecule accurately as it represents unequal bonds. According to experimental findings all carbon to oxygen bonds in  $CO_3^{2-}$  are equivalent. Therefore the carbonate ion is best described as a resonance hybrid of the canonical forms as shown in Fig. 10.9 b.



**Fig. 10.9 Resonance structures of (a) Ozone (b) Carbonate ion (c) Carbon dioxide (d) Nitrous oxide**

There are three canonical forms of  $CO_3^{2-}$ .

Structure of  $CO_2$  molecule is also an example of resonance, the experimental C-O bond length is found to be shorter than C-O single bond length and longer than C=O bond length and lies intermediate in value

between a pure single and a pure double bond lengths. Also the two C=O bond length in the  $\text{CO}_2$  molecule are equivalent and the properties of the two bonds are also the same. Therefore, a single lewis structure cannot depict the structure of  $\text{CO}_2$  as a whole and it is best described as a resonance hybrid of the canonical forms given in Fig. 10.9c.

In  $\text{N}_2\text{O}$  molecule which is a linear molecule, structures with charges on atoms can be written similar to  $\text{CO}_2$ .

- Here also the experimental bond length of N-N-bond lies between a double and triple bond and that of N-O bond length lies between a single and a double bond. Therefore  $\text{N}_2\text{O}$  exists as a hybrid structure of the two canonical forms with a linear geometry.

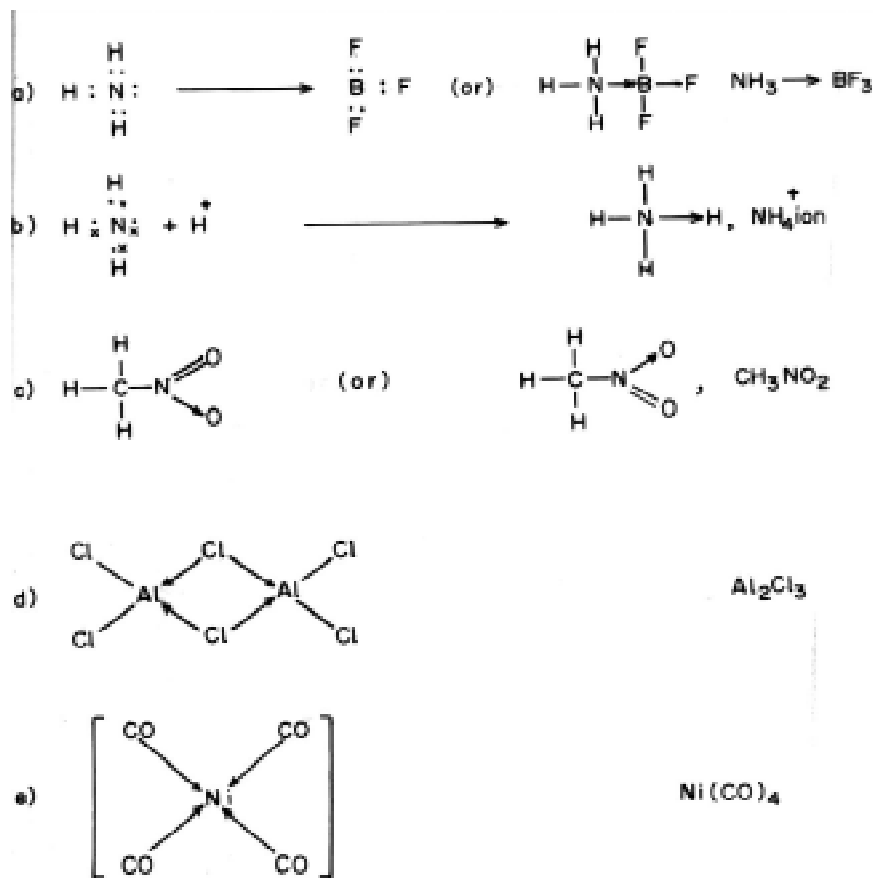
### 10.8 Co-ordinate-covalent bonding or Dative bonding

The electron contributions of combining atoms in a covalent bond are generally equal. In each shared pair of electrons one electron is contributed from each atom of the bond. However in some bond formation, the whole of the shared pair of electrons comes from only one of the combining atoms of the bond, which is referred as the donor atom. The other atom which does not contribute the electron to the shared pair but tries to pull the pair of electron towards itself is called as the acceptor atom. The bond thus formed is between the donor and acceptor atoms is called as the **co-ordinate or co-ordinate - covalent or dative bond**.

A coordinate bond is showed as an arrow which points from the donor to the acceptor atom. In some cases, the donated pair of electron comes from a molecule as a whole which is already formed to an already formed acceptor molecule as a whole.

For Example, coordination bond between  $\text{H}_3\text{N:}$  and  $\text{BF}_3$  molecules. The molecule, ammonia (donor) which gives a pair of electron (lone pair) to  $\text{BF}_3$  molecule which is electron deficient (acceptor) which has an empty orbital to accommodate the pair of electrons. Thus a dative bond is formed and the molecule as a whole is represented as  $\text{H}_3\text{N} \rightarrow \text{BF}_3$  (Fig. 10.10a).

When Proton is added to ammonia, a pair of electron is donated by nitrogen to proton and then proton shares the electron pair to form coordinate covalent bond.



**Fig. 10.10 Coordinate bonding in**  
**(a) ammonia-borontrifluoride (b) ammonium ion**  
**(c) nitromethane**  
**(d) Aluminium chloride and**  
**(e) Nickel tetracarbonyl**

Similarly in (NH<sub>4</sub>Cl) ammonium chloride, covalent - coordinate bond exists in NH<sub>4</sub><sup>+</sup> ion only and Cl<sup>-</sup> ion exists as it is.

Few examples of covalent - coordinate bond :

In nitro methane (CH<sub>3</sub> - NO<sub>2</sub>), one of the N-O-bond exists in a covalent coordinate type.



### Aluminum chloride $\text{Al}_2\text{Cl}_6$ (dimeric form)

Lone pairs of electron from chlorine are donated to electron deficient aluminium atoms in such a way that dimers of  $\text{AlCl}_3$  are formed easily (Fig. 10.10d). The two chlorine atoms act as bridge to link the two Aluminium atoms.

In some complex ion formations, if the central transition metal-ion has empty 'd' orbitals then lone pair of electrons from neutral molecules or anions are donated resulting in the formation of coordination bonds. Example : In Nickel tetracarbonyl, the four bonds between central Ni atom and the carbonyl ligands are mainly covalent -coordinate type. This complex exists in square planar geometry.

### Questions

#### A. Choose the correct answer

1. The crystal lattice of electrovalent compounds is composed of  
(a) Atoms (b) Molecules  
(c) Oppositely charged ions (d) Both molecules and ions
2. The compound which contains both ionic and covalent is  
(a)  $\text{CH}_4$  (b)  $\text{H}_2$  (c)  $\text{KCN}$  (d)  $\text{KCl}$

#### B. Fill in the blanks

3. In  $\text{NaCl}$ ,  $\text{Na}^+$  ion has \_\_\_\_\_ and  $\text{Cl}^-$  ion has \_\_\_\_\_ electron configurations.
4. Linear overlap of two atomic p-orbitals leads to \_\_\_\_\_.
5. Born-Haber cycle is related with \_\_\_\_\_.
6. Two atoms of similar electronegativity are expected to form \_\_\_\_\_ compounds.
7. Repulsion between bond pair-bond pair is than in between lonepair-lone pair.

#### C. Match the following

- |                          |                       |
|--------------------------|-----------------------|
| 1. Electrovalent bonding | a. Benzene            |
| 2. Covalent bonding      | b. Heitler and London |
| 3. Valence Bond theory   | c. Electron transfer  |
| 4. Polarised Bond        | d. Electron sharing   |
| 5. Resonance             | e. Fajan's theory     |
|                          | f. Aluminium chloride |

**D. Write in one or two sentence**

1. Arrange NaCl, MgCl<sub>2</sub> and AlCl<sub>3</sub> in the increasing order of covalent character.
2. Find  $\sigma$  and  $\pi$  bonds in the following :  
CH<sub>3</sub>-CH<sub>3</sub>, CH<sub>2</sub>=CH<sub>2</sub>, CH $\equiv$ CH
3. Among Na<sup>+</sup>, Ca<sup>+2</sup>, Mg<sup>+2</sup>, Al<sup>+3</sup> which has high polarising power ?
4. What is the structure of BeCl<sub>2</sub> ?
5. Write the differences between electrovalent and covalent bonds.
6. Give reason : CCl<sub>4</sub> is insoluble in H<sub>2</sub>O while NaCl is soluble.
7. sp<sup>3</sup> hybridisation is involved in CH<sub>4</sub>, H<sub>2</sub>O and NH<sub>3</sub>. Why are the bond angles different in three cases?
8. Explain the co-ordinate bond formation between BF<sub>3</sub> & NH<sub>3</sub>.
9. What is octet rule? Explain with an example.
10. What are the different types of bonds?
11. What is meant by electrovalent bond. Explain the bond formation in AlBr<sub>3</sub> and CaO.
12. Give the electron dot representation for PH<sub>3</sub> and ethane.
13. Write the Lewis dot structures for the following. S, S<sup>2-</sup>, P, P<sup>3-</sup>, Na, Na<sup>+</sup>, Al and Al<sup>3+</sup>.
14. What are the important features of valence bond theory?
15. What is meant by hybridisation?
16. Define resonance. Give the various resonance structures of CO<sub>2</sub> and CO<sub>3</sub><sup>2-</sup> ion.

**E. Explain briefly on the following**

1. Discuss the important properties of electrovalent compounds.
2. Calculate the lattice energy of NaCl using Born-Haber cycle.
3. Explain the important properties of covalent compounds.
4. Discuss the partial covalent character in ionic compounds using Fajan's rule.
5. Explain the polarity of covalent bonds in H<sub>2</sub>O and HCl.
6. Discuss the shapes of following molecules : NH<sub>3</sub>, H<sub>2</sub>O, CH<sub>4</sub>, PCl<sub>5</sub> and SO<sub>2</sub>.

7. Discuss VSEPR model applied for linear, trigonal planar, tetrahedral and octahedral geometries of molecules.
8. Explain the formation and difference between a sigma bond and a pi-bond. Which has more bond strength?
9. Calculate the lattice enthalpy of  $\text{CaCl}_2$  given that the enthalpy of :
  - i) Sublimation of Ca in  $121 \text{ kJ mol}^{-1}$
  - ii) Dissociation of  $\text{Cl}_2$  to  $2\text{Cl}$  is  $242.8 \text{ kJ mol}^{-1}$
  - iii) Ionisation of Ca to  $\text{Ca}^{2+}$  is  $2422 \text{ kJ mol}^{-1}$
  - iv) Electron gain for Cl to  $\text{Cl}^-$  is  $-355 \text{ kJ mol}^{-1}$
  - v)  $\Delta H_f^{(o)}$  overall is  $-795 \text{ kJ mol}^{-1}$

(Ans :  $2870.8 \text{ kJ mol}^{-1}$ )

### SUMMARY

- Chemical bonding is defined and Kossel-Lewis approach to understand chemical bonding by using the octet rule is studied. Except helium, atoms share or transfer valence electrons to attain the stable octet shell as the electronic configuration.
- Ionic bonding results due to complete electron transfer from electropositive elements to electronegative elements forming cation and anion. Electrostatic force of attraction between ions describe the ionic bonding. Mutual sharing of electrons between the two atoms result in covalent bonding. The directional character, partial ionic character by the pure orbital overlaps are also studied with suitable examples.
- The geometry of simple molecules are predicted using the postulates of VSEPR model  $\text{BeCl}_2$  : linear;  $\text{CH}_4$  : Tetrahedral;  $\text{BCl}_3$  : trigonal;  $\text{PCl}_5$  : trigonal bipyramidal;  $\text{SF}_6$  : Octahedral.
- The concept of hybridisation of C, N, O are learnt.  $\sigma$  and  $\pi$  bonds are studied and differentiated. Resonance in benzene, carbonate ion, molecules are understood.
- Formation of coordinate covalent (dative) bonding between Lewis acids and electron donors are studied.  $\text{Al}_2\text{Cl}_6$  is covalent but in water, it is ionic. Coordinate-covalent bonding in  $\text{Ni}(\text{CO})_4$  is also understood.

## 11. COLLIGATIVE PROPERTIES

### OBJECTIVES

- *To know about colligative properties and the scopes to determine molar mass of the non-volatile solute.*
- *To define Raoult's law and relate the relative lowering of vapour pressure to the molar mass of the solute in the solution.*
- *To determine experimentally the depression in freezing point by Beckmann method and use it to find the molar mass of a non-volatile solute.*
- *To know cottrell's method of elevation of boiling point and use it know the molar mass of a nonvolatile solute.*
- *To understand the concept of osmosis and to find the molar mass of a solute using osmotic pressure.*
- *To explain abnormal colligative properties as due to association and dissociation of solute molecules.*

### 11.1 Colligative Properties and its Scope

A solution may be considered as a homogeneous (single phase) mixture of two or more substances. It is said to be 'binary' if two substances are present and 'ternary' if three substances are present and 'quaternary' if four substances are being present etc. In a binary solution, the component present in larger amount is called as solvent and the component in smaller amounts is called as solute. Solvent and solute together make a solution. In dilute solutions, very small amount of the solute is present.

A colligative property of a solution depends purely on the number of particles dissolved in it, rather than on the chemical nature of the particles. The colligative properties can be regarded as the properties of the solvent in a given solution. Generally, the solute is considered as non-volatile. The various colligative properties are as below :

- i. Lowering of vapour pressure of the solvent ( $\Delta p$ )

- ii. Elevation of boiling point of the solvent ( $\Delta T_b$ )
- iii. Depression of freezing point of the solvent ( $\Delta T_f$ )
- iv. Osmotic pressure ( $\pi$ ).

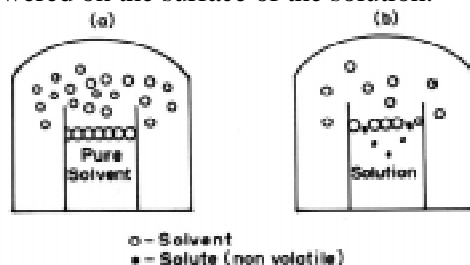
The important scope of the measurement of colligative properties lies on its use to determine the molar mass of the non-volatile solute dissolved in the dilute solution.

## 11.2 Lowering of Vapour Pressure ( $\Delta p$ )

If we take a pure liquid in a closed container, we find that a part of the liquid evaporates and fills the available space with its vapour. The vapour exerts a pressure on the walls of the container and exists in equilibrium with the liquid. This pressure is referred as the vapour pressure of the liquid.

When a non-volatile solute is dissolved in the solvent so that a dilute and homogeneous solution results, then again the vapour pressure of the solution will be made up of entirely from the solvent since the solute does not evaporate. This vapour pressure of the dilute solution is found to be lower than the vapour pressure of the pure solvent.

From Fig.11.1 it may be seen the surface of a dilute solution is partly occupied by solute molecules, thereby the number of solvent molecules at the surface being reduced. Consequently the vapour pressure of the solvent molecules gets lowered on the surface of the solution.



**Fig. 11.1 Effect of solute in the solution on the vapour pressure**

## 11.3 Raoult's Law

The relationship between the vapour pressure of the solution and its concentration is given by a French chemist named Francois Marie Raoult (1886). According to Raoult's law, at constant temperature the vapour pressure of the solution ( $p$ ) is directly proportional to the molefraction of

the solvent ( $X_1$ ) present in the solution. That is,  $p \propto X_1$  (or)  $p = kX_1$  where  $k$  is the proportionality constant. The value of  $k$  is known as follows: For a pure solvent,  $X_1 = 1.0$  and  $p$  becomes  $p^\circ$  corresponding to the vapour pressure of the pure solvent. Thus,  $p^\circ = k(1.0)$ . Substituting the value of  $k$ ,

$$\boxed{p = p^\circ X_1} \quad \dots 11.1$$

Equation 11.1 is generally known as Raoult's law.

When  $n_1$  and  $n_2$  are the number of moles of solvent and solute present in the solution, the molefraction of the solvent  $X_1 = n_1/(n_1 + n_2)$  and the mole fraction of solute  $X_2 = n_2/(n_1+n_2)$ . Also,  $X_1 + X_2 = 1.0$

If  $W_1$  and  $W_2$  are the weights of solvent and solute present, then  $n_1 = W_1/M_1$  and  $n_2 = W_2/M_2$ .  $M_1$  and  $M_2$  are the molar masses of solvent and solute respectively.

It is generally observed that  $p$  is lower than  $P^\circ$ . The lowering of vapour pressure of the solvent in the solution equals to  $(p^\circ - p) = \Delta p$ .

The relative lowering of the vapour pressure, is defined as the ratio of the lowering of vapour pressure to the vapour pressure of the pure solvent. Thus relative lowering of vapour pressure is given by

$$\begin{aligned} \frac{p^\circ - p}{p^\circ} &= \frac{\Delta p}{p^\circ} \\ \frac{p^\circ - p}{p^\circ} &= \frac{p^\circ - p^\circ X_1}{p^\circ} \quad \text{since } p = p^\circ X_1 \\ \frac{p^\circ(1-X_1)}{p^\circ} &= 1-X_1 = X_2 \dots \text{since } \{X_1+X_2 = 1\} \\ \boxed{\therefore \frac{p^\circ - p}{p^\circ} = X_2} &\quad \dots 11.2 \end{aligned}$$

Equation 11.2 represents the mathematical form of Raoult's law. Thus, the statement of Raoult's law for dilute solutions containing non-volatile

non-electrolyte solute is: Relative lowering of vapour pressure is equal to the mole fraction of the solute. Since mole fraction of the solute ( $X_2$ ) is given by  $n_2/(n_1+n_2)$ , the quantity  $(p^\circ - p)/p^\circ$  depends upon the number of moles or molecules of the solute in solution and not on its chemical nature. Thus, relative lowering of vapour pressure is a colligative property.

### 11.3.1 Determination of molecular weights from relative lowering of vapour pressure

In dilute solutions, the number of moles of solvent ( $n_1$ ) is large compared to the number of moles of solute ( $n_2$ ) and thus  $(n_1 + n_2)$  can be approximated to  $n_1$  and  $x_2$  becomes equal to  $n_2/n_1$ .

$$\text{Thus } \frac{\Delta p}{p^\circ} = \frac{n_2}{n_1} = \frac{W_2 \cdot M_1}{M_2 \cdot W_1} \quad \dots 11.3$$

Substituting for  $n_1$  and  $n_2$  as  $W_1/M_1$  and  $W_2/M_2$  we get  $\Delta p/p^\circ = M_1 \cdot W_2 / W_1 \cdot M_2$ . Knowing  $M_1, W_1$  and  $W_2$  and from the measurement of lowering of vapour pressure,  $M_2$  the molar mass of the solute can be determined using equation 11.3.

#### Problem 1

The vapour pressure of  $\text{CCl}_4$  at  $30^\circ\text{C}$  is 143 mm of Hg. 0.5 gm of a non-volatile non electrolyte substance with molar mass 65 is dissolved in 100 ml of  $\text{CCl}_4$ . What will be the vapour pressure of the solution. Density of  $\text{CCl}_4$  at  $30^\circ\text{C} = 1.58$  gm per cc.

#### Solution

Vapour pressure of pure solvent,  $P^\circ = 143$  mm of Hg.

Vapour pressure of solution,  $p = ?$

Weight of solute,  $W_2 = 0.5$  gm

Mol. wt of solute,  $M_2 = 65$

Mol. wt of solvent ( $\text{CCl}_4$ ),  $M_1 = 154$

Weight of solvent,  $W_1 = 100 \times 1.58 = 158$  gm

(mass = density x volume)

$$\frac{p^\circ - p}{P^\circ} = \frac{W_2}{M_2} \cdot \frac{M_1}{W_1} \quad (\text{By Raoult's law})$$

$$\frac{143 - P}{143} = \frac{0.5}{65} \times \frac{154}{158}$$

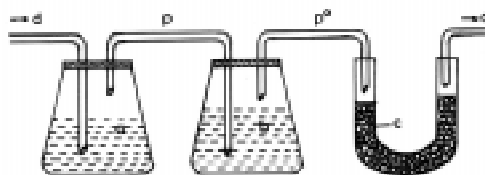
$$\therefore \frac{143 - P}{143} = \frac{0.5}{65} \times \frac{154}{158}$$

$$\therefore p = 141.93 \text{ mm of Hg.}$$

### 11.3.2 Experimental determination of relative lowering of vapour pressure

#### Dynamic method (or) Ostwald - Walker method

This method is based on the principle that when dry air is successively passed through a series of containers possessing solution and pure solvent respectively, the air becomes saturated with the solvent vapours and an equal amount of weight loss in solution and solvent containers takes place.



**Fig. 11.2 Ostwald - walker apparatus**

In Fig. 11.2 the first chamber (a) contains a weighed amount of the solution under examination and the next chamber (b) contains a weighed amount of the pure solvent. A weighed amount of anhydrous and dry calcium chloride is taken in the U-tube (c) connected at the end. The chambers and the U-tube are connected by a series of delivery tubes (d) through which air is passed. The dry air is first allowed to pass through the solution chamber until the air is saturated with the solvent vapour to maintain the vapour pressure of the solution 'p'. Consequently, a loss in weight of the solution results in the solution chamber since some amount solvent molecules have evaporated. When this air is allowed to pass through the pure solvent chamber some more solvent vapour gets in stream with air, until the vapour pressure of pure solvent  $p^\circ$ , is maintained. This



happens so because  $p^\circ$  is greater than  $p$ . Consequently, the weight loss registered in the solvent chamber is proportional to the  $(p^\circ - p)$  quantity.

The weight loss in solution chamber  $\propto p$

The weight loss in solvent chamber  $\propto p^\circ - p$

Sum of the loss in weights of solution

and solvent chamber  $\propto (p + p^\circ - p) \propto p^\circ$

When the air saturated with solvent vapours is passed through  $\text{CaCl}_2$  U-tube, the solvent vapours are absorbed and the dry air gets out. The gain in weight of the  $\text{CaCl}_2$  U-tube should be equal to the total loss in weight of solution and solvent chambers, which is in turn proportional to  $p^\circ$ .

$$\frac{\text{Loss in weight of the solvent chamber}}{\text{Gain in weight of } \text{CaCl}_2 \text{ tube}} = \frac{p^\circ - p}{p^\circ}$$

= relative lowering of the vapour pressure

Thus, using the experimental  $(p^\circ - p)/p^\circ$  values and applying Raoult's law, the molecular weight of the solute can be determined.

## Problem 2

Dry air was passed successively through a solution of 5 gm of solute dissolved in 80.0 gm of water and through pure water. The loss in weight of the solution was 2.5 gm and that of the pure solvent was 0.04 gm. What is the molecular weight of the solute?

$$p \propto 2.5 \text{ gm}; (p^\circ - p) \propto 0.04 \text{ gm}$$

$$\therefore p^\circ \propto 2.54 \text{ gm.}$$

$$\left. \begin{array}{l} \text{The relative lowering of} \\ \text{vapour pressure} \end{array} \right\} = \frac{p^\circ - p}{p^\circ} = \frac{W_2}{M_2} \cdot \frac{M_1}{W_1}$$

$$\therefore \frac{0.04}{2.54} = \frac{5 \times 18}{M_2 \times 80} \quad (\therefore M_2 = 71.43)$$

$$M_2 = \text{mol.wt of solute} = 71.43$$

### Problem 3

Calculate the vapour pressure of the solution. The molefraction of the solute is 0.25. The vapour pressure of the pure solvent is 0.8atm.

$$\frac{p^\circ - p}{p^\circ} = X_2$$

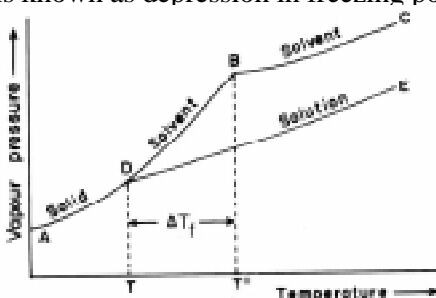
$$\frac{0.8 - p}{0.8} = 0.25$$

$$p = 0.6 \text{ atm}$$

Vapour pressure of the solution = 0.6 atm

### 11.4 Depression of freezing point of dilute solution

Freezing point is the temperature at which solid and liquid states of a substance have the same vapour pressure. According to Raoult's law, addition of a non-volatile solute to solvent lowers the vapour pressure of the solvent and hence, the vapour pressure of pure solvent is greater than the vapour pressure of solution. Thus the temperature at which the solution and its solid form existing in equilibrium and possessing the equal vapour pressures, is lowered. That is, the freezing point of solution is lowered. The lowering of the freezing point of the solution from that of the freezing point of the pure solvent is known as depression in freezing point of the solution.



**Fig. 11.3 Vapour pressure - temperature curves for depression in freezing point**

Consider the vapour pressure curves shown in Fig.11.3. Generally when

the temperature of a solid substance that is used as the solvent is raised, the vapour pressure also raises. AB curve depicts this. Similarly curve BC represents the increase in vapour pressure of the liquid solvent with increase in temperature. Curves AB and BC meet at B corresponding to  $T^{\circ}$  temperature which is the freezing point of the pure solvent. At  $T^{\circ}$ , the vapour pressure of the liquid and solid states of the solvent are equal at B. Since the vapour pressure of the solution is always lower than that of its pure solvent, the vapour pressure curve of the solution DE always lie below that of the pure solvent.

D is the point of intersection of the vapour pressure curves of solution and pure solvent. The temperature at D is the freezing point of the solution and is seen to be lower than  $T^{\circ}$ . The depression in freezing point is  $\Delta T_f = T^{\circ} - T$ . The measured depression in freezing point ( $\Delta T_f$ ) is found to be directly proportional to the molality (m) of the solute in solution. That is,  $\Delta T_f \propto m$  (or)  $\Delta T_f = K_f m$ , where  $K_f$  is called as the **cryoscopic constant (or) molal freezing point depression constant**. ' $K_f$ ' is defined as the depression in freezing point produced when one mole of solute is dissolved in 1 kg solvent. It is also the depression in freezing point of one molal solution. Freezing point depression of a dilute solution is found to be directly proportional to the number of moles (and hence the no. of molecules) of the solute dissolved in a given amount of the solvent. Also  $\Delta T_f$  is independent of the nature of the solute as long as it is non-volatile. Hence depression in freezing point is considered as a colligative property.

#### Determination of molecular weight from depression in freezing point

$$\Delta T_f = K_f \cdot m$$

where  $m$  = molality

$$m = \frac{n_2}{W_1} \quad \text{and} \quad n_2 = \frac{W_2}{M_2}$$

$W_1$  = Weight of the solvent in Kg;

$M_2$  = Molecular weight of solute

$$\therefore m = \frac{W_2}{M_2 W_1}$$

$$\therefore \Delta T_f = K_f \frac{W_2}{M_2 \cdot W_1}$$

$$\therefore M_2 = \frac{K_f \cdot W_2}{\Delta T_f \cdot W_1} \quad \frac{\text{K.kg mol}^{-1}\text{g}}{\text{K.kg}}$$

$$M_2 = \frac{K_f}{\Delta T_f} \cdot \frac{W_2}{W_1} \text{ g mol}^{-1}$$

Thus the molecular weight of the solute can be calculated.

#### Problem 4

1.00 g of a non-electrolyte dissolved in 50.5g of benzene lowered its freezing point by 0.40K. The freezing point depression constant of benzene is 5.12K.kg mol<sup>-1</sup>. Find the molecular mass of the solute.

#### Solution

$$\Delta T_f = 0.40\text{K}$$

$$K_f = 5.12\text{K.kg mol}^{-1}$$

$$W_2 = 1\text{g}$$

$$W_1 = 50.5 \text{ gm} = \frac{50.5}{1000} \text{ kg}$$

$$M_2 = \frac{K_f}{\Delta T_f} \times \frac{W_2}{W_1}$$

$$\therefore M_2 = \frac{5.12}{0.40} \times \frac{1}{50.5} \times 1000$$

$$= 256 \text{ g mol}^{-1}$$

Thus, the molecule mass of the solute = 256 g mol<sup>-1</sup>.

**Problem 5**

What is the freezing point of solution containing 3g of a non-volatile solute in 20g of water. Freezing point of pure water is 273K,  $K_f$  of water = 1.86 Kkg/mol. Molar mass of solute is 300 g/mol.

$$T^\circ - T = K_f m$$

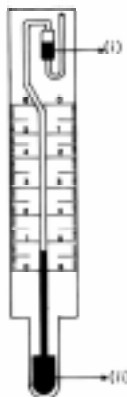
$$\begin{aligned} m &= \frac{W_2}{M_2 W_1} \\ &= \frac{3}{300 \times 20} \times 1000 \\ T^\circ - T &= \frac{1.86 \times 3 \times 1000}{300 \times 20} = 0.93 \text{ K} \end{aligned}$$

$$T = 273 \text{ K} - 0.93 \text{ K} = 272.07 \text{ K}$$

$\therefore$  Freezing point of the solution = 272.07 K

**11.4.1 Beckmann Method**

Beckmann thermometer is used to measure small temperature changes in the freezing point of pure solvent and solution. Beckmann thermometer is not used in determining the absolute value of freezing temperature of the solvent or that of the solution. It is therefore called a differential thermometer. Temperature differences of even 0.01K can easily be measured.

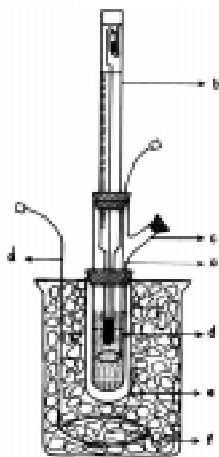


**Fig. 11.4 Beckmann thermometer**

Beckmann thermometer (Fig.11.4) consists of a large thermometer bulb at the bottom of a free capillary tube (ii) which is connected to a reservoir of mercury (i) placed at the top. As the capillary has fine bore, a small change of temperature causes a considerable change in the height of mercury column (level) in the capillary. The whole scale of a Beckmann thermometer covers only about 6K. Initially the level of mercury in the capillary should be on the scale. This is achieved by transferring mercury from the lower bulb to the reservoir and viceversa. When the Beckmann thermometer is used at high temperatures, some of the mercury from the thermometer bulb is transferred into the upper reservoir. At lower temperature mercury from the reservoir falls down in to the thermometer bulb.

#### **Measurement of freezing point depression by Beckmann method**

A simple Beckmann apparatus is shown in Fig.11.5. It consists of a freezing tube (a) with a side arm (c) through which a known amount of a solute can be introduced. A stopper carrying a Beckmann thermometer (b) and a stirrer (d) is fitted in to the freezing tube. To prevent rapid cooling of the contents of the freezing tube, A, a guard tube (e) surrounds the tube so that there is an air space between a and e. This assembly, as a whole, is placed in a wide vessel V which contains a freezing mixture (f) maintaining a low temperature around 5°C below the freezing point of the pure solvent.



**Fig. 11.5 Apparatus for Beckmann method**

A known weight of the pure solvent is placed in the tube (a). It is cooled with gentle and continuous stirring. As a result of super cooling, the temperature of the solvent will fall by about 0.5°C below its freezing point. Vigorous stirring is then set in when solid starts separating and the temperature rises to the exact freezing point. This temperature remains constant, for some time, until all the liquid solvent gets solidified and is noted as  $T^0$ .

The tube (a) is taken out, warmed to melt the solid and a known weight of the solute is added through the side arm (c). When the solute is dissolved in to the solvent forming a solution, the tube (a) is put back in to the original position and the freezing point of the solution (T) is redetermined in the same manner as before. The difference between the two readings gives the freezing point depression ( $\Delta T_f$ ).

Depression in freezing point  $\Delta T_f = T^0 - T$ . From this value, the molecular mass of the non-volatile solute can be determined using the expression and known  $K_f$  value.

$$M_2 = \frac{K_f}{\Delta T_f} \cdot \frac{W_2}{W_1} \quad \dots 11.4$$

**Table 11.1 Molal Depression (cryoscopic) constants,  $K_f$  (One mole of solute per 1000 grams of solvent)**

Solvent	F. Pt. K	$K_f$ (K.kg.mole <sup>-1</sup> )
Acetic acid	289.60	3.90
Bromoform	281.30	14.30
Benzene	278.53	5.10
Cyclohexane	279.55	20.20
Camphor	451.40	37.70
Naphthalene	353.25	7.00
Nitrobenzene	278.70	6.90
Phenol	314.10	7.27
Water	273.00	1.86

### 11.5 Elevation of boiling point of dilute solutions

The boiling point of a pure liquid is the temperature at which its vapour pressure becomes equal to the atmospheric pressure. Since the vapour pressure of a solution is always lower than that of the pure solvent, it follows that the boiling point of a solution will always be higher than of the pure solvent.

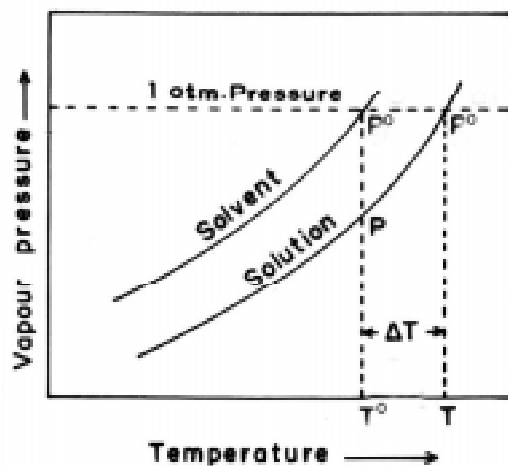


Fig. 11.6

In the Fig.11.6, the upper curve represents the vapour pressure - temperature dependence of the pure solvent. The lower curve represents the vapour pressure - temperature dependence of a dilute solution with known concentration. It is evident that the vapour pressure of the solution is lower than that of the pure solvent at every temperature. The temperature  $T^\circ$  gives the boiling point of the pure solvent and  $T$  the boiling point of the pure solution. This is because at these temperatures ( $T^\circ$ ,  $T$ ) the vapour pressures of pure solvent and solution becomes equal to the atmospheric pressure.

$$\text{The elevation of boiling point} = \Delta T_b = T - T^\circ.$$

Elevation of boiling point is found directly proportional to the molality of the solution (or) in turn the number of molecules of solute. Also it is independent of the nature of the solute for a non-volatile solute. Hence, boiling point elevation is a colligative property.



Thus it may be written as

$$\boxed{\Delta T_b \propto m} \quad \dots 11.5$$

### Determination of molecular weight from boiling point elevation

By measuring the boiling point elevation of a solution of a known concentration, it is possible to calculate molecular weight of a non-volatile non-electrolyte solute.

$$\Delta T_b \propto m$$

$$\therefore \Delta T_b = K_b m \quad \dots 11.6$$

The proportionality constant  $K_b$  is characteristic of the solvent and it is called the **molal boiling point elevation constant** or **ebullioscopic constant**. It is defined as the elevation of boiling point of one molal solution.

When  $n_2$  moles of the solute is dissolved in  $W_1$  kg of the solvent, the molality is given by  $n_2/W_1$ .

$$\Delta T_b = K_b \frac{n_2}{W_1} \quad \text{since} \quad n_2 = \frac{W_2}{M_2}$$

$$\Delta T_b = K_b \frac{W_2}{M_2 W_1}$$

Since  $W_2$ , is the weight of the solute, we can calculate the molecular weight of the solution using the following expression.

$$\boxed{\therefore M_2 = \frac{K_b \cdot W_2}{\Delta T_b \cdot W_1}}$$

**Table 11.2 Molal Elevation (Ebullioscopic) constants (One mole of solute per 1000 grams of solvent)**

Solvent	B. Pt K	$K_b$ (K.kg.mole <sup>-1</sup> )
Water	373.00	0.52
Benzene	353.10	2.57
Methanol	337.51	0.81
Ethanol	351.33	1.20
Carbon tetra chloride	349.72	5.01
Chloroform	334.20	3.88
Acetic acid	391.50	3.07
Acetone	329.15	1.72
Carbon disulphide	319.25	2.41
Phenol	455.10	3.56

**Problem 5**

A solution containing 2.5 g of a non-volatile solute in 100 gm of benzene boiled at a temperature 0.42K higher than at the pure solvent boiled. What is the molecular weight of the solute? The molal elevation constant of benzene is 2.67 K kg mol<sup>-1</sup>.

$$K_b = 2.67 \text{ K kg mol}^{-1}$$

$$\Delta T_b = 0.42 \text{ K}$$

$$100$$

$$W_1 = 100 \text{ g} = \frac{100}{1000} \text{ kg} = 0.1 \text{ Kg}$$

$$W_2 = \frac{K_b}{\Delta T_b} \cdot \frac{W_2}{W_1}$$

$$M_2 = \frac{2.67}{0.42} \times \frac{2.5}{0.1}$$

$$M_2 = 158.98 \text{ g mol}^{-1}$$

### 11.5.1 Determination of elevation of boiling point by Cottrell's Method

The apparatus (Fig.11.7) consists of a boiling tube (a) which is graduated and contains weighed amount of the liquid under examination. An inverted funnel tube (b) placed in the boiling tube collects the bubbles rising from a few fragments of a porous pot placed inside the liquid. When the liquid starts boiling, it pumps a stream of a liquid and vapour over the bulb of the Beckmann thermometer (f) held a little above the liquid surface. In this way, the bulb is covered with a thin layer of boiling liquid which is in equilibrium with the vapour. This ensures that the temperature reading is exactly that of the boiling liquid and that superheating is minimum. After determining the boiling point of the pure solvent, a weighed amount of the solute is added and procedure is repeated for another reading. The vapours of the boiling liquid is cooled in a condenser (C) which has circulation of water through (d) and (e). The cooled liquid drops into the liquid in (a).

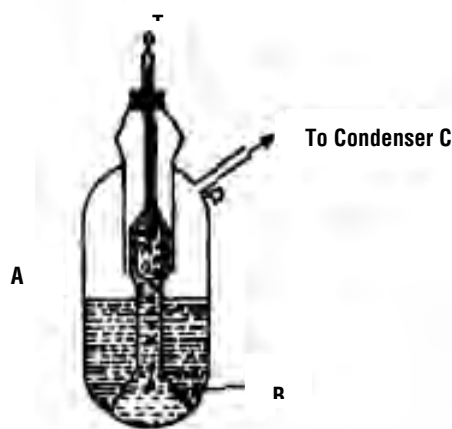


Fig. 11.7

#### Problem 7

0.900g of a solute was dissolved in 100 ml of benzene at 25°C when its density is 0.879 g/ml. This solution boiled 0.250°C higher than the boiling

point of benzene. Molal elevation constant for benzene is  $2.52 \text{ K.Kg.mol}^{-1}$ . Calculate the molecular weight of the solute.

**Solution**

$$\text{Weight of benzene} = 100 \times 0.879 = 87.9\text{g}$$

$$\begin{aligned} \text{Molality of solution, } m &= \frac{0.900/M_2}{87.9} \times 1000 \\ &= \frac{900}{87.9 M_2} \end{aligned}$$

$$\Delta T_b = K_b m \text{ (or) } 0.250 = 2.52 \times \frac{900}{87.9 M_2}$$

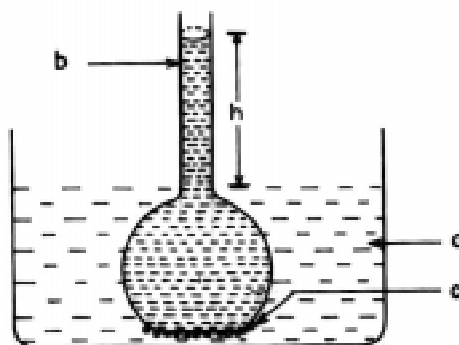
$$\therefore M_2 = \frac{900 \times 2.52}{87.9 \times 0.250}$$

$$M_2 = 103.2 \text{ g/mole}$$

$$\therefore \left. \begin{array}{l} \text{Molecular weight} \\ \text{of the solute} \end{array} \right\} = 103.2 \text{ g/mole}$$

**11.6 Osmosis in solution**

Spontaneous movement of solvent particles from a dilute solution or from a pure solvent towards the concentrated solution through a semipermeable membrane is known as **osmosis** (Greek word : 'Osmos' = to push).



**Fig. 11.8 Osmosis apparatus**

Fig. 11.8 depicts Osmosis in a simple way. The flow of the solvent from its side (a) to solution side (b) separated by semipermeable membrane (c) can be stopped if some definite extra pressure is applied on the solution risen to height (h). This pressure that just stops the flow of solvent is called **osmotic pressure** of the solution. This pressure ( $\pi$ ) has been found to depend on the concentration of the solution.

Osmosis is a process of prime importance in living organisms. The salt concentration in blood plasma due to different species is equivalent to 0.9% of aqueous sodium chloride. If blood cells are placed in pure water, water molecules rapidly move into the cell. The movement of water molecules into the cell dilutes the salt content. As a result of this transfer of water molecules the blood cells swell and burst. Hence, care is always taken to ensure that solutions that flow into the blood stream have the same osmotic pressure as that of the blood.

Sodium ion ( $\text{Na}^+$ ) and potassium ions ( $\text{K}^+$ ), are responsible for maintaining proper osmotic pressure balance inside and outside of the cells of organism. Osmosis is also critically involved in the functioning of kidneys.

#### **Characteristics of Osmotic Pressure ( $\pi$ )**

- It is the minimum external pressure which must be applied on solution side in order to prevent osmosis if separated by a solvent through a semi permeable membrane.
- A solution having lower or higher osmotic pressure than the other is said to be hypotonic or hypertonic respectively in respect to other solution.
- Two solutions of different substances having same osmotic pressure at same temperature are said to be isotonic to each other. They are known as isotonic solutions.

#### **11.6.1 Osmotic pressure and concerned laws**

Vant Hoff noted the striking resemblance between the behaviour of dilute solutions and gases. He concluded that, a substance in solution behaves exactly like gas and the osmotic pressure of a dilute solution is equal to the pressure which the solute would exert if it is a gas at the same temperature occupying the same volume as the solution. Thus it is proposed

that solutions also obey laws similar to gas laws.

### 1. Boyle's - Vant Hoff law

The osmotic pressure ( $\pi$ ) of the solution at constant temperature is directly proportional to the concentration (C) of the solution.

$\therefore \pi \propto C$  at constant T.

C = Molar concentration

### 2. Charle's - Vant Hoff law

At constant concentration the osmotic pressure ( $\pi$ ) of the solution is directly proportional to the temperature (T).

$\pi \propto T$  at constant C. Combining these two laws,  
 $\pi \propto C T$

$$\text{(or)} \quad \boxed{\pi = CRT} \quad 11.7$$

where R is the gas constant.

### Determination of molecular weight by osmotic pressure measurement

The osmotic pressure is a colligative property as it depends, on the number of solute molecules and not on their identity.

Solution of known concentration is prepared by dissolving a known weight ( $W_2$ ) of solute, in a known volume ( $V \text{ dm}^3$ ) of the solvent and its osmotic pressure ( $\pi$ ) is measured at room temperature (T)

Since  $\pi = CRT$

$$C = \frac{n_2}{V} = \frac{\text{number of moles of solute}}{\text{Volume of the solution in dm}^3}$$

$$C = \frac{W_2}{M_2 V}$$

Substituting in the equation 11.8,

$$\text{We get } \pi = \frac{W_2}{M_2 V} RT$$

(or)

$$M_2 = \frac{W_2 RT}{\pi V}$$

11.8

Thus  $M_2$ , molecular weight of the solute can be calculated by measuring osmotic pressure value.

#### 11.6.2 Determination of osmotic pressure by Berkley-Hartley method

The osmotic pressure of a solution can be conveniently measured by Berkley - Hartley method. The apparatus (Fig. 11.9) consists of two concentric tubes. The inner tube (a) is made of semipermeable membrane (c) with two side tubes. The outer tube (b) is made of gun metal which contains the solution. The solvent is taken in the inner tube. As a result of osmosis, there is fall of level in the capillary indicator (d) attached to the inner tube. The external pressure is applied by means of a piston (e) attached to the outer tube so that the level in the capillary indicator remains stationary at (d). This pressure is equal to the osmotic pressure ( $\pi$ ) and the solvent flow from inner to outer tube is also stopped.

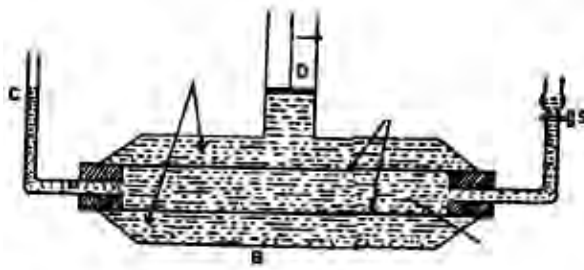


Fig. 11.9 Berkley - Hartley apparatus

#### Advantages of this Method

1. The osmotic pressure is recorded directly and the method is quick.
2. There is no change in the concentration of the solution during the measurement of osmotic pressure.
3. The osmotic pressure is balanced by the external pressure and there is minimum strain on the semipermeable membrane.

#### Problem 8

10g of an organic substance when dissolved in two litres of water gave an osmotic pressure of 0.59 atm, at 7°C. Calculate the molecular weight of the substance.

**Solution**

$$\pi = \frac{\text{Moles of solute}}{\text{Litres of solution}} \times RT$$

$$0.59 = \frac{10 \times 0.082 \times 280}{M \times 2}$$

$$M = \frac{10 \times 0.082 \times 280}{2 \times 0.59} = 194.6 \text{ g/mol}$$

Molecular weight = 194.6 g/mole

**11.7 Abnormal Colligative Properties**

The experimental values of colligative properties in most of the cases resemble closely to those obtained theoretically by their formula. However, in some cases experimental values of colligative properties differ widely from those obtained theoretically. Such experimental values are referred to as abnormal colligative properties.

The abnormal behaviour of colligative properties has been explained in terms of dissociation and association of solute molecules.

**a. Dissociation of solute molecules**

Such solutes which dissociate in solvent (water) i.e. electrolytes, show an increase in number of particles present in solution. This effect results in an increase in colligative properties obtained experimentally.

The Van't Hoff factor (i)

$$i = \frac{\text{Experimental colligative property}}{\text{Normal colligative property}}$$

$i > 1$  for dissociation. We can calculate the degree of dissociation ( $\alpha$ ) using the equation.

$$\alpha_{\text{dissociation}} = \frac{i - 1}{n - 1} \quad \dots 11.9$$



where 'n' is the total number of particles furnished by one molecule of the solute.

For example, sodium chloride in aqueous solution exists almost entirely as  $\text{Na}^+$  and  $\text{Cl}^-$  ions. In such case, the number of effective particles increases and therefore observed colligative property is greater than normal colligative property.

### Problem 9

A 0.5 percent aqueous solution of KCl was found to freeze at 272.76K. Calculate the Van't Hoff factor and degree of dissociation of the solute at this concentration ( $K_f$  for water =  $1.86 \text{ k.kg.mol}^{-1}$ ). Normal molar mass of KCl = 74.5.

$$T_f^\circ \text{ of water} = 273 \text{ K}$$

$$T_f \text{ of the solution} = 272.76 \text{ K}$$

$$\therefore \Delta T_f = T_f^\circ - T_f = +0.24 \text{ K}$$

$$M_2 = \frac{K_f \cdot W_2}{\Delta T_f \cdot W_1}$$

Observed molecular mass

$$M_2 = \frac{1.86 \times 0.5 \times 1000}{100 \times 0.24} = 38.75 \text{ g.mol}^{-1}$$

The colligative property is inversely related to the molar mass.

$\therefore$  Van't Hoff factor

$$i = \frac{\text{Observed colligative property}}{\text{Normal colligative property}} = \frac{\text{Theoretical molar mass}}{\text{Observed molar mass}}$$

$$\text{Vant Hoff factor (i)} = \frac{74.5}{38.75} = 1.92$$

$$\text{Degree of dissociation } \alpha = \frac{i-1}{n-1}$$

$n = 2$  for KCl

$$\begin{aligned} \therefore \alpha &= \frac{1.92-1}{2-1} \\ &= 0.92 \end{aligned}$$

$$\therefore \text{Degree of dissociation} = 0.92$$

#### **b. Association of the solute molecules**

Such solute which associate in a solvent show a decrease in number of particles present in solution. This effect results in a decrease in colligative properties obtained experimentally.

Here,

$$\text{Experimental Colligative Property} < \text{Normal Colligative Property}$$

$\therefore$  Vant Hoff factor

$$i = \frac{\text{Experimental Colligative Property}}{\text{Normal colligative property}}$$

$i < 1$  for association

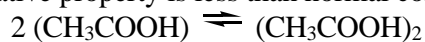
Using this, the degree of association ' $\alpha$ ' can be calculated from

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

... 11.10

where ' $n$ ' is the number of small molecules that associate into a single larger new molecule.

For example, molecules of acetic acid dimerise in benzene due to intermolecular hydrogen bonding. In this case, the number of particles is reduced to half its original value due to dimerisation. In such case, the experimental colligative property is less than normal colligative property.



### Problem

The depression in the freezing point of a benzene solution containing 0.784g of Acetic acid dissolved in 100ml of benzene is 0.35k. Calculate the van't Hoff factor and the degree of association of the solute at this concentration

( $k_f$  for benzene =  $5.10 \text{ k.kg.mol}^{-1}$ , molar mass of acetic acid is 60.01).

$$\begin{aligned} \Delta T_f &= \frac{k_f \cdot W_2}{M_2} \\ M_2 &= \frac{k_f \cdot W_2}{\Delta T_f} \\ &= \frac{5.10 \times 0.784 \times 1000}{100 \times 0.35} = 114.24 \end{aligned}$$

The colligative property is inversely related to molar mass.

∴ Van't Hoff factor

$$i = \frac{\text{Observed colligative property}}{\text{Normal colligative property}}$$

$$= \frac{\text{Theoretical molar mass}}{\text{Observed molar mass}}$$

$$\begin{aligned} \text{Van't Hoff factor } i &= \frac{60}{114.24} \\ &= 0.525 \end{aligned}$$

$$\text{Degree of association } \alpha = \frac{n(1-i)}{n-1}$$

$n = 2$  for dimerisation

Acetic acid exist as dimers in benzene

$$\alpha = 2 \frac{(1-0.525)}{2-1} = 0.95$$

$\therefore$  Degree of association = 0.95

### Summary

#### Relationship between colligative properties and molecular mass of the non-volatile solute

1.	Relative lowering of vapour pressure $\frac{p^\circ - p}{p^\circ}$	The ratio of lowering of vapour pressure of the pure solvent	$\frac{P^\circ - P}{P^\circ} = \frac{W_2 M_1}{M_2 W_1}$
2.	Elevation of boiling point ( $\Delta T_b$ )	Boiling point of the solution is greater than the solvent	$T - T^\circ = \Delta T_b$ $\Delta T_b = \frac{W_2}{M_2 W_1} \cdot K_b$
3.	Depression in freezing point ( $\Delta T_f$ )	Freezing point of the solution is lower than solvent.	$T^\circ - T = \Delta T_f$ $\Delta T_f = \frac{W_2}{M_2 W_1} \cdot K_f$
4.	Osmotic pressure ( $\pi$ )	Excess pressure applied on the concentrated solution side to stop the osmosis.	$\pi = CRT$
5.	Abnormal colligative property (i)	Due to dissociation and association of molecules, there is a change in the experimental colligative property value	Van't Hoff factor $i = \frac{\text{Observed colligative property}}{\text{Theoretical colligative property}}$

## Questions

### A. Choose the correct answer

- Properties which depend only on number of particles present in solution are called  
(a) Additive (b) Constitutive (c) Colligative (d) None
- Which solution would possess the lowest boiling point  
(a) 1% NaCl solution (b) 1% Urea solution  
(c) 1% glucose solution (d) 1% sucrose solution
- In cold countries, ethylene glycol is added to water in the radiators of cars during winters. It results in :  
(a) Lowering boiling point (b) Reducing viscosity  
(c) Reducing specific heat (d) Lowering freezing point
- Which of the following 0.1M aqueous solutions will have the lowest freezing point?  
(a) Potassium sulphate (b) Sodium chloride  
(c) Urea (d) Glucose
- The Van't Hoff factor of 0.005M aqueous solution of KCl is 1.95. The degree of ionisation of KCl is  
(a) 0.94 (b) 0.95 (c) 0.96 (d) 0.59

### B. Fill in the blanks

- Relative lowering of vapour pressure is equal to \_\_\_\_\_ in solution.
- A liquid having high vapour pressure has \_\_\_\_\_ boiling point.
- The least count of Beckmann's thermometer is \_\_\_\_\_.
- Molal elevation constant is a characteristic constant for a given \_\_\_\_\_.
- Semipermeable membrane allows the passage of \_\_\_\_\_ through it.
- For a deliquescence to occur, the vapour pressure of water in the air must be \_\_\_\_\_ than that of the saturated solution.
- Depression in freezing point is \_\_\_\_\_ pronounced if camphor is used as a solvent in place of water for same amount of solute and solvent.
- Every solution behaves as ideal solution \_\_\_\_\_.
- The osmotic pressures of 0.1M glucose and 0.1M NaCl solutions are \_\_\_\_\_.
- Solutions that have same osmotic pressure are called solutions.

### C. Answer the following in one (or) two sentences

- What are colligative properties?
- Define relative lowering of vapour pressure.

## 12. THERMODYNAMICS - I

### OBJECTIVES

- *To predict the possibility of a process.*
- *To differentiate system and surroundings from universe.*
- *To define various processes, properties; state and path functions; spontaneous and non-spontaneous; exo- and endo-thermic processes.*
- *To learn to interrelate work, heat and energy.*
- *To define Zeroth and first laws of thermodynamics.*
- *To measure changes in internal energy and enthalpy.*
- *To relate E and H.*
- *To determine enthalpy changes of various physical processes.*
- *To determine enthalpy changes in formation, combustion, neutralisation.*
- *To understand non-conventional energy resources and to identify different renewable energy resources.*

### 12.1 Introduction

The term **thermodynamics** is derived from Greek word, '**Thermos**' meaning heat and '**dynamics**' meaning flow. Thermodynamics deals with the inter-relationship between heat and work. It is concerned with the interconversions of one kind of energy into another without actually creating or destroying the energy. **Energy** is understood to be the capacity to do work. It can exist in many forms like electrical, chemical, thermal, mechanical, gravitational etc. Transformations from one to another energy form and prediction of the feasibility (possibility) of the processes are the important aspects of thermodynamics.

As an illustration, from our common experience steam engines are seen to transform heat energy to mechanical energy, by burning of coal which is a fossil fuel. Actually, the engines use the energy stored in the fuel to perform mechanical work. In chemistry, many reactions are encountered that can be utilised to provide heat and work along with the required products. At present thermodynamics is widely used in physical, chemical

and biological sciences focussing mainly on the aspect of predicting the possibility of the processes connected with each sciences. On the other hand, it fails to provide insight into two aspects: Firstly, the factor of time involved during the initial to final energy transformations and secondly, on the quantitative microscopic properties of matter like atoms and molecules.

## **12.2 Terminology used in Thermodynamics**

It is useful to understand few terms that are used to define and explain the basic concepts and laws of thermodynamics.

### **System**

Thermodynamically a system is defined as any portion of matter under consideration which is separated from the rest of the universe by real or imaginary boundaries.

### **Surroundings**

Everything in the universe that is not the part of system and can interact with it is called as surroundings.

### **Boundary**

Anything (fixed or moving) which separates the system from its surroundings is called **boundary**.

For example, if the reaction between A and B substances are studied, the mixture A and B, forms the system. All the rest, that includes beaker, its walls, air, room etc. form the surroundings. The boundaries may be considered as part of the system or surroundings depending upon convenience. The surroundings can affect the system by the exchange of matter or energy across the boundaries.

### **Types of systems**

In thermodynamics different types of systems are considered, which depends on the different kinds of interactions between the system and surroundings.

#### **Isolated system**

A system which can exchange neither energy nor matter with its surroundings is called an isolated system. For example, a sample in a sealed thermos flask with walls made of insulating materials represents an isolated

system (Fig.12.1).

### **Closed system**

A system which permits the exchange of energy but not mass, across the boundary with its surroundings is called a closed system.

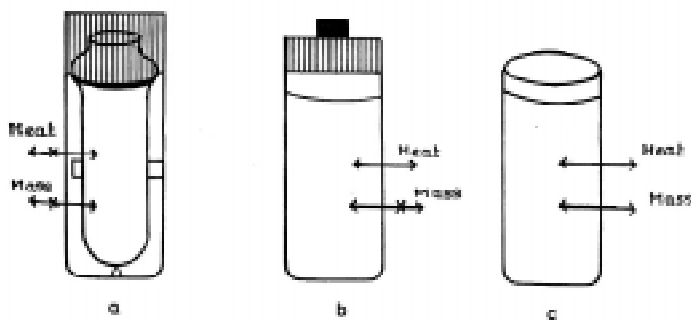
For example: A liquid in equilibrium with its vapours in a sealed tube represents a closed system since the sealed container may be heated or cooled to add or remove energy from its contents while no matter (liquid or vapour) can be added or removed.

### **Open system**

A system is said to be open if it can exchange both energy and matter with its surroundings.

For eg. a open beaker containing an aqueous salt solution represents open system. Here, matter and heat can be added or removed simultaneously or separately from the system to its surroundings.

All living things (or systems) are open systems because they continuously exchange matter and energy with the surroundings.



↔ exchange impossible ↔ exchange possible

**Fig. 12.1 Examples of**

- (a) isolated (thermos flask)**
- (b) closed (closed beaker)**
- (c) open (open beaker) systems**



### **Homogeneous and Heterogeneous systems**

A system is said to be **homogeneous** if the physical states of all its matter are uniform. For eg. mixture of gases, completely miscible mixture of liquids etc.

A system is said to be **heterogeneous**, if its contents does not possess the same physical state. For eg: immiscible liquids, solid in contact with an immiscible liquid, solid in contact with a gas, etc.

### **Macroscopic properties of system**

The properties which are associated with bulk or macroscopic state of the system such as pressure, volume, temperature, concentration, density, viscosity, surface tension, refractive index, colour, etc. are called as macroscopic properties.

### **Types of macroscopic properties of system**

Measurable properties of a system can be divided into two types.

#### **Extensive properties**

The properties that depend on the **mass** or **size** of the system are called as extensive properties. Examples: volume, number of moles, mass, energy, internal energy etc. The value of the extensive property is equal to the sum of extensive properties of smaller parts into which the system is divided. Suppose  $x_1$  ml,  $x_2$  ml,  $x_3$  ml of 1,2,3 gases are mixed in a system, the total volume of the system equals to  $(x_1 + x_2 + x_3)$  ml. Thus volume is an extensive property.

#### **Intensive properties**

The properties that are independent of the mass or size of the system are known as intensive properties. For eg. refractive index, surface tension, density, temperature, boiling point, freezing point, etc., of the system. These properties do not depend on the number of moles of the substance in the system.

If any extensive property is expressed per mole or per gram or per ml, it becomes an intensive property. For eg: mass, volume, heat capacity are extensive properties while density, specific volume, specific heat are intensive properties.

### 12.2.1 State functions

#### State of a system

A system is said to be in a particular physical state when specific values of the macroscopic properties of the system are known. For eg. The gaseous state of matter can be described by parameters like Pressure (P), Volume (V), Temperature (T) etc. The values of these parameters change when the matter is in liquid state. Thus, the **state of a system** is defined by specific measurable macroscopic properties of the system.

The **initial state** of system refers to the starting state of the system before any kind of interaction with its surroundings.

The **final state** of system refers to the state after the interaction of system with its surroundings. A system can interact with its surroundings by means of exchange of matter or heat or energy or all.

The variables like P,V,T, composition (no. of moles) 'n' that are used to describe the state of a system are called as **state variables or state functions**. When the state of the system changes, the values of the state variables of the system also change. Thus, state functions depend only on the initial and final states of system and not on how the changes occur. Also, if the values of state functions of a system are known, all other properties like mass, viscosity, density etc. of the system become specified.

For specifying a state of the system, it is not necessary to know all the state variables, since they are interdependent and only a few of them (state variables) are sufficient. A system which satisfies the conditions of thermal, mechanical and chemical equilibria and contains the macroscopic properties which are independent of time is said to be in **thermodynamic equilibrium**.

**Thermodynamic equilibrium** sets the condition that there should be no flow of heat from one portion or part of the system to another portion or part of the same system. ie. temperature of the system remaining constant at every point of the system.

**Mechanical equilibrium** implies that there is no work done by one portion or part of the system over another portion or part of the same system. ie. Pressure of the system being constant at all its points.

**Chemical equilibrium** demands that the composition of one or more phases of chemicals present in the system should remain constant.

### 12.2.2 Thermodynamic processes

A thermodynamic (physical or chemical) process may be defined as the pathway of series of intermediate changes that occur when a system is changed from initial to final state. Processes starting with the same initial state and ending at different final states correspond to different thermodynamic processes.

Different types of processes are commonly used in the study of thermodynamics.

**Isothermal process** is defined as one in which the temperature of the system remains constant during the change from its initial to final states. During the isothermal process, the system exchanges heat with its surroundings and the temperature of system remains constant.

**Adiabatic process** is defined as that one which does not exchange heat with its surroundings during the change from initial to final states of the system.

A thermally and completely insulated system with its surroundings can have changes in temperature during transformation from initial to final states in an adiabatic process. This is because, the system cannot exchange heat with its surroundings.

**Isobaric process** is that process in which the pressure of the system remains constant during its change from the initial to final state.

**Isochoric process** shows no change in volume of system during its change from initial to final state of the process.

**Cyclic process:** The process which brings back the system to its original or initial state after a series of changes is called as cyclic process.

**Spontaneous process** are those that occur on their own accord. For example heat flowing from a hotter end of a metal rod to a colder end. In these processes, the transformation of the system from initial, to final state is favourable in a particular direction only. Many of the spontaneous processes are natural processes and are also, irreversible processes.

**Non-spontaneous process** are those that does not occur on their own accord. For example, although carbon burns in air evolving heat to form carbon dioxide, on its own carbon does not catch fire and an initial heat supply is required. Since many of the non-spontaneous processes are slow processes, they also exist as equilibrium processes.

**Reversible process.** In a reversible process the series of changes carried out on the system during its transformation from initial to final state may be possibly reversed in an exact manner.

This is possible when the changes are carried out very slowly in many smaller steps on the system during its change from initial to final state. By doing so, each of its intermediate state will be in equilibrium with its surroundings. Under such conditions the initial and final states of the system become reversible completely.

For example, when ice melts a certain amount of heat is absorbed. The water formed can be converted back to ice if the same amount of heat is removed from it. This indicates that many reversible processes are non-spontaneous processes also.

### **Irreversible Process**

An irreversible process is one which cannot be retraced to the initial state without making a permanent change in the surroundings. Many of the spontaneous processes are irreversible in nature.

For eg. Biological ageing is an irreversible process. Water flowing down a hill on its own accord is an irreversible process.

Some of the characteristics of thermodynamically reversible and irreversible processes are compared as below:

<b>Reversible process</b>	<b>Irreversible process</b>
It is a slow process going through a series of smaller stages with each stage maintaining equilibrium between the system and surroundings.	In this process the system attains final state from the initial state with a measurable speed. During the transformation, there is no equilibrium maintained between the system and surroundings.
A reversible process can be made to proceed in forward or backward direction.	Irreversible process can take place in one direction only.

The driving force for the reversible process is small since the process proceeds in smaller steps.	There is a definite driving force required for the progress of the irreversible process.
Work done in a reversible process is greater than the corresponding work done in irreversible process.	Work done in a irreversible process is always lower than the same kind of work done in a reversible process.
A reversible process can be brought back to the initial state without making an change in the adjacent surroundings.	An irreversible process cannot be brought back to its initial state without making a change in the surroundings.

### Exothermic and endothermic processes

When the thermodynamic process is a chemical reaction or a physical transformation, process is classified as either exothermic or endothermic depending on the nature of heat involved in the over all process. These two processes are differentiated as follows:

Endothermic process	Exothermic process
A process when transformed from initial to final states by absorption of heat is called as an endothermic process.	A process when transformed from initial to final states by evolution of heat is called as exothermic process.
The final state of the system possesses higher energy than the initial state. The excess energy needed is absorbed as heat by the system from the surroundings.	The final state of the system possesses lower energy than the initial state. The excess energy is evolved as heat. Example: All combustion processes are exothermic.
Generally in a physical transformation which is endothermic heat is supplied to bring about the initial to final state. Example: melting of a solid by supplying heat is an endothermic process.	If the physical transformation is exothermic heat is removed to bring about the initial to final state. Example: Freezing of a liquid at its freezing point is an exothermic process.

## 12.3 Nature of thermodynamic functions

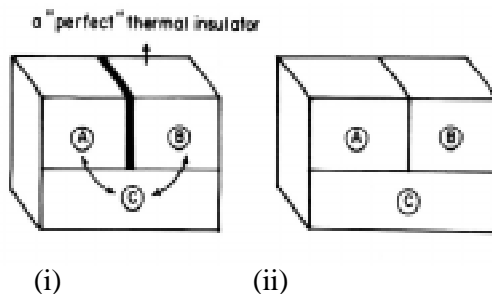
The properties of a thermodynamic system depend on variables which are measurable and change in values when the state of the system changes. These variables are classified as state variables or state functions and path variables (or) path functions.

The **state functions** considered in a gaseous system like,  $P$ ,  $V$  and  $T$  are called as state variables. A **state function** is a thermodynamic property of a system which has a specific value for each state of the system and does not depend on the path (or manner) in which a particular state is reached. Other than  $P, V, T$  there are other important thermodynamic properties existing as state functions like internal energy ( $U$ ), enthalpy ( $H$ ), free energy ( $G$ ) etc. (The properties of  $U, H$  and  $G$  are to be studied later).

A **path function** is a thermodynamic property of the system whose value depends on the path or manner by which the system goes from its initial to final states. It also depends on the previous history of the system. For example, work ( $w$ ) and heat ( $q$ ) are some of the thermodynamic properties of the system that are path functions. Their values change when there is a change in manner in which the system goes from initial to final states.

#### 12.4 Zeroth law of thermodynamics

Consider any two objects each maintained at different temperature, when brought in thermal contact with each other such that heat is exchanged until a thermal equilibrium is reached, then the two objects are considered to have equal temperatures. For example, if a beaker containing water and a thermometer are the two objects, while reading the temperature of the water in the beaker using the thermometer, a thermal equilibrium is reached between the two objects having a contact with each other. Also, when the temperatures of the thermometer bulb and that of water in the beaker are same, thermal equilibrium has said to be occurred.



**Fig. 12.2 i) A and B are in thermal equilibrium with C**  
**ii) A, B and C are in thermal equilibrium with each other**

**Zeroth law of thermodynamics** is also known as the law of thermal

equilibrium. It provides a logical basis for the concept of temperature of a system. It can be stated as follows.

`If two systems at different temperatures are separately in thermal equilibrium with a third one, then they tend to be in thermal equilibrium with themselves'.

Conversely, the Zeroth law can be stated in another manner as,

`When two objects are in thermal equilibrium with the third object, then there is thermal equilibrium between the two objects itself'.

## 12.5 Work, heat and energy

In order to formulate the laws of

$1 \text{ Torr} = 1 \text{ mm of Hg}$
---------------------------------------

thermodynamics it becomes necessary to know the properties and nature of work (w) heat (q) and energy (u).

### Work (w)

In thermodynamics work is generally defined as the force (F) multiplied by the distance of displacement(s). That is,

$$w = F.s.$$

Several aspects should be considered in the definition of work which are listed below:

- (i) work appears only at the boundary of the system.
- (ii) work appears during the change in the state of the system.
- (iii) work brings in a permanent effect in the surroundings.
- (iv) work is an algebraic quantity.
- (v) work is a path function and it is not a state function.

### Types of work

Many types of work are known. Some of the types of work are as follows:

**(i) Gravitational work**

This work is said to be done when a body is raised to a certain height against the gravitational field. If a body of mass ' $m$ ' is raised through a height ' $h$ ' against acceleration due to gravity ' $g$ ', then the gravitational work carried out is ' $mgh$ '. In this expression, force is ' $mg$ ' and the distance is ' $h$ '.

**(ii) Electrical work**

This type of work is said to be done when a charged body moves from one potential region to another. The electrical work is  $Q \cdot V$ . if  $V$  is the potential difference causing the quantity of electricity ' $Q$ ' during its movement

**(iii) Mechanical work**

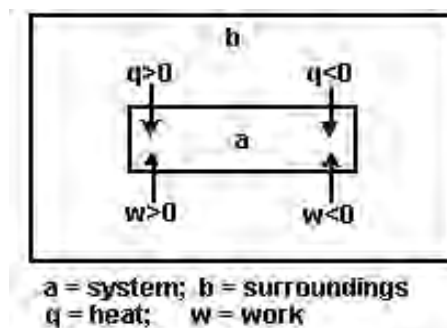
This type of work is associated with changes in volume of a system when an external pressure is applied or lowered. This pressure-volume work is also referred to as the mechanical work.

**Heat**

Like work, heat ( $q$ ) is regarded in thermodynamics as energy in transit across the boundary separating a system from its surroundings. Heat changes result in temperature differences between system and surroundings. Heat cannot be converted into work completely without producing permanent change either in the system or in the surroundings. Some of the characteristics of heat ( $q$ ) are:

- (i) heat is an algebraic quantity.
- (ii) heat is a path function and is not a state function.
- (iii) heat changes are generally considered as temperature changes of the system.

Sign convention for heat ( $q$ ) and work ( $w$ )





- when, (i) heat is absorbed by the system (or) heat is lost by surroundings to the system:  $+q$
- (ii) heat is evolved by the system (or) heat is gained by surroundings:  $-q$ .
- (iii) work is done by the system :  $-w$
- (iv) work is done on the system :  $+w$

If heat ( $q$ ) is supplied to the system, the energy of the system increases and ' $q$ ' is written as a positive quantity. If work is done on the system, the energy of the system increases and ' $w$ ' is written as a positive quantity. When  $w$  or  $q$  is positive, it means that energy has been supplied to the system as work or as heat. In such cases internal energy ( $U$ ) of the system increases. When  $w$  or  $q$  is negative, it means that energy is lost by the system as work or as heat. In such cases, the internal energy ( $U$ ) of the system decreases.

### **Energy ' $U$ '**

Energy is easily, defined as the capacity to do work. Whenever there is a change in the state of matter of a system, then there is a change in energy ( $\Delta U$ ) of the system. For example energy changes are involved in processes like melting, fusion, sublimation, vapourisation etc. of the matter in a system. Energy ( $U$ ) exists in many forms. Kinetic energy (K.E.) arises due to motion of a body and potential energy (P.E.) arises due to its position in space.

In chemical systems, there are two types of energy available. The energies acquired by the system like electrical, magnetic, gravitational etc. and termed as external energies of the system. The internal energy is

generally referred to as the energy ( $U$ ) of a thermodynamic system which is considered to be made up of mainly by P.E. and K.E.

Characteristics of energy ( $U$ ) are:

- (i)  $U$  is a state function. Its value depend on the initial and final states of the system.
- (ii)  $U$  is an extensive property. Its magnitude depend on the quantity of material in the system.
- (iii)  $U$  is not a path function. Its value remains constant for fixed initial and final states and does not vary even though the initial and final states are connected by different paths.

In S.I. system the unit of energy is Joules 'J' or kJ.

## 12.6 First law of thermodynamics

First law of thermodynamics is also known as the law of conservation of energy which may be stated as follows:

"Energy may be converted from one form to another, but cannot be created or be destroyed".

There are many ways of enunciating the first law of thermodynamics. Some of the selected statements are given below:

- (i) "Energy of an isolated system must remain constant although it may be changed from one form to another".
- (ii) "The change in the internal energy of a closed system is equal to the energy that passes through its boundary as heat or work".
- (iii) "Heat and work are equivalent ways of changing a system's internal energy".
- (iv) "Whenever other forms of energies are converted into heat or vice versa there is a fixed ratio between the quantities of energy and heat thus converted".

Significance of first law of thermodynamics is that, the law ascertains an exact relation between heat and work. It establishes that ascertain quantity of heat will produce a definite amount of work or vice versa. Also, when a system apparently shows no mechanical energy but still capable of

doing work, it is said to possess internal energy or intrinsic energy.

## 12.7 Enthalpy

In chemistry most of the chemical reactions are carried out at constant pressure. To measure heat changes of system at constant pressure, it is useful to define a new thermodynamic state function called Enthalpy 'H'.

H is defined as sum of the internal energy 'U' of a system and the product of Pressure and Volume of the system.

That is,

$$H = U + PV$$

### Characteristics of H

Enthalpy, H depends on three state functions U, P, V and hence it is also a state function. H is independent of the path by which it is reached. Enthalpy is also known by the term 'heat content'.

#### 12.7.1 Relation between enthalpy 'H' and internal energy 'U'

When the system at constant pressure undergoes changes from an initial state with  $H_1$ ,  $U_1$ ,  $V_1$ , P parameters to a final state with  $H_2$ ,  $U_2$ ,  $V_2$ , P parameters the change in enthalpy  $\Delta H$ , is given by,

$$\Delta H = (H_2 - H_1) = (U_2 - U_1) + P(V_2 - V_1)$$

$$\text{i.e. } \Delta H = \Delta U + P\Delta V$$

Considering  $\Delta U = q - w$  or  $q - P\Delta V$  (assuming p - V work),  $\Delta U + P\Delta V$  becomes equal to 'q<sub>p</sub>'. 'q<sub>p</sub>' is the heat absorbed by the system at constant pressure for increasing the volume from  $V_1$  to  $V_2$ . This is so because, -w indicates that work is done by the system. Therefore volume increase against constant pressure is considered.

$$\begin{aligned} \therefore \text{eqn. becomes } q_p &= \Delta U + P\Delta V \\ &= \Delta H. \end{aligned}$$

or

$$\Delta H = q_p.$$

' $q_p$ ' is the heat absorbed by the system at constant pressure and is considered as the heat content of the system.

Heat effects measured at constant pressure indicate changes in enthalpy of a system and not in changes of internal energy of the system. Using calorimeters operating at constant pressure, the enthalpy change of a process can be measured directly.

Considering a system of gases which are chemically reacting to produce product gases with  $V_r$  and  $V_p$  as the total volumes of the reactant and product gases respectively, and  $n_r$  and  $n_p$  as the number of moles of gaseous reactants and products, then using ideal gas law we can write that, at constant temperature and constant pressure,

$$PV_r = n_r RT \text{ and } PV_p = n_p RT.$$

Then considering reactants as initial state and products as final state of the system,

$$P(V_p - V_r) = RT (n_p - n_r)$$

$$\therefore P\Delta V = \Delta n_g RT \text{ where,}$$

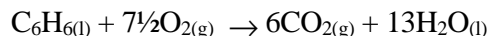
$\Delta n_g$  refers to the difference in the number of moles of product and reactant gases. But, we already know that,  $\Delta H = \Delta U + P\Delta V$ .

$$\therefore \boxed{\Delta H = \Delta U + \Delta n_g RT}$$

In certain processes internal energy change  $\Delta U = \Delta E$  also.

### **Example 1**

From the following data at constant volume for combustion of benzene, calculate the heat of this reaction at constant pressure condition.



$$\Delta E_{25^\circ C} = -781.1 \text{ kcal}$$

$$\Delta H = \Delta E + \Delta n_g RT$$

$$\Delta E = -781.1 \text{ K.cal}$$

$$\Delta n_g = 6 - 7\frac{1}{2} = -1.5$$

$$(-1.5) \times 1.987 \times 298$$

$$-781.1 +$$

$$\Delta H = \frac{\quad}{1000}$$

$$= -781.1 - 0.888$$

$$\therefore \Delta H = -782 \text{ k.cal}$$

### 12.7.2 Standard enthalpy changes

The standard enthalpy of a reaction is the enthalpy change for a reaction when all the participating substances (elements and compounds) are present in their standard states.

The standard state of a substance at any specified temperature is its pure form at 1 atm pressure. For example standard state of solid iron at 500 K is pure iron at 500 K and 1 atm. Standard conditions are denoted by adding the superscript 0 to the symbol  $\Delta H$ .

For a reaction, the standard enthalpy change is denoted by  $\Delta_r H^0$ . Similarly, the standard enthalpy changes for combustion, formation, etc. are denoted by  $\Delta_c H^0$  and  $\Delta_f H^0$  etc respectively. Generally the reactants are presented in their standard states during the enthalpy change.

### 12.8 Thermochemical equations

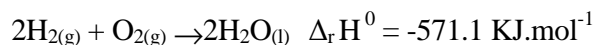
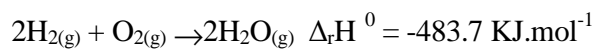
A balanced chemical equation together with standard conventions adopted and including the value of  $\Delta H$  of the reaction is called a thermochemical equation.

The following conventions are necessarily adopted in a thermochemical equation :

- (i) The coefficients in a balanced thermochemical equation refers to number of moles of reactants and products involved in the reaction.
- (ii) The enthalpy change of the reaction  $\Delta_r H$  has unit  $\text{KJ mol}^{-1}$  and will remain as it is, even if more than one mole of the reactant or product are involved but with only the magnitude changing.

- (iii) When a chemical equation is reversed the value of  $\Delta H$  is reversed in sign with the magnitude remaining the same.
- (iv) Physical states of all species is important and must be specified in a thermochemical equation since  $\Delta H$  depends on the phases of reactants and products.
- (v) If the thermochemical equation is multiplied throughout by a number, the enthalpy change is also be multiplied by the same number value.
- (vi) The negative sign of  $\Delta_r H^0$  indicates the reaction to be an exothermic reaction and positive sign of  $\Delta_r H^0$  indicates an endothermic type of reaction.

For example, consider the following reaction,



The above thermochemical equations can be interpreted in several ways.

483.7 KJ given off per mole of the reaction  $\equiv$

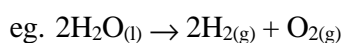
483.7 KJ given off per 2 moles of  $\text{H}_{2(g)}$  consumed  $\equiv$

483.7KJ given off per mole of  $\text{O}_{2(g)}$  consumed  $\equiv$

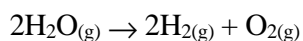
483.7 KJ given off per 2 moles of water vapour formed

The above equation describes the combustion of  $\text{H}_2$  gas to water in a general sense. The first reaction can be considered as the formation reaction of water vapour and the second reaction as the formation of liquid water. Both the reaction refer to constant temperature and pressure.

The negative sign of  $\Delta H$  indicates that it is an exothermic reaction. The reaction which is exothermic in the forward direction is endothermic in the reverse direction and vice-versa. This rule applies to both physical and chemical processes.



$$\Delta_r H^0 = +571.1 \text{ KJ.mol}^{-1}$$



$$\Delta H_r^0 = +483.7 \text{ KJ.mol}^{-1}$$

## 12.9 Enthalpy of combustion

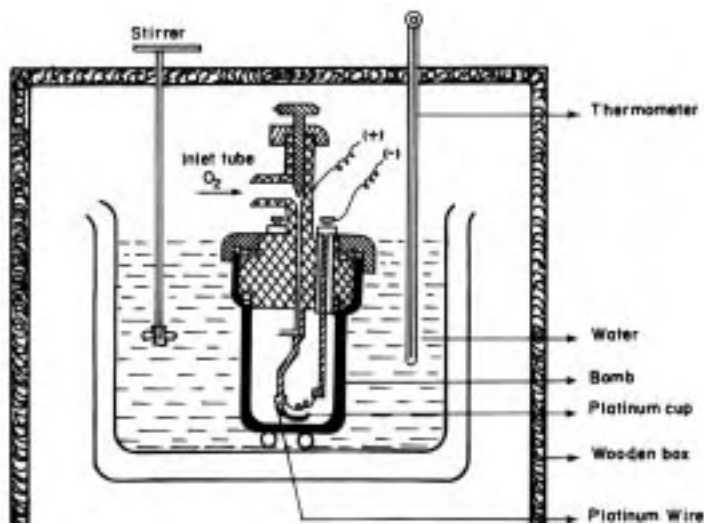
Generally combustion reactions occur in oxygen atmosphere (excess oxygen) with evolution of heat. These reactions are exothermic in nature. Enthalpy changes of combustion reactions are used in industrial heating and in rocket fuels and in domestic fuels.

Enthalpy change of combustion  $\Delta_c H$ , of a substance at a given temperature is defined as the enthalpy change of the reaction accompanying the complete combustion of one mole of the substance in presence of excess oxygen at that temperature. The enthalpy change of combustion of substances in their standard states are known as standard enthalpy change of combustion ( $\Delta_c H^\circ$ ). These values are useful to experimentally determine the standard enthalpy change of formation of organic compounds.

### 12.9.1 Bomb calorimeter

Enthalpy changes of combustion of chemical substances are experimentally determined using a bomb calorimeter.

The bomb calorimeter apparatus is shown in Fig.12.3. The inner vessel or the bomb and its cover are made of strong steel. The cover is fitted tightly to the vessel by means of metal lid and screws. A weighed amount of the substance is taken in a platinum cup or boat connected with electrical wires for striking an arc instantly to kindle combustion. The bomb is then tightly closed and pressurised with excess oxygen. The bomb is lowered in water which is placed inside the calorimeter. A stirrer is placed in the space between the wall of the calorimeter and the bomb, so that water can be stirred, uniformly. The reaction is started in the bomb by heating the substance through electrical heating. During burning, the exothermic heat generated inside the bomb raises the temperature of the surrounding water bath. The enthalpy measurements in this case corresponds to the heat of reaction at constant volume. Although the temperature rise is small (only by few degrees), the temperature change can be measured accurately using Beckmann thermometer.



### Fig. 12.3 Bombcalorimeter

In a typical bomb calorimeter experiment, a weighed sample of benzoic acid ( $w$ ) is placed in the bomb which is then filled with excess oxygen and sealed. Ignition is brought about electrically. The rise in temperature ( $\Delta T$ ) is noted. Water equivalent ( $w_c$ ) of the calorimeter is known from the standard value of enthalpy of combustion of benzoic acid.

$$\Delta H_c^\circ \text{C}_6\text{H}_5\text{COOH}_{(s)} = -3227 \text{ kJ mol}^{-1}$$

$w$

$$\therefore \Delta H_c^\circ \text{C}_6\text{H}_5\text{COOH} \times \frac{w}{M_2} = w_c \cdot \Delta T$$

(where  $M_2$  = mol.wt benzoic acid).

Knowing  $w_c$  value, the enthalpy of combustion of any other substance is determined adopting the similar procedure and using the substance in place of benzoic acid. By this experiment, the enthalpy of combustion at constant volume ( $\Delta H_{c(\text{Vol})}$ ) is known

$$\Delta H_{c(\text{Vol})}^\circ = w_c \cdot \Delta T.$$

Enthalpy of combustion at constant pressure of the substance is calculated from the equation,

$$\Delta H_{c(\text{Pr})}^\circ = \Delta H_{c(\text{Vol})}^\circ + \Delta n_{(g)}RT$$



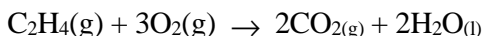
and  $\Delta n_{(g)}$  is known from the difference in the number of moles of the products and reactants in the completely balanced equation of combustion of the substance with excess oxygen.

### Example 2

Calculate the enthalpy of combustion of ethylene at 300K at constant pressure if its enthalpy of combustion at constant volume is  $-1406 \text{ kJ mol}^{-1}$ .

### Solution

The complete ethylene combustion reaction can be written as,



$$\Delta H = \Delta E + RT \Delta n_{(g)},$$

$$\text{where } \Delta n_{(g)} = n_{p(g)} - n_{r(g)}.$$

$$\therefore \Delta n_{(g)} = 2 - (3+1) = -2.$$

$$\text{Enthalpy of combustion at constant volume} = \Delta E = -1406 \text{ kJ mol}^{-1}$$

$$\therefore \text{Overall enthalpy of combustion}$$

$$= \Delta H_c = -1406 + (-2 \times 8.314 \times 10^{-3} \times 300)$$

$$= -1406 - 4.9884$$

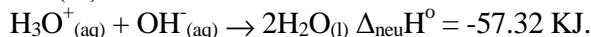
$$\Delta H_c = -1410.9 \text{ kJ mol}^{-1}.$$

## 12.10 Enthalpy of neutralisation

The **enthalpy change of neutralisation** is defined as the enthalpy change accompanied by the complete neutralisation of one gram – equivalent amount of a strong acid by a gram-equivalent amount of strong base under fully ionised state in dilute conditions. It is found that the enthalpy of neutralisation of a strong acid and a strong base is a constant value equal to  $-57.32 \text{ kJ}$ . This value is independent of the nature of the strong acid and strong base. Strong acids and strong bases exist in the fully ionised form in aqueous solutions as below:



(or)

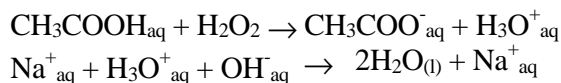


The  $\text{H}^+$  ions produced in water by the acid molecules exist as  $\text{H}_3\text{O}^+$ . During the neutralisation reaction, water and salt (existing as ions) are produced in solution. Thus, enthalpy change of neutralisation is essentially

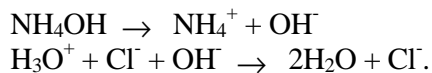
due to enthalpy change per mole of water formed from  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions. Therefore, irrespective of the chemical nature, the enthalpy of neutralisation of strong acid by strong base is a constant value. At infinite dilutions, complete ionisation of acids and bases are ensured and also the inter ionic interactions exist in the lowest extents.

In case of neutralisation of a weak acid like acetic acid ( $\text{CH}_3\text{COOH}$ ) by a strong base ( $\text{NaOH}$ ) or neutralisation of weak base ( $\text{NH}_4\text{OH}$ ) by a strong acid, two steps are involved. The first step is the ionisation of weak acid or weak base since these molecules are only partially ionised. The second step being the neutralisation step of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions. Since ionisation of weak acids and weak bases in water are endothermic and some energy will be used up in dissociating weak acid and weak base molecules.

Thus, acetic acid with  $\text{NaOH}$  and ammonium hydroxide with  $\text{HCl}$  neutralisation reactions can be written as,



and



Enthalpy of neutralisation of a weak acid or a weak base is equal to  $-57.32 \text{ kJ}$  + enthalpy of ionisation of weak acid (or) base. Since enthalpy of ionisation of weak acid or base is endothermic it is a positive value, hence enthalpy of neutralisation of a weak acid or base will be lower than the neutralisation of strong acid and strong base.

### **Example 3**

- The measured heats of neutralization of acetic acid, formic acid, hydrocyanic acid, and hydrogen sulphide are 13.20, 13.40, 2.90 and 3.80 KCal per g.equiv. respectively. Arrange these acids in a decreasing order of strength.
- Heat of neutralization of formic acid by  $\text{NH}_4\text{OH}$  is 11.9 KCal per g.equiv. What is the heat of ionization of  $\text{NH}_4\text{OH}$ ?

### Solution

$$(a) \Delta H_{(\text{neutralization})} = \Delta H_{(\text{ionization})} + \Delta H_{(\text{H}^+ + \text{OH}^-)}$$

$$\therefore \Delta H_{(\text{ionization})} = \Delta H_{(\text{neutralization})} - \Delta H_{(\text{H}^+ + \text{OH}^-)}$$

$$57.32 \text{ KJ} = 13.2 \text{ Kcal.}$$

$\Delta H_{(\text{neutralization})}$  for all acids have a -ve sign.

$\Delta H$  for ionisation of acetic acid.

$$= -13.20 - (-13.70)$$

$$= +0.50 \text{ Cal/g.equiv}$$

$\Delta H$  for ionisation of formic acid

$$= -13.40 + 13.70$$

$$= +0.30 \text{ Cal/g.equiv.}$$

$\Delta H$  for ionization of hydrocyanic acid

$$= -2.90 + 13.70$$

$$= +10.80 \text{ kCal/g. equiv.}$$

$\Delta H$  for ionisation of hydrogen sulphide

$$= -3.80 + 13.70$$

$$= +9.90 \text{ KCal/g.equiv.}$$

The acid with the lowest positive value of heat of ionization will be the strongest acid. Thus formic acid is the strongest and hydrocyanic acid the weakest acid. The trend in decreasing strength of acids is:

Formic acid > acetic acid > hydrocyanic acid > hydrogen sulphide.

(b) The thermochemical equations are:



The sum of reactions (2), (3) and (4) should equal reaction (1).

$$\therefore \Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4$$

$$-11.90 = 0.30 + x - 13.70$$

$$x = -11.90 - 0.30 + 13.70$$

$$= +1.50 \text{ KCal.g.equiv}^{-1}$$

$\Delta H$  for ionization of

$$\text{NH}_4\text{OH} = +1.50 \text{ kCal/g.equiv.}$$

## Questions

### A. Choose the correct answer :

1. Which of the following is not a state functions?  
(a)  $q$  (b)  $q + w$  (c)  $\Delta H$  (d)  $V + PV$
2. Which of the following is an extensive property?  
(a) volume (b) density (c) refractive index (d) molar volume
3. Which of the following is an exothermic reaction?  
(a) melting of ice (b) combustion reactions  
(c) hydrolysis (d) boiling of water
4. Which of the following is reversible process?  
(a) Diffusion (b) melting (c) neutralization (d) combustion
5. In which process, work is maximum?  
(a) reversible (b) irreversible (c) exothermic (d) cyclic

### B. Fill in the blanks

1. Translational energy of molecules is a part of \_\_\_\_\_ energy of the system.
2. Specific heat of a liquid system is \_\_\_\_\_ property.
3. Work done in the reversible expansion is \_\_\_\_\_
4. Combustion is an \_\_\_\_\_ process.
5. Heat of neutralisation of a strong acid is \_\_\_\_\_ than that of a weak acid.

### C. Write in one or two sentence:

1. Name the equipment using which heat of combustion of compounds are determined?
2. Energy can be created and be destroyed. State whether this is true or false.
3. Define zeroth law of thermodynamics.
4. Give the relation between  $\Delta U$  and  $\Delta H$ .
5. Define an adiabatic process.
6. Write the differences between an exothermic and an endothermic process.
7. What are intensive and extensive properties?.
8. Define first law of thermodynamics.
9. Explain thermal and mechanical equilibrium processes.

### D. Explain briefly on the following

10. Describe a bomb calorimeter and explain how heat of formation of an organic compound is determined.

## 13. CHEMICAL EQUILIBRIUM - I

### OBJECTIVES

- *to understand the scopes of chemical equilibrium and to know the extent of completeness of chemical reactions.*
- *to compare and learn about the reversible and irreversible reactions.*
- *to study the dynamic nature of the chemical equilibrium.*
- *to explain the equilibrium existing in physical and chemical changes.*
- *to define law of chemical equilibrium and the equilibrium constant. To express equilibrium constant in terms of concentration and partial pressures and inter relate them.*
- *to deduce expressions for equilibrium constants of homogeneous and heterogeneous chemical equilibria and study suitable examples in each.*

### Equilibrium in Chemical Reactions

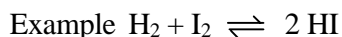
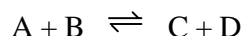
Consider a chemical reaction between A and B to form products C and D. After allowing sufficient period of time for the reaction, upon analyses, when A and B are absent in the reaction mixture, then the reaction is understood to be complete and only the presence of C and D will be detected. For example, when sodium reacts with water, sodium hydroxide and hydrogen gas are produced, and the reverse reaction to form back the reactants never occurs even when the reaction vessel is a closed one. Reactions when go to completion and never proceed in the reverse direction are called as **irreversible reactions**. The chemical equations of such reactions are represented with a single arrow as  $A + B \rightarrow C + D$ .

For Example.  $2\text{Na} + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{H}_2$

However, even after allowing sufficient period of time for reaction, when the presence of A and B are always detected along with C and D, then such reactions are understood to be never complete.

For example, when  $\text{H}_2$  and  $\text{I}_2$  are reacted,  $2\text{HI}$  is formed. Initially the reaction proceeds to form  $\text{HI}$  until a certain period of time and with further increase in the reaction time,  $\text{HI}$  molecules dissociate to produce back  $\text{H}_2$  and  $\text{I}_2$  in such a way that, the reaction mixture always contain  $\text{H}_2$ ,  $\text{I}_2$  and  $\text{HI}$  for any length of time until external factors like temperature, pressure, catalyst etc. are applied. Reactions which never proceed to completion in both forward and backward direction are called as **Equilibrium reactions**.

The chemical equation of such reactions are represented as,



when both forward and reverse reaction rates are equal, the concentration of reactants and products do not change with any length of reaction time. Physical transformations of matter like change of solid to liquid states or liquid to vapour states also take place under equilibrium conditions with both the states of matter being present together. For example, at 0°C, melting ice and freezing water are both present.

### 13.1 Scope of Chemical Equilibrium

Study of chemical equilibria possesses many scopes. The knowledge on whether the equilibrium lies in favour of reactants or products under certain experimental conditions is useful to increase yields in industrial processes, to establish the exact proton transfer equilibria in aqueous protein solutions. Since small changes in equilibrium concentration of hydrogen ion may result in protein denaturing and cell damage etc. This study is also useful or certain acids, bases and salts in water exist in ionic equilibria which control their use as buffers, colour indicators etc.

### 13.2 Reversible and Irreversible Reactions

A reaction which can go in the forward and backward direction simultaneously under the same conditions, is called a **reversible reaction**.

If the forward reaction is written as

$k_f$

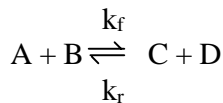


then, the reverse reaction is written as

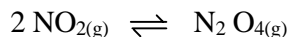
$k_r$

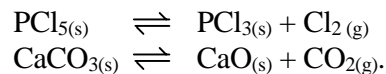


The reversible reaction is represented as

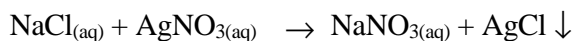


Some examples of reversible reactions are :





In a reaction when the product molecules never react to produce back the reactants, then such a reaction is called as **irreversible reaction**. For example,

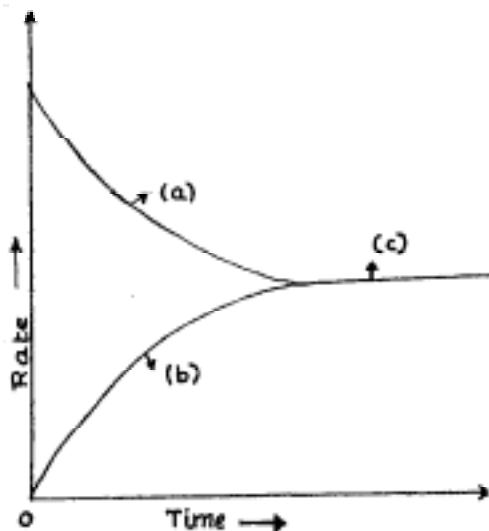


In irreversible reactions only forward reaction takes place and the reaction goes to completion. After the completion, only products exist.

### 13.3 Nature of Chemical Equilibrium

The occurrence of chemical equilibrium is seen in reversible reactions only. Chemical equilibrium may be defined as the state of a reversible reaction when the two opposing reactions occur at the same rate and the concentration of reactants and products do not change with time. The true equilibrium of a reaction can be attained from both sides.

For  $X \rightarrow Y$  reaction,  $a = \frac{-d[x]}{dt}$ ;  $b = \frac{d[Y]}{dt}$



**Fig. 13.1. (a) Forward rate (b) reverse rate (c) Equilibrium condition.**

The equilibrium concentrations of reactants and products do not change

with time. This is because, since the forward reaction rate equals with backward reaction rate as and when the products are formed, they react back to form the reactants in equal capacity. The equilibrium concentrations of reactants are different from their initial concentrations.

The equilibrium concentrations are represented by square brackets with subscript 'eq' or as  $[ ]_{eq}$ . Thus  $[A]_{eq}$  denotes the equilibrium concentration of A in moles per litre. In modern practice, the subscript 'eq' is not used.

### 13.3.1 Dynamic Equilibrium

When a reversible reaction attains equilibrium it appears that the concentrations of individual reactants and that of the products remain constant with time. Apparently, the equilibrium appears as dead (or) as not proceeding. Actually, the reactant molecules are always reacting to form the product molecules. When the product molecules are able to react with themselves under the same experimental condition to form the same amount of reactants simultaneously (at the same time) in an equal rate of the forward reaction, then the process is a ceaseless phenomenon. Thus chemical equilibrium is **dynamic** when the forward and reverse reactions take place **endlessly and simultaneously with equal rates**. Therefore chemical equilibrium is called as dynamic equilibrium.

### 13.3.2 Characteristics of Chemical Equilibrium

#### (i) Constancy of concentrations

When a chemical equilibrium is established in a closed vessel at constant temperature, the concentrations of various species like reactants and products remain unchanged.

The reaction mixture consisting of reactants and products at equilibrium is called as equilibrium mixture.

The concentrations of reactants and products at equilibrium are called as equilibrium concentrations.

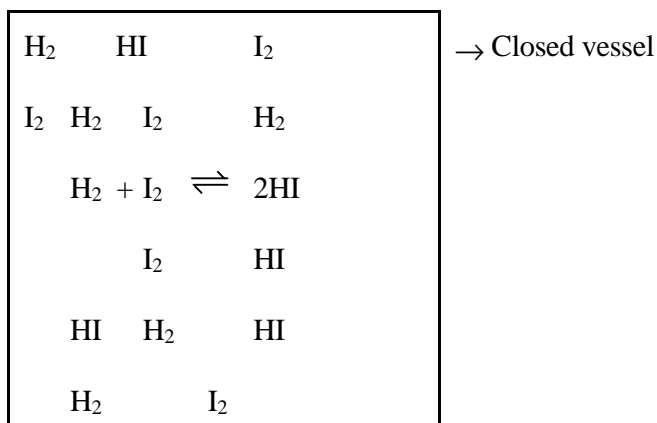
#### (ii) **Equilibrium can be initiated from either side.** The state of equilibrium of a reversible reaction can be arrived at whether we start from reactants or products.

For example, this equilibrium  $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$  can be achieved whether we start with  $H_2$  and  $I_2$  or with HI.

#### (iii) Equilibrium cannot be attained in an open vessel



Only in a closed vessel, a reaction can be considered to attain equilibrium since no part of reactants or products should escape out. In an open vessel, gaseous reactants or products may escape so that no possibility of attaining equilibrium exists. Equilibrium can be attained when all the reactants and products are in contact with each other.



**Fig. 13.2 A chemical equilibrium between H<sub>2</sub> + I<sub>2</sub> and 2HI**

(iv) Catalyst does not alter the equilibrium

When a catalyst is added to the equilibrium system, it speeds up the rates of both forward and reverse reactions to an equal extent. Therefore the equilibrium is not changed but the state of equilibrium is attained earlier.

(v) The value of equilibrium constant does not depend upon the initial concentration of reactants.

(vi) At equilibrium, the free energy change is minimum or zero.

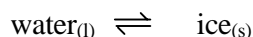
(vii) When temperature is changed, the forward and backward reaction rates are changed and the equilibrium concentrations of reactants and products are changed.

### 13.3.3 Equilibrium in physical processes

When there is a change in the state of occurrence of matter, then a physical transformation is said to have occurred. The equilibrium concepts are also applicable to physical state transformations of matter.

**(i) Solid-liquid equilibria**

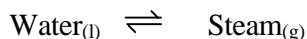
Here, the solid and the liquid forms of a substance co exist at characteristic temperature and pressure. At 1 atm and at the melting point of a substance, there is a solid-liquid equilibrium existing. For example, the solid-liquid equilibrium of water at 0°C,



occurs at 1 atm pressure. Here, both the liquid and ice exist together. Also, at melting point of ice or freezing point of water, the rate of melting of ice equals with rate of freezing of water. With change in pressure the temperature at which this equilibrium onsets changes.

**(ii) Liquid-vapour equilibrium**

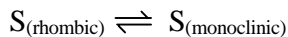
Here the vapour and the liquid forms of a substance exist simultaneously at a characteristic temperature called as boiling point and at 1 atm pressure. For example at 100°C which is the boiling point of water, and 1 atm pressure,



both liquid water and water vapour (steam) exist simultaneously, provided the vapour does not escape.

**(iii) Solid-solid equilibrium**

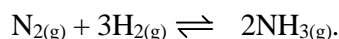
When a substance existing in a particular crystalline solid transforms to another crystalline form retaining its solid nature at a characteristic temperature called the transition temperature with both the solid forms coexisting, at 1 atm pressure then it is said to be in solid-solid equilibrium. For example, solid sulphur exhibits equilibrium with rhombic to monoclinic forms at its transition temperature.



**13.3.4 Equilibrium in chemical processes**

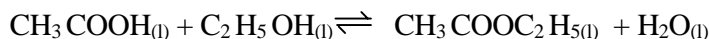
Chemical equilibrium exists in two types such as homogeneous and heterogeneous equilibria. In a chemical reaction existing in equilibrium, if all the reactants and products are present in the same phase, then a homogeneous equilibria is said to have occurred.

For example,



Here all the reactants and products exist in gaseous state. This is an example of gas-phase equilibrium.

The chemical equilibrium in which all the reactants and products are in the liquid phase are referred to as liquid equilibria. For example,

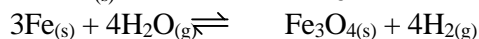


Both gas phase and liquid phase equilibria are collectively called as homogeneous equilibria.

### **Heterogeneous equilibrium**

In a chemical equilibrium, if the reactants and products are in different phases then heterogeneous equilibrium is said to have occurred.

Examples :



Here, only when the reaction is carried out in closed vessel, the equilibrium state is established.

## **13.4 Law of chemical equilibrium and equilibrium constant**

### **Law of Mass action**

Two Norwegian Chemists, Guldberg and Waage, studied experimentally a large number of equilibrium reactions. In 1864, they postulated a generalisation called the **Law of Mass action**. It states that:

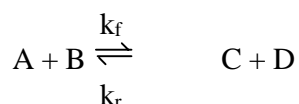
"the rate of a chemical reaction is proportional to the active masses of the reactants". By the term 'active mass', it is meant the molar concentration i.e., number of moles per litre.

### **Law of Mass Action based on the Molecular Collision theory**

We assume that a chemical reaction occurs as the result of the collisions between the reacting molecules. Although some of these collisions are ineffective, the chemical change produced is proportional to the number of collisions actually taking place. Thus at a fixed temperature the rate of a reaction is determined by the number of collisions between the reactant molecules present in unit volume and hence its concentration, which is generally referred as the active mass.

#### 13.4.1 Equilibrium constant and equilibrium law

Let us consider a general reaction



and let [A], [B], [C] and [D] represent the molar concentrations of A, B, C and D at the equilibrium point. According to the Law of Mass action,

Rate of forward reaction  $\propto [A] [B] = k_f [A] [B]$

Rate of reverse reaction  $\propto [C] [D] = k_r [C] [D]$

where  $k_f$  and  $k_r$  are rate constants for the forward and reverse reactions.

At equilibrium, rate of forward reaction = rate of reverse reaction.

Therefore,

$$k_f [A] [B] = k_r [C] [D]$$

$$\text{or } \frac{k_f}{k_r} = \frac{[C] [D]}{[A] [B]} \quad \dots (1)$$

At any specific temperature  $k_f/k_r$  is a constant since both  $k_f$  and  $k_r$  are constants. The ratio  $k_f/k_r$  is called **equilibrium constant** and is represented by the symbol  $K_c$ . The subscript 'c' indicates that the value is in terms of concentration of reactants and products. The equation (1) may be written as

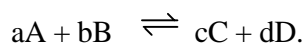
$$K_f = \frac{[C] [D] \leftarrow \text{Products concentration}}{[A] [B] \leftarrow \text{Reactants concentrations}} \dots (2)$$

Equilibrium constant

This equation is known as the equilibrium constant expression or equilibrium law. Hence [C], [D] [A] and [B] values are the equilibrium concentrations and are equal to equilibrium concentrations.

### 13.4.2 Equilibrium Constant Expression for a Reaction in General Terms

The general reaction may be written as



where a,b,c and d are numerical quotients of the substance A,B,C and D respectively. The equilibrium constant expression is

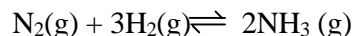
$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \dots (3)$$

where  $K_c$  is the Equilibrium constant. The general definition of the equilibrium constant may thus be stated as :

**The product of the equilibrium concentrations of the products divided by the product of the equilibrium concentrations of the reactants, with each concentration term raised to a power equal to the coefficient of the substance in the balanced equation.**

*For Example*

(a) Consider the equilibrium constant expression for the reaction



- (1) The equation is already balanced. The numerical quotient of  $H_2$  is 3 and  $NH_3$  is 2.
- (2) The concentration of the 'product'  $NH_3$  is  $[NH_3]^2$ .

(3) The product of concentrations of the reactants is  $[N_2] [H_2]^3$ .

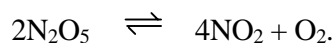
(4) Therefore, the equilibrium constant expression is

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

(b) Consider the equilibrium constant expression for the reaction



(1) The equation as written is not balanced. Balancing yields



(2) The coefficient of the product  $NO_2$  is 4 and of the reactant  $N_2O_5$  is 2.

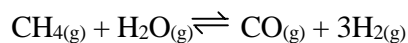
(3) The product of the concentrations of products is  $[NO_2]^4 [O_2]$ .

(4) The concentration of the reactant is  $[N_2O_5]^2$

(5) The equilibrium constant expression can be written as

$$K_c = \frac{[NO_2]^4 [O_2]}{[N_2O_5]^2}$$

(c) Consider the equilibrium constant expression of the reaction.



(i) Write the product of concentrations of 'products' divided by the product (multiplication) of concentrations of 'reactants'.

(ii) The concentration of  $H_2$  is to be raised by its coefficient in the balanced equation. Thus, the equilibrium constant expression is :

$$K_c = \frac{[CO] [H_2]^3}{[CH_4] [H_2O]}$$

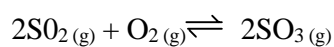
### 13.4.3 Equilibrium Constant Expression for Gaseous Equilibrium

When all the reactants and products are gases, we can formulate the equilibrium constant expression in terms of partial pressures exactly similar to equation (1).

The partial pressure of a gas in the equilibrium mixture is directly proportional to its molar concentration at a given temperature.

Considering equation (1) :  $K_p = \frac{p_C^c p_D^d}{p_A^j p_B^k}$

The gaseous equilibrium reaction of SO<sub>2</sub> can be written as follows



$$K_p = \frac{(p_{\text{SO}_3})^2}{(p_{\text{SO}_2})^2 \cdot p_{\text{O}_2}} \text{ atm}^{-1}$$

As an example, K<sub>p</sub> value can be calculated from the following data:

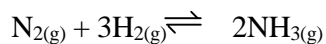
The total pressure in the reaction flask is 1 atm and the partial pressures of oxygen, SO<sub>2</sub> and SO<sub>3</sub> at equilibrium are 0.1 atm, 0.57 atm, 0.33 atm respectively.

$$\therefore K_p = \frac{(0.33)^2}{(0.57)^2 \times 0.1} \text{ atm}^{-1}$$

$$= \frac{(0.33)^2}{0.03249} \text{ atm}^{-1}$$

$$K_p = 3.3518 \text{ atm}^{-1}.$$

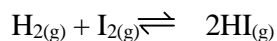
In the ammonia formation reaction, the gaseous chemical equilibrium exists as:



where p = partial pressure

Similarly for HI formation in the gaseous state from H<sub>2</sub> and I<sub>2</sub> gases, the

equilibrium constant ( $K_p$ ) can be written as



$$K_p = \frac{p_{\text{HI}}^2}{p_{\text{H}_{2(g)}} p_{\text{I}_{2(g)}}}$$

here  $K_p$  has no units.

### Problem 1

Equivalent amounts of hydrogen and iodine are allowed to reach equilibrium at a given temperature.  $\text{H}_{2(g)} + \text{I}_{2(g)} \rightarrow 2\text{HI}_{(g)}$ . If 80% of the hydrogen can be converted to hydrogen iodide, what is the value of  $K_c$  and  $K_p$  at this temperature.

	$\text{H}_2$	$\text{I}_2$	$\text{HI}$
Initial concentration mol dm <sup>-3</sup>	1	1	0
Equilibrium concentration	1-0.8	1-0.8	1.6
	= 0.2	= 0.2	1.6

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{1.6 \times 1.6}{0.2 \times 0.2} = 64.$$

$$K_p = K_c(RT)^{\Delta n}$$

In this reaction  $\Delta n = 0$

$$\therefore K_p = K_c$$

$$K_c = 64$$

### 13.4.4 Degree of dissociation (x)

In the study of dissociation equilibrium, it is easier to derive the equilibrium constant expression in terms of **degree of dissociation (x)**. It is considered as the fraction of total molecules that actually, dissociate into the simpler molecules x has no units. If x is the degree of dissociation then

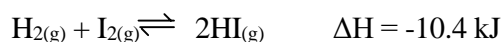


for completely dissociating molecules  $x = 1.0$ . For all dissociations involving equilibrium state,  $x$  is a fractional value. If  $x$  is known,  $K_c$  or  $K_p$  can be calculated and vice-versa.

### Equilibrium constants in terms of degree of dissociation

#### (i) Formation of HI from $H_2$ and $I_2$

The formation of HI from  $H_2$  and  $I_2$  is an example of gaseous homogeneous equilibrium reaction. It can be represented as



This equilibrium is an exothermic one.

Let us consider that one mole of  $H_2$  and one mole of  $I_2$  are present initially in a vessel of volume  $V \text{ dm}^3$ . At equilibrium let us assume that  $x$  mole of  $H_2$  combines with  $x$  mole of  $I_2$  to give  $2x$  moles of HI. The concentrations of  $H_2$ ,  $I_2$  and HI remaining at equilibrium can be calculated as follows :

	$H_{2(g)}$	$I_{2(g)}$	$HI_{(g)}$
Initial number of moles	1	1	0
Number of moles reacted	$x$	$x$	$-$
Number of moles remaining at equilibrium	$1-x$	$1-x$	$2x$

$$\text{Equilibrium concentration} \quad \left( \frac{1-x}{V} \right) \left( \frac{1-x}{V} \right) \left( \frac{2x}{V} \right)$$

According to the law of mass action,

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

Substituting the values of equilibrium concentrations in the above equation, we get

$$K_c = \frac{\left( \frac{2x}{V} \right)^2}{\left( \frac{1-x}{V} \right) \left( \frac{1-x}{V} \right)} = \frac{4x^2}{(1-x)^2} \times \frac{V^2}{V^2}$$

$$K_c = \frac{4x^2}{(1-x)^2}$$

If the initial concentration of  $H_2$  and  $I_2$  are equal to  $a$  and  $b$  moles  $dm^{-3}$  respectively, then it can be shown that

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

### Derivation of $K_p$ in terms of $x$

Let us consider one mole of  $H_2$  and one mole of  $I_2$  are present initially. At equilibrium, let us assume that  $x$  mole of  $H_2$  combines with  $x$  mole of  $I_2$  to give  $2x$  moles of  $HI$ . Let the total pressure at equilibrium be  $P$  atmosphere. The number of moles of  $H_2$ ,  $I_2$  and  $HI$  present at equilibrium can be calculated as follows :

	$H_{2(g)}$	$I_{2(g)}$	$HI_{(g)}$
Initial number of moles	I	I	O
Number of moles reacted	x	x	-
Number of moles remaining at equilibrium	I-x	I-x	2x
$\therefore$ The total number of moles at equilibrium	$= 1 - x + 1 - x + 2x = 2$		

We know that partial pressure is the product of mole fraction and the total pressure. Mole fraction is the number of moles of that individual component divided by the total number of moles in the mixture. Therefore,

$$p_{H_2} = \frac{1-x}{2}P, p_{I_2} = \frac{1-x}{2}P, p_{HI} = \frac{2x}{2}P$$

$$\text{We know that } K_p = \frac{p_{HI}^2}{p_{H_2} \cdot p_{I_2}}$$

Substituting the values of partial pressures in the above equation, we get

$$K_p = \frac{\left(\frac{2x}{2}P\right)^2}{\left(\frac{1-x}{2}\right)P\left(\frac{1-x}{2}\right)P} = \frac{4x^2P^2}{4} \times \frac{4}{(1-x)^2P^2}$$

$$\therefore \boxed{K_p = \frac{4x^2}{(1-x)^2}}$$

we see that  $K_p$  and  $K_e$  are equal in terms of  $x$  values. The influence of various factors on the chemical equilibrium can be explained as below:

**(i) Influence of pressure :** The expressions for the equilibrium constants  $K_c$  and  $K_p$  involve neither the pressure nor volume term. So the equilibrium constants are independent of pressure and volume. Pressure has therefore no effect on the equilibrium.

**(ii) Influence of concentration :** The addition of either  $H_2$  or  $I_2$  to the equilibrium mixture will increase the value of the denominator in the equation  $K_e = [HI]^2/[H_2][I_2]$  and hence tends to decrease the value of  $K_e$ . In order to maintain the constancy of  $K_c$ , the increase in the denominator value will be compensated by the corresponding increase in the numerator value. In other words, the forward reaction will be favoured and there will be corresponding increase in the concentration of HI.

**(iii) Influence of catalyst :** A catalyst affects both the forward and reverse reactions to the same extent. So it does not change the relative amounts of reactants and products at equilibrium. The values of  $K_e$  and  $K_p$  are not affected. However the equilibrium is attained quickly in the presence of a catalyst.

## **(ii) Dissociation of $PCl_5$**

Phosphorus pentachloride dissociates in gas phase to give  $PCl_3$  and  $Cl_2$ . This is an example of gaseous homogeneous equilibrium. It can be represented as



For this reaction  $\Delta n = 1 \quad \therefore K_p = K_c (RT)$

Let us consider that one mole of  $\text{PCl}_5$  is present initially in a vessel of volume  $V \text{ dm}^3$ . At equilibrium let  $x$  mole dissociates to give  $x$  mole of  $\text{PCl}_3$  and  $x$  mole of  $\text{Cl}_2$ . The equilibrium concentrations of the components can be given as follows :

	$\text{PCl}_{5(g)}$	$\text{PCl}_{3(g)}$	$\text{Cl}_{2(g)}$
Initial number of moles	1	0	0
Number of moles reacted	$x$	-	-
Number of moles at equilibrium	$1-x$	$x$	$x$
Equilibrium concentration	$(1-x) \left( \frac{1}{V} \right)$	$x \left( \frac{1}{V} \right)$	$x \left( \frac{1}{V} \right)$

According to law of mass action,

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}$$

Substituting the values of equilibrium concentrations in the above equation we get,

$$K_c = \frac{\left( \frac{x}{V} \right) \left( \frac{x}{V} \right)}{\left( \frac{1-x}{V} \right)} = \frac{x^2}{V^2} \frac{V}{1-x}$$

$$K_c = \frac{x^2}{(1-x)V}$$

### Derivation of $K_p$ in terms of $x$

Let us consider that one mole of  $\text{PCl}_5$  is present initially. At equilibrium, let us assume that  $x$  mole of  $\text{PCl}_5$  dissociates to give  $x$  mole of

$\text{PCl}_3$  and  $x$  mole of  $\text{Cl}_2$ . Let the total pressure at equilibrium be  $P$  atmosphere. The number of moles of  $\text{PCl}_5$ ,  $\text{PCl}_3$  and  $\text{Cl}_2$  present at equilibrium can be given as follows :

	$\text{PCl}_{5(g)}$	$\text{PCl}_{3(g)}$	$\text{Cl}_{2(g)}$
Initial number of moles	1	0	0
Number of moles reacted	$x$	-	-
Number of moles at equilibrium	$1-x$	$x$	$x$
$\therefore$ Total number of moles at equilibrium = $1 - x + x + x$			
	= $1 + x$		

We know that partial pressure is the product of mole fraction and the total pressure. Mole fraction is the number of moles of that component divided by the total number of moles in the mixture. Therefore

$$p_{\text{PCl}_5} = \frac{1-x}{1+x} P; \quad p_{\text{PCl}_3} = \frac{x}{1+x} P; \quad p_{\text{Cl}_2} = \frac{x}{1+x} P$$

$$\text{we know that } K_p = \frac{p_{\text{PCl}_3} \cdot p_{\text{Cl}_2}}{p_{\text{PCl}_5}}$$

substituting the values of partial pressures in this expression

$$K_p = \frac{\left[ \frac{x}{1+x} P \right] \left[ \frac{x}{1+x} P \right]}{\left[ \frac{1-x}{1+x} P \right]}$$

$$= \frac{x^2 \cdot P^2}{(1+x)^2} \cdot \frac{(1+x)}{(1-x)} \cdot \frac{1}{P}$$

$$K_p = \frac{x^2 P}{1-x^2}$$

When  $x \ll 1$ ,  $x^2$  value can be neglected when compared to one.

$$\therefore K_p \simeq x^2 P$$

This equation can be used to predict the influence of pressure on this equilibrium.

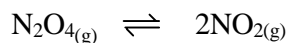
**(i) Influence of pressure :** The expression for  $K_c$  contains the volume term and the expression for  $K_p$  contains the pressure term. Therefore this equilibrium is affected by the total pressure. According to the above equation, increase in the value of  $P$  will tend to increase the value of  $K_p$ . But  $K_p$  is a constant at constant temperature. Therefore, in order to maintain the constancy of  $K_p$  the value of  $x$  should decrease. Thus, increase in total pressure favours the reverse reaction and decreases the value of  $x$ .

**(ii) Influence of concentration :** Increase in the concentration of  $\text{PCl}_5$  favours the forward reaction, while increase in the concentration of either  $\text{PCl}_3$  or  $\text{Cl}_2$  favours the reverse reaction. Increase in the concentration of a substance in a reversible reaction will favour the reaction in that direction in which the substance is used up.

**(iii) Influence of catalyst :** A catalyst will affect the rates of the forward and reverse reactions to the same extent. It does not change either the amount of reactants and products present at equilibrium or the numerical value of  $K_p$  or  $K_c$ . However, the equilibrium is obtained quickly in the presence of a catalyst.

## Problem 2

At  $100^\circ\text{C}$  and 1 atm pressure, the degree of dissociation of  $\text{N}_2\text{O}_4$  is 0.9114. Calculate its equilibrium constant. What will be the degree of dissociation if temperature remains constant and pressure is doubled?



$$(1-x) \qquad 2x$$

$x$  = degree of dissociation

$1-x$  = fraction undissociated

$P$  = total pressure

Total no. of molecules in equilibrium

$$= 1 - x + 2x = (1+x)$$

$$4x^2P$$

$$K_p = \frac{4x^2P}{1-x^2}$$

$P = 1$  atm and  $x = 0.9114$  (given)

$$\therefore K_p = \frac{1 \times 4 \times 0.9114^2}{1 - 0.9114^2} = 19.63$$

Let  $y$  be the degree of dissociation at  $P = 2$  atm

$$4y^2P \quad 4y^2 \times 2$$

$$\text{Then } K_p = 19.63 = \frac{4y^2P}{1-y^2} = \frac{4y^2 \times 2}{1-y^2}$$

Solving for  $y$ ,  $y = 0.8428$

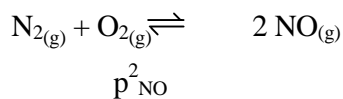
i.e., degree of dissociation at  $P = 2$  atm is 0.8428.

In this case, increase in pressure lowers the degree of dissociation.

### Problem 3

In the reaction  $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$

at 298K, the partial pressures of  $NO_{(g)}$ ,  $O_{2(g)}$ ,  $N_{2(g)}$  at equilibrium are 0.9, 0.3 and 0.01 atoms respectively. Calculate the value of  $K_p$ .



$$K_p = \frac{p_{NO}^2}{p_{N_2} \times p_{O_2}}$$

where  $p$  = partial pressure.

$$K_p = \frac{0.9 \times 0.9}{0.3 \times 0.01} = 270.0$$

#### 13.4.5 Characteristics of Equilibrium constant

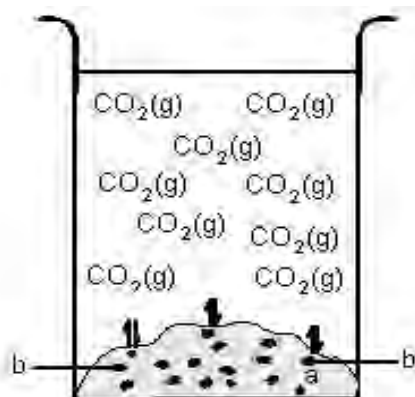
- (i) The  $K_{eq}$  ( $K_c$  or  $K_p$ ) values do not depend on the initial concentrations of reactants but depend only on the equilibrium concentration values.
- (ii) When  $K_{eq}$  values are greater than unity, the equilibrium is favourable towards product formations and vice-versa.
- (iii)  $K_{eq}$  values do not change in presence of catalyst catalyst only speeds up the forward and backward reactions.
- (iv) Temperature changes on the chemical equilibrium changes the  $K_{eq}$  values. For exothermic equilibrium reactions increase in temperature, lowers the  $K_{eq}$  values and for endothermic equilibrium, increase in temperature increases the  $K_{eq}$  values. Generally, when  $T$  is raised, the equilibrium shifts in a direction in which heat is absorbed.
- (v) Pressure changes on gaseous equilibrium alters the  $K_p$  values. For dissociation equilibrium, increase in pressure lowers the  $K_p$  values, while for association equilibrium (number of product molecules < number of reactant molecules) increase in pressure increases the  $K_p$  values. When the number of product and reactant molecules are equal, there is no pressure effect.

#### 13.5 Heterogeneous equilibria

The chemical equilibrium in which the reactants and products are not in the same phases are called **heterogeneous equilibrium**. An example of heterogeneous equilibrium can be the decomposition of calcium carbonate which upon heating forms calcium oxide and carbondioxide under equilibrium conditions. When the reaction is carried out in a closed vessel, the following heterogeneous equilibrium is established.







**Fig. 13.3 Heterogeneous equilibrium**

**a =  $\text{CaCO}_3$  Solid ; b =  $\text{CaO}$  Solid**

The equilibrium constant expression for  $\text{CaCO}_3$  dissociation can be written as

$$K = \frac{[\text{CO}_2] [\text{CaO}]}{[\text{CaCO}_3]}$$

But  $\text{CaO}$  and  $\text{CaCO}_3$  are pure solids. The activity or concentration of pure solids is unity.

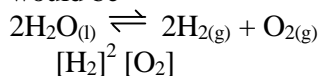
Thus  $K_c = [\text{CO}_2]$

in terms of partial pressures,

$K_p = p_{\text{CO}_2}$ , where  $p_{\text{CO}_2}$  is the pressure of  $\text{CO}_2$  alone in equilibrium.

There are many examples of heterogeneous chemical equilibria with  $K_p$  and  $K_c$  values different depending on the number of product and reactant molecules.

(i) The equilibrium constant expression for decomposition of liquid water would be



$K = \frac{[\text{H}_2]^2 [\text{O}_2]}{[\text{H}_2\text{O}]^2}$  but activity of liquid  $\text{H}_2\text{O} = 1.0$

$\therefore K_c = [\text{H}_2]^2 [\text{O}_2]$

and  $K_p = (p_{H_2})^2 (p_{O_2})$   $p$  = partial pressure.

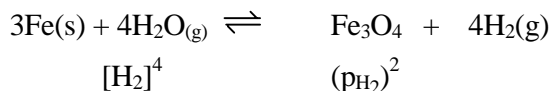
(ii) Consider the equilibrium reaction of decomposition of  $NH_4Cl$ .



$$K_c = [NH_3] [HCl] \text{ because } [NH_4Cl_{(s)}] = 1.0$$

$$K_p = p_{NH_3} p_{HCl}. p = \text{partial pressure}$$

(iii) Consider the hydrogen gas evolution equilibrium such as

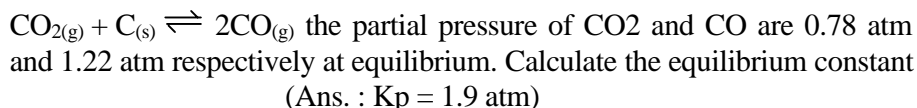


$$K_c = \frac{[H_2O]^4}{[H_2]^4} \text{ and } K_p = \frac{(p_{H_2O})^4}{(p_{H_2})^4}$$

since activities of  $Fe_{(s)}$  and  $Fe_3O_4_{(s)}$  are 1.0.

#### Problem 4

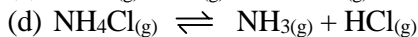
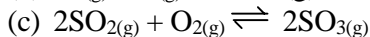
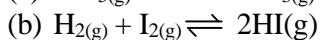
In the equilibrium reaction



#### Questions

A. Choose the correct answer :

1. In which equilibrium pressure has no effect



2. For the equilibrium  $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ , the  $K_p$  and  $K_c$  values are related as

(a)  $K_p = K_c(RT)$  (b)  $K_p = K_c (RT)^2$  (c)  $K_p = K_c (RT)^{-1}$  (d)  $K_p = K_c (RT)^{-2}$

3. For endothermic equilibrium, increase in temperature changes the  $K_{eq}$  value as

- (a) No change (b) Increases (c) Decreases
4. In the heterogeneous equilibrium  
 $\text{CaCO}_{3(s)} \rightleftharpoons \text{CaO}_{(s)} + \text{CO}_{2(g)}$  the  $K_{eq}$  value is given by  
 (a) partial pressure of  $\text{CO}_2$   
 (b) activity  $\text{CaO}$   
 (c) activities of  $\text{CaCO}_3$   
 (d)  $[\text{CaO}]/[\text{CaCO}_3]$
5. For the equilibrium reaction  $\text{H}_{2(g)} + \text{I}_{2(g)} \rightleftharpoons 2\text{HI}_{(g)}$   
 (a)  $K_p = K_c$  (b)  $K_p > K_c$  (c)  $K_p < K_c$  (d)  $K_p = 1/K_c$

**B. Fill in the blanks**

6. In endothermic equilibrium reaction the increase in temperature \_\_\_\_\_ the reaction.
7. When the reactant is a liquid which decomposes to gaseous products.  
 Then the equilibrium is called as \_\_\_\_\_
8. When reactants and products are in gaseous state, the equilibrium constant can be expressed in terms of \_\_\_\_\_
9. Value of the equilibrium constant is \_\_\_\_\_ of the initial concentration of reactants.
10. According to law of mass action, the rate of a chemical reaction is proportional to \_\_\_\_\_ of reactants.

**C. Match the following**

- |   |                              |
|---|------------------------------|
| 11. $K_p$   | a. homogeneous equilibrium   |
| 12. $\text{CaCO}_3 \rightleftharpoons \text{CaO}_{(s)} + \text{CO}_{2(g)}$  | b. active mass of reactants  |
| 13. Rate of reaction  | c. irreversible reaction     |
| 14. $\text{H}_{2(g)} + \text{I}_{2(g)} \rightleftharpoons 2\text{HI}_{(g)}$ | d. Degree of dissociation    |
| 15. $\text{C}_{(s)} + \text{O}_{2(g)} \rightarrow \text{CO}_{2(g)}$         | e. $K_c(RT)^{\Delta n}$      |
|   | f. Heterogeneous equilibrium |

**D. Write in one or two sentence**

16. Define law of mass action
17. Write the  $K_p$  expression for  $\text{PCl}_{5(g)} \rightleftharpoons \text{PCl}_{3(g)} + \text{Cl}_{2(g)}$
18. Relate  $K_p$  and  $K_c$  when  $\Delta n = 0$ ,  $\Delta n = 1$ ;  $\Delta n = 2.0$
19. Give an example of irreversible reaction
20. Reason out why equilibrium concentrations remain constant.

**E. Explain briefly on the following**

21. Differentiate irreversible and reversible reactions.
22. Explain the characteristics of a chemical equilibrium.
23. Write a note on heterogeneous equilibrium reaction.
24. Two moles of  $\text{H}_2$  and three moles of  $\text{I}_2$  are taken in  $2 \text{ dm}^3$  vessel and

## 14. CHEMICAL KINETICS - I

### OBJECTIVES

- *To study the scope of chemical kinetics as to know the mechanism of reactions for maximum yield and rate in industrial processes.*
- *To define rate of chemical reactions and to deduce the rate constant of the overall process. Also, the factors affecting the rate and the rate constant are studied. To write the differential rate equations for simple reactions.*
- *To study the effects of nature of the reactant, temperature, concentration of the reactants, presence of catalyst surface area of reactants and irradiation on the overall rate of the processes are to be learnt.*
- *To write the rate law and to understand rate constant, order of the reaction. Different units of the rate constant for various orders of the reaction are to be deduced.*
- *Classification of rates of reactions based on order of the reaction is studied with suitable examples. Hence, zero, first, second, pseudo first order, fractional order, third order reactions are studied.*

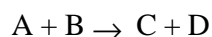
### 14.1 Scope of chemical kinetics

Chemical kinetics is the study of the rates and the mechanism of chemical reactions. Commonly the measure of how fast the products are formed and the reactants consumed is given by the rate values.

The study of chemical kinetics has been highly useful in determining the factors that influence the rate, maximum yield and conversion in industrial processes. The mechanism or the sequence of steps by which the reaction occurs can be known. It is also useful in selecting the optimum conditions for maximum rate and yield of the chemical process.

#### 14.1.1 Rate of chemical reactions

The rate of a reaction tells us how fast the reaction occurs. Let us consider a simple reaction.



As the reaction proceeds, the concentration of the reactant A and B decreases with time and the concentration of the products C + D increase with time simultaneously. The rate of the reaction is defined as the change in the concentration of any reactant or product in the reaction per unit time.

For the above reaction,

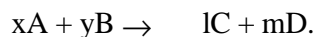
Rate of the reaction

$$\begin{aligned} &= \text{Rate of disappearance of A} \\ &= \text{Rate of disappearance of B} \\ &= \text{Rate of appearance of C} \\ &= \text{Rate of appearance of D} \end{aligned}$$

During the reaction, changes in the concentration is infinitesimally small even for small changes in time when considered in seconds. Therefore differential form of rate expression is adopted. The negative sign shows the concentration decrease trend and the positive sign shows the concentration increase trend.

$$\begin{aligned} \therefore \text{Rate} &= \frac{\text{concentration change}}{\text{time taken}} = \frac{-\Delta[A]}{\Delta t} \\ &= \frac{-d[A]}{dt} = \frac{-d[B]}{dt} = \frac{+d[C]}{dt} = \frac{+d[D]}{dt} \end{aligned}$$

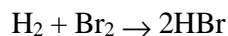
For a general balanced reaction, written with stoichiometries like x,y, for the reactant and l,m for the product, such as



The reaction rate is

$$\begin{aligned} \text{Rate} &= \frac{-1}{x} \frac{d[A]}{dt} = \frac{-1}{y} \frac{d[B]}{dt} = \frac{+1}{l} \frac{d[C]}{dt} \\ &= + \frac{1}{m} \frac{d[D]}{dt} \end{aligned}$$

For example : In the reaction,



The overall rate of the reaction is given by

$$\text{Rate} = \frac{-d[\text{H}_2]}{dt} = \frac{-d[\text{Br}_2]}{dt} = \frac{1}{2} \frac{d[\text{HBr}]}{dt}$$

Consider the reaction,  $2\text{NO} + 2\text{H}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$

$$\text{Rate} = -\frac{1}{2} \frac{d[\text{NO}]}{dt} = -\frac{1}{2} \frac{d[\text{H}_2]}{dt} = \frac{d[\text{N}_2]}{dt} = \frac{1}{2} \frac{d[\text{H}_2\text{O}]}{dt}$$

### Units of Rate

Reaction rate has units of concentration divided by time. Since concentration is expressed in  $\text{mol lit}^{-1}$  or  $\text{mol dm}^{-3}$  the unit of the reaction rate is  $\text{mol lit}^{-1} \text{s}^{-1}$  or  $\text{mol dm}^{-3} \text{s}^{-1}$ .

### 14.1.2 Factors influencing reaction rates

There are number of factors which influence the rate of the reaction. These are :

- (i) Nature of the reactants and products
- (ii) Concentration of the reacting species
- (iii) Temperature of the system
- (iv) Presence of catalyst
- (v) Surface area of reactants
- (vi) Exposure to radiation

#### (i) Effect of nature of the reactant and product

Each reactant reacts with its own rate. Changing the chemical nature of any reacting species will change the rate of the reaction. For example, in halogenation reactions, the reactions involving iodine is found to be slower than those involving chlorine.

In case of products, some of them are capable of reacting back to form reactants or some other kind of products. In such cases, the overall rate will be altered depending on the reactivity of the products.

#### (ii) Effect of reacting species

As the initial concentration of the reactants increase in the reaction mixture, the number of reacting molecules will increase. Since the chemical reaction occurs when the reacting species come close together and collide, the collisions are more frequent when the concentrations are higher. This effect increases the reaction rate.

### **(iii) Effect of temperature**

Increase in temperature of the system increases the rate of the reaction. This is because, as the temperature increases the kinetic energy of the molecules increases, which increases the number of collisions between the molecules. Therefore the overall rate of the reaction increases. This condition is valid only for endothermic reaction. For exothermic reaction the overall rate decreases with increasing temperature.

### **(iv) Effect of presence of catalyst**

A catalyst is a substance that alters the rate of a chemical reaction, while concentration of catalyst remaining the same before and after the reaction. The addition of catalyst generally increases the rate of the reaction at a given temperature. Also, catalyst is specific for a given reaction.

### **(v) Effect of surface area of reactants**

In case of reactions involving solid reactants and in case of heterogeneous reactions, surface area of the reactant has an important role. As the particle size decreases surface area increases for the same mass. More number of molecules at the surface will be exposed to the reaction conditions such that the rate of the reaction increases. Thus the reactants in the powdered form (or) in smaller particles react rapidly than when present in larger particles.

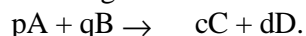
### **(vi) Effect of radiation**

Rates of certain reactions are increased by absorption of photons of energy. Such reactions are known as photochemical reactions. For example,  $\text{H}_2$  and  $\text{Cl}_2$  react only in the presence of light. With increase in the intensity of the light (or) radiation, the product yield increases. For photosynthesis light radiation is essential and the process does not proceed in the absence of light.

### **14.1.3 Rate law**

According to concepts of chemical kinetics, the rate of the reaction is proportional to the product of the initial concentration of all the reactants with each reactant concentration raised to certain exponential powers.

Consider a general reaction



The rate law is given by the expression,

$$\begin{aligned}\text{Rate} &\propto [\text{A}]^p [\text{B}]^q \\ \therefore \text{Rate} &= k[\text{A}]^p [\text{B}]^q\end{aligned}$$

where  $k$  is proportionality constant also known as the rate constant or velocity constant of the reactions.  $p$  and  $q$  represent the order of the reaction with respect to  $\text{A}$  and  $\text{B}$ . The values of  $k$ ,  $p$  and  $q$  are experimentally determined for a given reaction. Values of  $p$  and  $q$  need not be same as the stoichiometric coefficients of the reaction.

### Rate constant

In the above general equation  $k$  represents the rate constant. Rate constant or velocity constant (or) specific reaction rate is defined as the rate of the reaction when the concentration of each of the reactants is unity in the reaction.

When concentration of  $\text{A}$  and  $\text{B}$  is unity then, the rate constant is equal to the rate of the reaction. When the temperature of the reaction mixture changes, the value of rate constant changes.

#### 14.1.4 Order of the reaction

Order of a reaction is defined as the sum of the exponential powers to which each concentration is raised in the rate expression. For example, if the overall rate is given by the expression

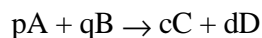
$$\text{Rate} = k[\text{A}]^p [\text{B}]^q$$

Then, the overall order of the reaction is  $(p+q)$ . The order with respect to  $\text{A}$  is  $p$ . The order with respect to  $\text{B}$  is  $q$ . If  $p=1$ ;  $q=0$  and vice versa, the order of the reaction is 1, and the reaction is called first order. If  $p=1$ ,  $q=1$ , the order of the reaction is 2 and the reaction is called second order and so on.

A zero order reaction is one where the reaction rate does not depend upon the concentration of the reactant. In this type of reaction, the rate constant is equal to the rate of the reaction.

#### 14.1.5 Unit of rate constant

In general, rate expression for the reaction,





$$\text{Rate} = k [A]^p [B]^q$$

$$k = \frac{\text{Rate}}{[A]^p [B]^q}$$

The unit for the rate constant 'k' depends upon the rate of the reaction, the concentration of the reactants and the order of the reaction.

In the case of the first order reaction.

$$k = \frac{\text{Rate}}{[A]^1 [B]^0}$$

$$k = \frac{\text{mol dm}^{-3} \text{sec}^{-1}}{\text{mol dm}^{-3}}$$

Unit of

$$k = \text{sec}^{-1} \text{ for first order reaction.}$$

Similarly unit of  $k = \text{mol}^{-1} \text{dm}^3 \text{sec}^{-1}$  for second order reaction

unit of  $k = \text{mol}^{-(n-1)} \text{dm}^{3(n-1)} \text{sec}^{-1}$  for  $n^{\text{th}}$  order reaction

Following are the important differences between rate and rate constant of a reaction

Rate of reaction	Rate constant of reaction
1. It represents the speed at which the reactants are converted into products at any instant.	1. It is the constant of proportionality in the rate law expression.
2. At any instant of time, the rate depends upon the concentration of reactants at that instant.	2. It refers to the rate of a reaction at the specific point when concentration of every reacting species is unity.
3. It decreases as the reaction proceeds.	3. It is constant and does not depend on the progress of the reaction.
4. Rate of rate determining step determines overall rate value.	4. It is an experimental value. It does not depend on the rate determining step.

## 14.2 Molecularity of the reaction

Molecularity is defined as the number of atoms or molecules taking part in an elementary step leading to a chemical reaction. The overall chemical reaction may consist of many elementary steps. Each elementary reaction has its own molecularity which is equal to number of atoms or molecules participating in it. If the reaction takes place in more than one step there is no molecularity for the overall reaction. However molecularity and order are identical for elementary reaction (one step).

There are many differences between the concepts of order and molecularity.

Order of a reaction	Molecularity of a reaction
1. It is the sum of powers raised on concentration terms in the rate expression.	1. It is the number of molecules of reactants taking part in elementary step of a reaction.
2. Order of a reaction is an experimental value, derived from rate expression.	2. It is a theoretical concept.
3. Order of a reaction can be zero, fractional or integer.	3. Molecularity can neither be zero nor fractional.
4. Order of a reaction may have negative value.	4. Molecularity can never be negative.
5. It is assigned for overall reaction.	5. It is assigned for each elementary step of mechanism.
6. It depends upon pressure, temperature and concentration (for pseudo order)	6. It is independent of pressure and temperature.

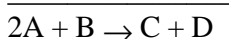
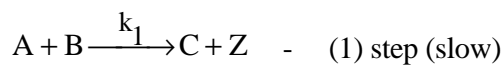
### 14.2.1 Rate determining step

Most of the chemical reactions occur by multistep reactions. In the sequence of steps it is found that one of the steps is considerably slower than the others. The overall rate of the reaction cannot be lower in value

than the rate of the slowest step. Thus in a multistep reaction the experimentally determined rate corresponds to the rate of the slowest step. Thus the step which has the lowest rate value among the other steps of the reaction is called as the rate determining step (or) rate limiting step.

Consider the reaction,

$2A + B \rightarrow C + D$  going by two steps like,



Here, the overall rate of the reaction corresponds to the rate of the first step which is the slow step and thus, the first step is called as the rate determining step of the reaction. In the above reaction, the rate of the reaction depends upon the rate constant  $k_1$  only. The rate of 2<sup>nd</sup> step doesn't contribute experimentally determined overall rate of the reaction.

### Example

For a reaction  $A + B \rightarrow \text{Products}$ , the following data has been provided to you for determining rate expression. Derive it and suggest order of reaction.

[A]	[B]	rate concentration in mole litre <sup>-1</sup> & rate in mol litre <sup>-1</sup> time <sup>-1</sup>
1	2	4
2	2	4
2	4	16

We can write

$$\begin{aligned} \text{rate} &= K[A]^m [B]^n \\ 4 &= K[1]^m [2]^n && \dots(i) \\ 4 &= K[2]^m [2]^n && \dots(ii) \\ 16 &= K[2]^m [4]^n && \dots(iii) \end{aligned}$$

By (i) & (ii)  $m = 0$

By (i) & (iii)  $n = 2$

$$\therefore \text{rate} = k[A]^0 [B]^2 \text{ \& order of the reaction}$$

$$= 0 + 2 = 2.$$

### 14.3 Classification of rates based on the order of the reaction

The rate law for a reaction must be determined by experiment. Usually the order of the reaction determined experimentally does not coincide with the stoichiometric coefficients of the reactants or products in the balanced chemical equation. Each reaction proceeds by a rate value determined by the rate constant and initial concentrations of the reacting species. Rate constant values differ for different 'order' reactions even if concentrations are maintained the same. Therefore chemical reactions are classified according to its rate of chemical transformation which in turn depend on the order of the reaction. Let us consider a general rate equation such as

$$\text{rate} = k[A]^p [B]^q$$

Total order is  $p + q$  and order with respect to A is  $p$  and with respect to B is  $q$  respectively.

#### Zero order reaction

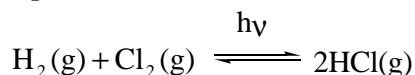
A reactant whose concentration does not affect the reaction rate is called as zero order reaction,

rate law is,

$$\text{rate} = k[A]^0 \quad (\text{or})$$

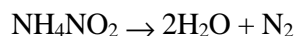
$$\frac{-d[A]}{dt} = k \quad \text{or} \quad k = \frac{[A]_0 - [A]_t}{t}$$

Examples of zero order reaction is



#### The first order reaction

when aqueous solution of  $NH_4NO_2$  is warmed it decomposes rapidly to  $H_2O$  and  $N_2$ .



This reaction goes by first order manner  
rate constant  $k$  is given by

$$K = \frac{2.303}{t} \log \frac{V_{\infty}}{V_{\infty} - V_t} \text{sec}^{-1}$$

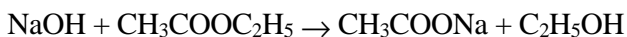
$V_{\infty}$  and  $V_t$  are volume of  $N_2$  collected at room temperature and 1 atm when a fixed amount of  $NH_4NO_2$  decomposes at  $t = \infty$  (after completion of reaction) and at any time 't'.

### Second order reaction

A reaction is said to be second order if its reaction rate is determined by the variation of two concentration terms or square of a single concentration term.

#### Example

Saponification of an ester is second order



or if  $A = NaOH$  ;  $B = \text{ester}$

$$\text{then rate} = \frac{-d[A]}{dt} = \frac{-d[B]}{dt} = k.C_A C_B$$

$$k = \frac{2.303}{t\{[A]_0 - [B]_0\}} \log \frac{[A]_t [B]_0}{[A]_0 [B]_t}$$

$[A]_0$  ;  $[B]_0$  = initial concentrations of A and B at  $t = 0$

$[A]_t$  ;  $[B]_t$  = concentration of A and B at time = t

for  $2A \rightarrow \text{products}$ ,

$$\text{rate} = k[A]^2$$

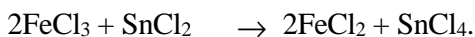
then

$$k = \frac{1}{t} \left[ \frac{1}{[A]_t} - \frac{1}{[A]_0} \right] \quad \text{or} \quad k = \frac{1}{t} \left[ \frac{x}{a(a-x)} \right] \text{lit mol}^{-1} \text{sec}^{-1}$$

### Third order reactions

A reaction is said to be third order if its rate is determined by the variation of three concentration terms.

#### Example



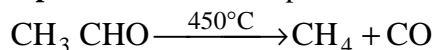


$$\text{Rate} = k[A]^3 \quad (\text{or})$$

$$k = \frac{1}{2t} \left[ \frac{1}{[A]_t^2} - \frac{1}{[A]_o^2} \right] \quad (\text{or}) \quad k = \frac{1}{2t} \left[ \frac{x(2a-x)}{a^2(a-x)^2} \right] \text{ lit}^2 \text{ mol}^{-2} \text{ sec}^{-1}$$

A second (or) third (or) any other high order reaction can be experimentally followed in an easy way by reducing the overall order to first order type by adopting pseudo order conditions. In this method, excluding the concentration of one of reactants, concentrations of all other reactant are kept in excess (at least 10 times) of the concentration of one of the reactant whose concentrations are to be varied to study the changes in the rate.

**Example :** Thermal decomposition of acetaldehyde.



Order = 1.5. Here a chain mechanism has been proposed. Polymerisation reactions also show fractional orders.

### Questions

#### A. Choose the correct answer

- mol.dm<sup>-3</sup> sec<sup>-1</sup> is the unit of  
(i) rate (ii) rate constant (iii) order (iv) active mass
- The elementary step with slow rate represents  
(i) rate determining step (ii) maximum rate step  
(iii) third order rate (iv) overall order
- Molecularity is determined for  
(i) an elementary reaction (ii) an overall reaction  
(iii) an over all stoichiometric reaction (iv) a fractional order reaction

#### B. Fill up the blanks

- Decomposition of aqueous NH<sub>4</sub>NO<sub>2</sub> proceeds by \_\_\_\_\_ reaction.
- Fractional orders are found in \_\_\_\_\_ reaction.
- In a \_\_\_\_\_ reaction rate does not depend on the reactant concentration.

#### C. Match the following

- |                 |                              |
|-----------------|------------------------------|
| 7. slow step    | a. experimentally determined |
| 8. order        | b. zero order                |
| 9. molecularity | c. rate determining step     |

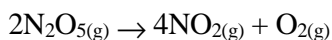
10. unit of first order 'k' d. maximum rate  
 11. rate is independent of reactant e. theoretical concept concentration  
 f.  $\text{sec}^{-1}$

**D. Write very short answers**

12. Define half life period.  
 13. Name the factors that affect the rate of reaction.  
 14. What is molecularity?  
 15. What is a rate determining step?  
 16. List the factors on which an order of the reaction depend.  
 17. Write the rate law of  $pA + qB \rightarrow lC + mD$  reaction.  
 18. Define the rate of a reaction.

**E. Explain briefly on the following**

19. Compare and contrast the terms, order and molecularity of a reaction.  
 20. Describe the factors on which the rate of a reaction depends.  
 21. What is a pseudo order reactions? How do you experimentally determine the pseudo first order rate constant of acid hydrolysis ester reaction?  
 22. Discuss the rate of the reaction



**Problems**

23. One ml of methyl acetate was added to 20 ml of 0.5 N sulphuric acid. 2 ml of the reaction mixture was with drawn at various time intervals and titrated against a solution of standard alkali. The titre values are tabulated. Show that the reaction is first order and calculate the rate constant and half life period of the reaction.

Time (s)	0	600	1200	2400	$\infty$
Volume of alkali (ml)	19.3	19.9	20.5	21.7	41.9

[Ans : mean  $k=4.570 \times 10^{-5} \text{ sec}^{-1}$ ;  $t_{1/2}=1.570 \times 10^4 \text{ sec}$ ]

24. In I order reaction the initial concentration of the reactant as 0.05 mole/litre and the rate constant  $1.5 \times 10^{-3} \text{ min}^{-1}$ . What is the initial rate of the reaction. [Ans :  $7.5 \times 10^{-5} \text{ mol lit}^{-1} \text{ min}^{-1}$ ]  
 25. If a reaction with  $t_{1/2}=69.3$  second, has a rate constant value of  $10^{-2}$  per second. Calculate the order of the reaction. [One]  
 26. The time for half life of a first order reaction is 1 hr. what is the time

taken for 87.5% completion of the reaction? [3 hrs]

27. The following results were obtained for the saponification of ethyl acetate using equal concentrations of ester and alkali.

Time	0	4.89	10.07	23.66	$\infty$
Acid in ml	47.65	38.92	32.62	22.58	11.84

Show that the reaction is of the second order.

[Ans : Mean Value of  $k = 9.68 \times 10^{-4} \text{ lit mol}^{-1} \text{ sec}^{-1}$ ].

### SUMMARY

- Basic concepts of chemical kinetics used in writing the rate law of a general reaction along with order and rate constant units and various expressions are understood.
- Identification of rate determining step examples of reactions with measurable rates are studied. Decomposition of  $\text{N}_2\text{O}_5$  reaction with various forms of rate expressions are studied.
- Order and molecularity are differentiated and various experimental methods of determination of order of the reaction was understood.
- Classification of rates based on the order of the reaction are understood with suitable examples each of the zero, first, second, pseudo first, third and fractional order reactions.

Order	Unit of k
Zero	$\text{mol litre}^{-1} \text{ time}^{-1}$
I	$\text{time}^{-1}$
II	$\text{litre mol}^{-1} \text{ time}^{-1}$
III	$\text{litre}^2 \text{ mol}^{-2} \text{ time}^{-1}$
$n^{\text{th}}$	$\text{litre}^{(n-1)} \text{ mol}^{(1-n)} \text{ s}^{-1}$

### REFERENCES

1. Physical Chemistry by Lewis and Glasstone.



## 15. BASIC CONCEPTS OF ORGANIC CHEMISTRY

### OBJECTIVES

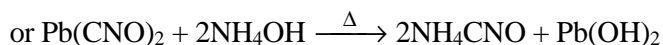
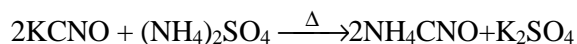
*This topic explains the nature of organic compounds and explores the possibilities of all basic concepts of organic chemistry.*

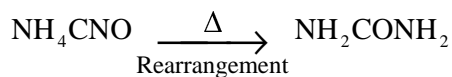
- *Catenation and the reason for innumerable number of organic compounds.*
- *Classification of organic compounds based on functional groups.*
- *IUPAC method of naming all types of organic compounds.*
- *Details about isomerism.*
- *Fission of bonds and types of organic reactions.*
- *Nature of reagents, electrophiles and Nucleophiles.*
- *Knowledge about carboniumion and carbanion and free radicals.*
- *Different types of electron displacements in organic chemistry.*

### Introduction

Initially (before 1828), the name organic chemistry was given for the chemistry of compounds obtained from plants and animals (i.e, from living organisms). The word organic signifies life. Lavoisier (who is considered as the father of chemistry) showed that the compounds obtained from plants are often made of C, H and O and the compounds obtained from animals contain C, H, O, N, S, P. .... etc.

Berzelius proposed vital force theory (a theory of life process) to deal with organic compounds. The vital force theory suffered blow in 1828 when Wohler synthesized the first organic compound urea in the laboratory from an inorganic compound, i.e, from ammonium cyanate ( $\text{NH}_4 \text{CNO}$ ).





Later on, a further blow to vital force theory was given by Kolbe (1845) who prepared acetic acid, the first organic compound, in laboratory from its elements.

Now a days organic chemistry is defined as **the chemistry of carbon compounds or the chemistry of hydrocarbons and their derivatives**. Organic compounds obey the same fundamental laws of chemistry as the inorganic compounds. However they are studied as a separate branch of chemistry because of two reasons:

- i. The total number of organic compounds known so far exceeds several times the total number of inorganic compounds known.
- ii. There are marked differences between the structure, composition and behaviour of organic and inorganic compounds. The phenomenon of **isomerism** and tendency of **catenation** are unique properties of organic compounds.

### 15.1 Catenation

1. The tendency of atoms of an element to unite with each other forming a chain of covalent bond is known as **catenation**.
2. Catenation may give rise to open chain or closed chain compounds.
3. Carbon possesses maximum tendency for catenation i.e. **Bond energy (kcal mol<sup>-1</sup>) for catenation of C is maximum.**

C-C,	Si-Si,	N-N,	P-P,	O-O,	S-S
85	54	39	50	35	54

4. Carbon also forms double as well as triple bonds.
5. A large number of compounds of carbon are known due to catenation.
6. The stability or strength of bond decreases as the bond energy decreases. Hence the catenation order among the following is  $\text{C} > \text{Si} \approx \text{S} > \text{P} > \text{N} > \text{O}$ .

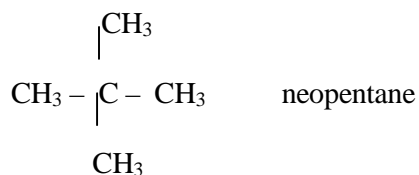
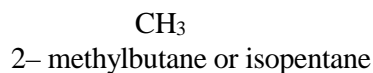
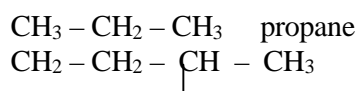
### 15.2 Classification into open chain and cyclic compounds

The organic compounds are classified into two main types, namely.

### (1) Open - chain or acyclic compounds or aliphatic compounds

The open chain or acyclic compounds are those in which carbon atoms are linked to each other either in linear or branched fashion such that the molecule is having open chain structure. These compounds are also called aliphatic compounds (Greek word : aliphar meaning fat).

Examples



### (2) Closed chain or cyclic compounds

Organic compounds with closed chain of atoms are called closed chain compounds or ring compounds.

These compounds are further classified into

- (a) Homocyclic or carbocyclic compounds
- (b) Heterocyclic compounds

**(a) Homocyclic compounds :** In these compounds the ring structure is made up of only carbon atoms.

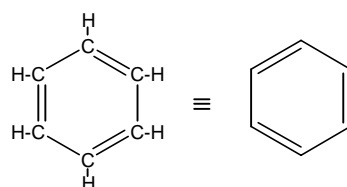
These compounds are further classified into

- (i) Aromatic compounds and
- (ii) Alicyclic compounds

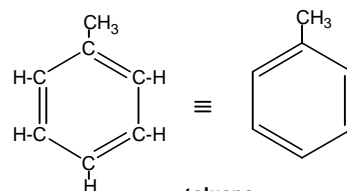
**(i) Aromatic compounds (Benzenoid) :** Compounds containing one or more benzene rings in their structure are classified as aromatic benzenoid compounds. Most of these compounds have pleasant odour (Greek : Aroma - sweet smell).

## Examples

### Monocyclic

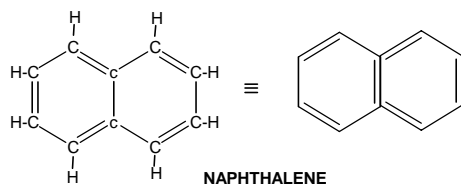


benzene

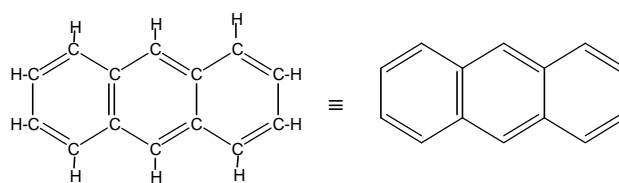


toluene

### Polycyclic



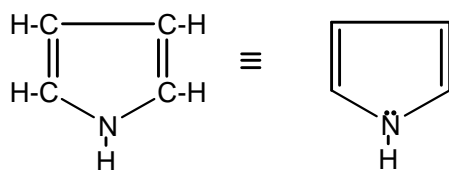
NAPHTHALENE



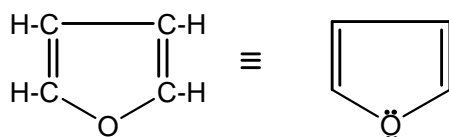
ANTHRACENE

**Heterocyclic compounds** (Non - benzenoid aromatic) : Cyclic compounds in which the ring atoms are made up of hetero atoms like nitrogen, oxygen and sulphur in addition to carbon atoms are called heterocyclic compounds.

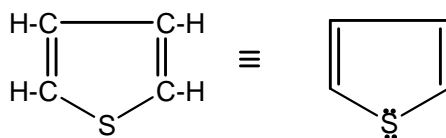
### Examples



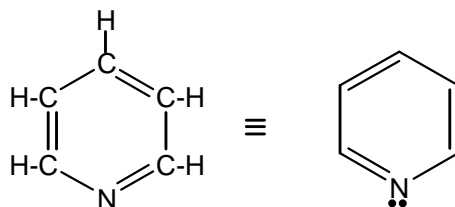
**pyrrole**



**furan**



**thiophene**

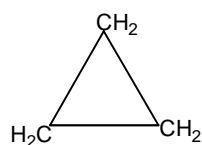


**pyridine**

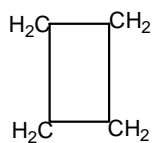
The above compounds are aromatic non-benzenoid compounds.

- (ii) **Alicyclic compounds** : Cyclic compounds with ring structure containing only carbon atoms are called alicyclic or carbocyclic compounds. Though these compounds possess a ring structure, they behave more like aliphatic compounds.

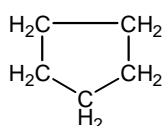
## Examples



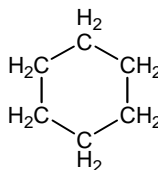
**cyclopropane**



**cyclobutane**

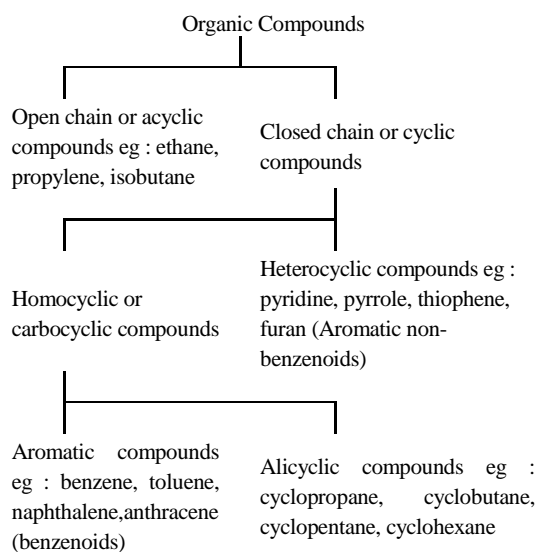


**cyclopentane**



**cyclohexane**

The above classification can be schematically represented as follows :



## Characteristics of organic compounds

All organic compounds have the following characteristic properties

- (1) Many organic compounds are inflammable
- (2) They are mostly covalent compounds

- (3) They are generally soluble in non - polar solvents like carbon tetrachloride, benzene etc.
- (4) They have generally low boiling point and melting point.
- (5) They exhibit isomerism

### **Homologous series**

A group or class of organic compounds related to each other by a general molecular formula constitutes homologous series.

### **Characteristics of homologous series**

Homologous series have the following characteristics :

- (1) All members of a series contain same elements and the same functional groups.
- (2) All the members of a homologous series can be represented by a general formula

### **Examples**

Alkanes	$C_nH_{2n+2}$
Alkenes	$C_nH_{2n}$
Alkynes	$C_nH_{2n-2}$

- (3) All the members of a homologous series can be prepared by similar methods.
- (4) All members of a homologous series usually undergo similar chemical reactions.
- (5) Successive members in a series differ by a  $-CH_2$  group
- (6) The physical properties of the members of a homologous series vary in a regular way down the series. For example, boiling point, melting point and density of the alkane series vary in a regular way with increasing number of carbon atoms.

### **15.3 Functional groups**

The chemical properties of all the members of a homologous series are characterised by a group called the functional group. It is characteristic of a particular series.

The following table gives a list of functional groups and names.

Halide	$-X$
Alcohol	$-OH$
Ether	$-O-$

Aldehyde	- CHO
Ketone	$\begin{array}{c} \text{---C---} \\    \\ \text{O} \end{array}$
Carboxylic acid	- COOH
Ester	- COOR
Amide	$\begin{array}{c} \text{---C---NH}_2 \\    \\ \text{O} \end{array}$
Acid halide	$\begin{array}{c} \text{---C---X} \\    \\ \text{O} \end{array}$ (X = -Cl, -Br, -I)
Acid anhydride	$\begin{array}{c} \text{---C---O---C---} \\    \qquad \qquad    \\ \text{O} \qquad \qquad \text{O} \end{array}$
Amine	- NH <sub>2</sub>
Nitro compounds	- NO <sub>2</sub>

#### 15.4 IUPAC system of nomenclature (1993)

The international union of pure and applied chemistry (abbreviated as IUPAC) has done a commendable job in framing set rules for naming organic compounds. Two commonly used systems of nomenclature are described below.

- (1) Common or Trivial system      (2) IUPAC system

#### IUPAC Nomenclature of Aliphatic Compounds

The IUPAC name of a compound essentially consists of three parts.

- (a) Root word   (b) Suffix   (c) Prefix

##### Root words for alkanes

The root words for the first four members are taken from their trivial or common names.

e.g.

Meth	-	for Methane
Eth	-	for Ethane
Prop	-	for Propane
But	-	for Butane

For the higher homologue, root words are derived from the Greek/Latin number indicating the total number of carbon atoms.



- e.g. Pent - is derived from penta for five  
 Hex - is derived from hexa for six  
 Hept - is derived from hepta for seven  
 Oct - is derived from octa for eight

### Suffix

There are two types of suffixes **Primary suffix** and secondary suffix.

### Primary suffix

A primary suffix is added to the **Root word** to indicate whether the parent chain is saturated or unsaturated. Some primary suffixes are given below.

Sl. No.	Nature of carbon chain (parent chain)	Primary suffix
1.	Saturated	ane
2.	Unsaturated with One double bond Two double bond Three double bond	ene diene triene
3.	Unsaturated with One triple bond Two triple bond	yne diyne

Sl. No.	Structural formula	No. of C atoms	Root word	Primary suffix	IUPAC name
1.	$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_3$	4	But	ane	Butane
2.	$\text{CH}_3\text{-CH=CH}_2$	3	Prop	ene	Propene
3.	$\text{CH}\equiv\text{CH}$	2	Eth	yne	Ethyne
4.	$\text{CH}_2\text{=CH-CH=CH}_2$	4	Buta <sup>*</sup>	diene	Butadiene
5.	$\text{HC}\equiv\text{C-C}\equiv\text{CH}$	4	Buta <sup>*</sup>	diyne	Butadiyne

\* extra 'a' has been added to the root word since the primary suffix, ie diene or diyne begins with a consonant (d).

### Secondary suffix

Secondary suffix is used to indicate the functional group in the organic compound secondary suffixes for various functional groups are given below.

Sl. No.	Class	Functional group	Secondary suffix	IUPAC name
1.	Alcohols (R-OH)	-OH	-ol	Alkanols
2.	Aldehyde (R-CHO)	-CHO	-al	Alkanals
3.	Ketones (RCOR')	$>C=O$	-one	Alkanones
4.	Carboxylic acids (R-COOH)	-COOH	-oic acid	Alkanoic acid
5.	Ester (RCOOR')	-COOR	-alkanoate	alkyl alkanoates

Secondary suffix is added to the primary suffix; ie written after the primary suffix. While adding the secondary suffix to the primary suffix following rules should be followed.

- If the secondary suffix begins with a vowel, then the terminal **e** of the primary suffix is dropped before adding the secondary suffix.
- If the secondary suffix begins with a consonant, then the last (terminal) **e** is retained and the secondary suffix is added after e.
- If the secondary suffix has some **numerical prefix**, such as, **di, tri etc.**, before it then the terminal **e** of the primary suffix is retained.

The addition of the secondary suffix to the primary suffix is illustrated below

Sl. No.	Structural formula	No. of C atoms	Root word	Primary suffix	Secondary suffix	IUPAC name	Remarks
1.	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_2\text{-OH} \end{array}$	2	Eth	ane	ol	Ethanol	'e' of primary suffix dropped

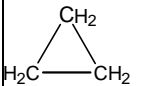
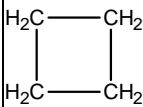
2.	$\begin{array}{c} \text{CH}_2\text{-OH} \\   \\ \text{CH}_2\text{-OH} \end{array}$	2	Eth	ane	diol	Ethane diol	'e' of prim suffix not dropped
3.	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_2 \\   \\ \text{CHO} \end{array}$	3	Prop	ane	al	Propanal	'e' of the prim suffix dropped
4.	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_2 \\   \\ \text{CH}_2 \\   \\ \text{COOH} \end{array}$	4	But	ane	oic acid	Butanoic acid	'e' of prim suffix dropped

### Prefix

Prefix is a part of the name which appears before the root word. There are two types of prefixes - primary prefix and secondary prefix.

#### Primary prefix

A primary prefix is used to distinguish alicyclic (aliphatic cyclic compounds) from acyclic (open chain) compounds. If the given compound is an alicyclic compound, then a prefix cyclo is used just before the root word. For example.

Structural formula	No. of C atoms	Root word	Primary suffix	Primary prefix	IUPAC name
	3	Prop	ane	Cyclo	Cyclo propane
	4	But	ane	Cyclo	Cyclo butane

### Secondary prefix

In the IUPAC system of nomenclature, certain characteristic groups are not considered as functional groups. Such characteristic groups are considered as the **substituents**. Each such group or substituent is denoted by a secondary prefix. Some typical secondary prefixes are listed below.

Substituent group	Secondary prefix
- F	Fluoro
- Cl	Chloro
- Br	Bromo
- I	Iodo
- CH <sub>3</sub>	Methyl
- C <sub>2</sub> H <sub>5</sub>	Ethyl
CH <sub>3</sub> - CH <sub>2</sub> - CH <sub>2</sub> -	n-propyl
(CH <sub>3</sub> ) <sub>2</sub> CH -	Iso propyl
(CH <sub>3</sub> ) <sub>3</sub> C -	t - Butyl
- NO <sub>2</sub>	Nitro
- NH <sub>2</sub>	Amino
- NO	Nitroso
N $\equiv$ N	Diazo
- OCH <sub>3</sub>	Methoxy
- OC <sub>2</sub> H <sub>5</sub>	Ethoxy

In the case of open chain compounds, the secondary prefix is added just before the root word in the **alphabetical** order. This is illustrated below.

Sl. No.	Structural formula	No. of C atoms	Root word	Suffix		Prefix		IUPAC Name
				Primary	Sec	Pri	Sec	
1.	CH <sub>3</sub> -CH <sub>2</sub> -Cl	2	Eth	ane	-	-	Chloro	Chloro ethane
2.	CH <sub>3</sub> -NO <sub>2</sub>	1	Meth	ane	-	-	Nitro	Nitro methane

### Saturated Hydrocarbons : Alkanes

**General formula :**  $C_nH_{2n+2}$       **Suffix :** ane

Sl. No.	Structural formula	Common Name	IUPAC name
1.	CH <sub>4</sub>	Methane	Methane
2.	H <sub>3</sub> C - CH <sub>3</sub>	Ethane	Ethane
3.	H <sub>3</sub> C - CH <sub>2</sub> - CH <sub>3</sub>	Propane	Propane
4.	H <sub>3</sub> C - CH <sub>2</sub> - CH <sub>2</sub> - CH <sub>3</sub>	n-butane	Butane

### Alkyl groups

The univalent hydrocarbon unit derived from an alkane by the loss of one hydrogen atom is termed as alkyl group.

The alkyl groups are named after their parent alkanes by replacing the suffix-**ane** by- **yl**.

### Continuous straight chain alkyl groups (or, normal alkyl (n-) groups)

Sl. No.	Alkane		Alkyl group	
	Formula	Name	Formula	Name
1.	CH <sub>4</sub>	Methane	CH <sub>3</sub> -	Methyl
2.	CH <sub>3</sub> - CH <sub>3</sub>	Ethane	CH <sub>3</sub> - CH <sub>2</sub> -	Ethyl
3.	CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>3</sub>	Propane	CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -	Propyl

### Branched chain alkyl groups

When a hydrogen atom from a secondary or tertiary carbon atom in any carbon chain is removed, a branched chain alkyl group is obtained. The common prefixes used are,

a) iso - b) sec - c) tert - d) neo –

a) **iso** – The alkyl group in which a - CH<sub>3</sub> branch is present at the end of the chain is designated as isoalkyl group. In other words, the alkyl group in which the second last carbon atom in the chain is branched to one - CH<sub>3</sub> group is called on isoalkyl group.

Sl.No.	Structure	IUPAC name
1.	$\begin{array}{c} \text{CH}_3 - \text{CH} - \\   \\ \text{CH}_3 \end{array}$	1-methyl ethyl (iso-propyl)
2.	$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 - \\   \\ \text{CH}_3 \end{array}$	2-methyl propyl (iso-butyl)
3.	$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_2 - \\   \\ \text{CH}_3 \end{array}$	3-methyl butyl (iso-pentyl)

**b) Sec -** The prefix sec - before the name of the alkyl group indicates that the H-atom was removed from a secondary carbon atom.

Sl.No.	Structure	IUPAC name
1.	$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_3 \\   \end{array}$	1 - Methyl ethyl (Sec - propyl)
2.	$\begin{array}{c} \text{CH}_3 - \text{CH}_2 - \text{CH} - \\   \\ \text{CH}_3 \end{array}$	1 - methyl propyl (Sec - butyl)
3.	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH} - \end{array}$	1 - methyl butyl (Sec - pentyl)

**c) Tert - (or) t -**

The prefix tert - before the name of the alkyl group indicates that the H - atom has been removed from a tertiary carbon atom.

Sl. No.	Structure	IUPAC name
1.	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3 - \text{C} - \\   \\ \text{CH}_3 \end{array}$	1,1 - dimethyl ethyl (tert - butyl)
2.	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3 - \text{CH}_2 - \text{C} - \\   \\ \text{CH}_3 \end{array}$	1,1 - dimethyl propyl (tert - pentyl)

## Alkenes

**General formula :**  $C_nH_{2n}$  **Suffix : ene**

The common name of alkene is obtained by replacing the ending - **ane** from the name of its parent alkane with - **ylene**.

The IUPAC name of an alkene is obtained by replacing - **ane** of the alkane by - **ene**.

Structural formula	Common Name	IUPAC name
$CH_2 = CH_2$	Ethylene	Ethene
$CH_3 - CH = CH_2$	Propylene	Propene
$CH_3-CH_2-CH=CH_2$ (double bond starts at $C_1$ )	1- Butylene	But-1-ene
$CH_3-CH=CH-CH_3$ (double bond starts at $C_2$ )	2- Butylene	But-2-ene

## Alkenyl group

The group obtained by removing a hydrogen atom from an alkene molecule, are called **alkenyl** group.

The IUPAC name of alkenyl group is obtained by replacing - **e** of the alkene by the suffix - **yl**.

Sl. No.	Structure	Common name	IUPAC name
1.	$CH_2 = CH_2$	vinyl	ethenyl
2.	$CH_2=CH-CH_2-$	allyl	Prop - 2 - enyl

## Alkynes

**General formula :**  $C_nH_{2n-2}$  **Suffix : - yne**

The IUPAC name of an alkyne is obtained by replacing the ending - **ane** from the name of the parent alkane with - **yne**.

Sl. No.	Structural formula	Common Name	IUPAC name
1.	$\text{HC} \equiv \text{CH}$	Acetylene	Ethyne
2.	$\text{CH}_3 - \text{C} \equiv \text{CH}$	Methyl acetylene	Propyne
3.	$\text{CH}_3 - \text{C} \equiv \text{C} - \text{CH}_3$	Dimethyl acetylene	But-2-yne

### Alkyl halides

The general formula of alkyl halides is R-X where R stands for alkyl group and "X" stands for halogen (F, Cl, Br, I). They are named by introducing the prefix halo (chloro, bromo, iodo, fluoro) to the name of the parent alkane.

Formula	Common name	IUPAC name
$\text{CH}_3\text{-Cl}$	Methyl chloride	Chloromethane
$\text{CH}_3\text{-CH}_2\text{-Br}$	Ethyl bromide	Bromoethane
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-Br}$	n-propyl bromide	1-bromopropane
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_3 \\   \\ \text{I} \end{array}$	Iso-propyl iodide	2-iodopropane
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-Cl}$	n-butyl chloride	1-chlorobutane
$\begin{array}{c} \text{CH}_3\text{-CH}_2\text{-CH-CH}_3 \\   \\ \text{Br} \end{array}$	Sec-butyl bromide	2-bromobutane
$\begin{array}{c} \text{CH}_3\text{-CH-CH}_2\text{-Cl} \\   \\ \text{CH}_3 \end{array}$	Isobutyl chloride	1-chloro-2-methyl propane
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3 - \text{C} - \text{I} \\   \\ \text{CH}_3 \end{array}$	ter-butyl iodide	2-iodo-2-methyl propane
$\text{CH}_2=\text{CH-Cl}$	Vinyl chloride	Chloroethene
$\text{CH}_2=\text{CH-CH}_2\text{-Cl}$	Allyl chloride	3-Chloro-1-propene



## Alcohols

The term alcohol is applied to all organic compounds obtained by replacing one or more hydrogen atoms of an open-chain hydrocarbon by hydroxyl groups. The alcohols are further classified into **mono-**, **di-**, **tri-**hydric alcohols according to the number of hydroxyl groups which they may contain.

In IUPAC nomenclature, the terminal "e" of the alkane is replaced by "ol".

### Monohydric alcohols

Alcohols which contain only one hydroxyl group per molecule are called monohydric alcohols.

Formula	Common name	IUPAC name
CH <sub>3</sub> -OH	Methyl alcohol	methanol
CH <sub>3</sub> -CH <sub>2</sub> -OH	Ethyl alcohol	ethanol
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -OH	n-propyl alcohol	1-propanol
CH <sub>3</sub> -CH - CH <sub>3</sub>   OH	Isopropyl alcohol	2-propanol
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -OH	n-butyl alcohol	1-butanol
CH <sub>3</sub> - CH <sub>2</sub> -CH - CH <sub>3</sub>   OH	sec-butyl alcohol	2-butanol
CH <sub>3</sub> -CH - CH <sub>2</sub> - OH   CH <sub>3</sub>	Isobutyl alcohol	2-methyl-1-propanol
CH <sub>3</sub> - C - OH   CH <sub>3</sub>	tert-butyl alcohol	2-methyl-2-propanol
CH <sub>2</sub> =CH-CH <sub>2</sub> -OH	Allyl alcohol	2-propene-1-ol

### Dihydric alcohols

Alcohols which contain two -OH groups per molecule are called dihydric alcohols.

Structural formula	Common name	IUPAC name
$\begin{array}{c} \text{CH}_2\text{-OH} \\   \\ \text{CH}_2\text{-OH} \end{array}$	Ethylene glycol	1,2-Ethanediol

### Trihydric alcohols

Alcohols which contain three -OH groups per molecule are called trihydric alcohols.

Structural formula	Common name	IUPAC name
$\begin{array}{c} \text{CH}_2\text{ - OH} \\   \\ \text{CH - OH} \\   \\ \text{CH}_2\text{ - OH} \end{array}$	Glycerol	1,2,3-propanetriol

### Ethers

An ether is a substance that has two organic groups bonded to the same oxygen atom, **R-O-R'**. The organic group may be alkyl or aryl. When the groups attached to the oxygen atom are the same, they are termed as simple ethers. When the groups attached to the oxygen atom are different, they are termed as mixed ethers.

In IUPAC system, ethers are considered to be alkoxy derivatives of hydrocarbons.

Structural formula	Common name	IUPAC name
<b>Simple ethers</b>		
$\text{CH}_3\text{-O-CH}_3$	Dimethyl ether	Methoxymethane
$\text{CH}_3\text{-CH}_2\text{-O-CH}_2\text{-CH}_3$	Diethyl ether	Ethoxyethane
<b>Mixed ethers</b>		
$\text{CH}_3\text{-O-CH}_2\text{-CH}_3$	Ethyl methyl ether	Methoxyethane
$\text{CH}_3\text{-O-CH}_2\text{-CH}_2\text{-CH}_3$	Methyl n-propyl ether	1-methoxypropane
$\begin{array}{c} \text{CH}_3\text{ - O - CH - CH}_3 \\   \\ \text{CH}_3 \end{array}$	Isopropyl methyl ether	2-methoxypropane

## Aldehydes

Aldehydes and ketones are two important classes of compounds containing the carbonyl group  $\text{—}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\text{—}$ . In aldehydes the  $\text{—}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\text{—}$  group is

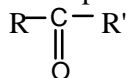
linked to an alkyl group and a hydrogen or two hydrogens. Aldehydes are represented by the general formula  $\text{R-CHO}$ .

IUPAC names of aldehydes are obtained by replacing the terminal "e" of alkane with "al".

Structural formula	Common name	IUPAC name
$\text{H-CHO}$	Formaldehyde	Methanal
$\text{CH}_3\text{-CHO}$	Acetaldehyde	Ethanal
$\text{CH}_3\text{-CH}_2\text{-CHO}$	Propionaldehyde	Propanal
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CHO}$	Butyraldehyde	1-Butanal
$\begin{array}{c} \text{CH}_3\text{-CH-CHO} \\   \\ \text{CH}_3 \end{array}$	Isobutyraldehyde	2-Methylpropanal

## Ketones

In ketones  $\text{—}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\text{—}$  group is united with 2 alkyl groups. These compounds are represented by the general formula.



Ketones are named by replacing the terminal "e" of the corresponding alkane name with "one".

Structural formula	Common name	IUPAC name
$\text{CH}_3-\overset{\text{O}}{\underset{\text{  }}{\text{C}}}-\text{CH}_3$	Acetone (Dimethyl ketone)	Propanone
$\text{CH}_3\text{-CH}_2-\overset{\text{O}}{\underset{\text{  }}{\text{C}}}-\text{CH}_3$	Ethylmethyl ketone	Butanone
$\text{CH}_3\text{-CH}_2-\overset{\text{O}}{\underset{\text{  }}{\text{C}}}-\text{CH}_2\text{-CH}_3$	Diethyl ketone	3-pentanone

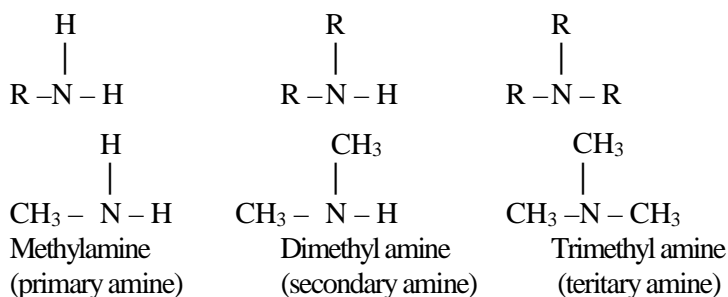
## Carboxylic acids

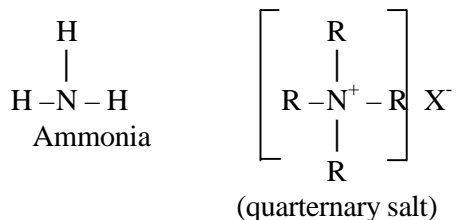
These are represented by the general formula  $R\text{-COOH}$ . IUPAC name is derived by replacing the terminal "e" of the alkane name with "**oic acid**". These compounds are further classified into **mono-** and **di-**carboxylic acids.

Structural formula	Common name	IUPAC name
<b>Monocarboxylic acids</b>		
$\text{H-COOH}$	Formic acid	Methanoic acid
$\text{CH}_3\text{-COOH}$	Acetic acid	Ethanoic acid
$\text{CH}_3\text{-CH}_2\text{-COOH}$	Propionic acid	Propanoic acid
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-COOH}$	Butyric acid	Butanoic acid
<b>Dicarboxylic acids</b>		
$\begin{array}{c} \text{COOH} \\   \\ \text{COOH} \end{array}$	Oxalic acid	Ethanedioic acid
$\begin{array}{c} \text{COOH} \\ / \quad \backslash \\ \text{CH}_2 \\ \backslash \quad / \\ \text{COOH} \end{array}$	Malonic acid	Propanedioic acid
$\begin{array}{c} \text{CH}_2\text{-COOH} \\   \\ \text{CH}_2\text{-COOH} \end{array}$	Succinic acid	Butanedioic acid

## Amines

Amines are the derivatives of ammonia in which one or more H-atoms have been replaced by alkyl groups. They are designated as primary, secondary and tertiary amines according as one, two or three hydrogen atoms in ammonia molecule have been replaced by alkyl groups.





When one alkyl group is attached to N-atom, it is called primary amine, when two alkyl groups are attached to nitrogen atom, then it is called secondary amine. When three alkyl groups are attached to nitrogen atom it is called tertiary amine. When four alkyl groups are attached to nitrogen atom it is called quarternary salt.

Structural formula	Common	IUPAC name
<b>Primary Amines</b>		
$\text{CH}_3\text{-NH}_2$	Methyl amine	aminomethane
$\text{CH}_3\text{-CH}_2\text{-NH}_2$	Ethyl amine	aminoethane
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-NH}_2$	n-propyl amine	1-aminopropane
$  \begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_3 \\   \\ \text{NH}_2 \end{array}  $	Isopropyl amine	2-aminopropane
<b>Secondary Amines</b>		
$\text{CH}_3\text{-NH-CH}_3$	Dimethyl amine	(N-methylamino) methane
$\text{CH}_3\text{-CH}_2\text{-NH-CH}_2\text{-CH}_3$	Diethyl amine	(N-ethylamino) ethane
$\text{CH}_3\text{-NH-CH}_2\text{-CH}_3$	Ethylmethyl amine	(N-methylamino) ethane

Structural formula	Common name	IUPAC name
<b>Tertiary Amines</b>		
$  \begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3 - \text{N} \\   \\ \text{CH}_3 \end{array}  $	Trimethyl amine	(N,N - dimethyl amino) methane
$  \begin{array}{c} \text{CH}_3 \\   \\ \text{C}_2\text{H}_5 - \text{N} \\   \\ \text{CH}_3 \end{array}  $	Ethyldimethyl amine	(N,N - dimethyl amino) ethane

## Nitro compounds

These compounds are represented by the general formula  $RNO_2$ . IUPAC names are obtained by adding the prefix "**nitro**" to the alkane.

Structural formula	Common/IUPAC name
1. $CH_3 - NO_2$	Nitromethane
2. $CH_3 - CH_2 - NO_2$	Nitroethane
3. $CH_3 - CH_2 - CH_2 - NO_2$	1-Nitropropane
4. $\begin{array}{c} CH_3 - CH - CH_3 \\   \\ NO_2 \end{array}$	2-Nitropropane

## 15.5 Isomerism

The molecular formula of an organic compound represents only the number of different atoms present in a molecule. But the molecular formula does not tell about the arrangement of atoms. A given molecular formula may lead to more than one arrangement of atoms such that there are many compounds which may have same molecular formula but with different physical and chemical properties. This phenomenon in which the same molecular formula may exhibit different structural arrangement is called isomerism.

Compounds that have the same molecular formula but different structural formulae are called isomers (from the Greek word isos + meros, "made of the same parts").

There are two types of isomerism, namely,

1. Structural isomerism
2. Stereoisomerism

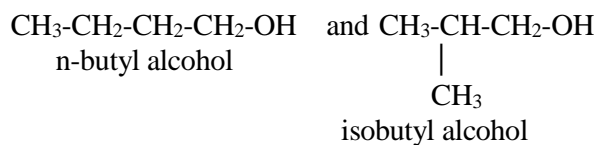
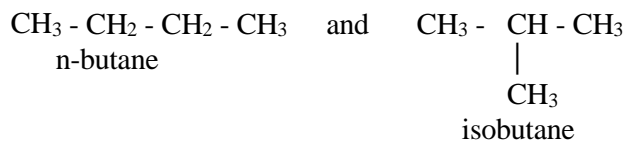
### Structural isomerism

When two or more compounds possess the same molecular formula but different structural formulae, they are said to exhibit structural isomerism. Structural isomerism is divided into.

#### 1. Chain isomerism or Nuclear isomerism

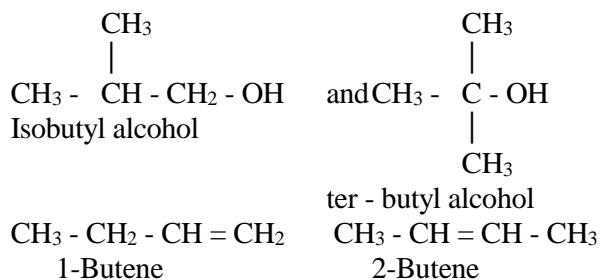
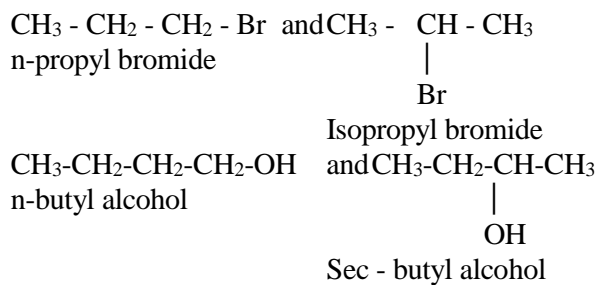
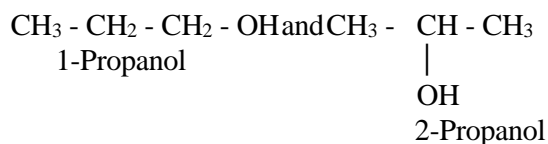
Chain isomers are compounds that have the same molecular formula but have different carbon skeletons.

### Examples



### 2. Position Isomerism

Position isomers are compounds that have the same formula, carbon skeleton and functional groups but have the functional groups located at different positions along the carbon skeleton.



### Functional isomerism

Functional isomers are compounds that have the same molecular formula but have different functional groups.

#### Examples

- $\text{CH}_3 - \text{CH}_2 - \text{OH}$  and  $\text{CH}_3 - \text{O} - \text{CH}_3$   
Ethyl alcohol                  Dimethyl ether
- $\text{CH}_3 - \underset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{CH}_3$  and  $\text{CH}_3 - \text{CH}_2 - \text{CHO}$   
Acetone                  Propionaldehyde
- $\text{CH}_3 - \text{CH}_2 - \text{COOH}$  and  $\text{CH}_3 - \text{COO} - \text{CH}_3$   
Propionic acid                  Methyl acetate

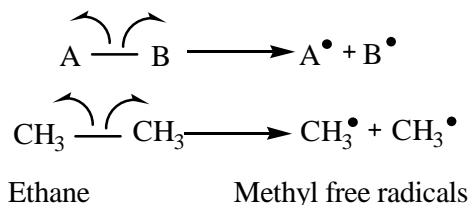
### 15.6 Fission of bonds

#### How bond fission occurs?

A covalent bond ( $\sigma$  bond) joining two atoms exist because of the shared pair of electrons. When two atoms are separated from each other, bond fission is said to have taken place. The fission process can take place in two ways.

#### Homolytic fission

A covalent bond between two atoms A and B may be shown as  $\text{A} \cdot \cdot \text{B}$  or  $\text{A}-\text{B}$ . This bond may undergo fission in such a way that each atom retains the electrons of the shared pair. Such species are known as **free radicals** or odd electron molecules.

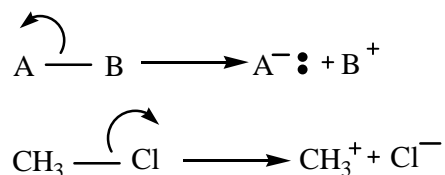


#### Heterolytic fission

A covalent bond breaks in such a way that the shared pair of electron



stay on any one of the atoms. Breaking of the bond in this manner is known as heterolytic fission or heterolysis.



The atom or group which carries the unshared pair of electrons are represented with a negative sign as  $\text{A}^-$  is known as anions. The carbonium ion carries the positive charge which lacks a pair of electrons. Heterolysis occurs only when the initially bonded atoms are of different in electronegativities and in that the electron pair becomes attached to the more electronegative atom.

An organic reaction may be represented as :

Reactants + attacking agent  $\rightarrow$  [intermediate]  $\rightarrow$  product

Depending upon the nature of the reaction which the intermediate species undergo, the reactions of the organic compounds are classified as substitution reactions, addition reactions, elimination reactions, polymerisation reactions, condensation reaction, hydrolysis, oxidation and reduction reactions.

## 15.7 Types of Reactions

### Substitution or Displacement reactions

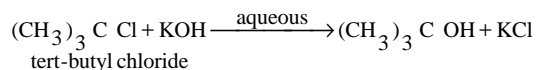
Displacement reaction is one in which an atom or group linked to a carbon atom is removed and in its place another atom or group is attached.

The substitution reactions are classified into three types.

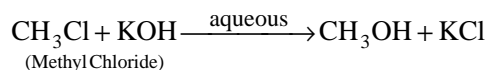
#### a) Nucleophilic substitution reaction ( $\text{S}_\text{N}$ )

When a substitution reaction is brought about by a nucleophile, the reaction is termed as  $\text{S}_\text{N}$  (S stands for substitution and N for nucleophile). These reactions are divided into two classes :

(1)  $\text{S}_\text{N}^1$  (substitution, nucleophilic, unimolecular)



(2) S<sub>N</sub><sup>2</sup> (Substitution, nucleophilic, bimolecular)

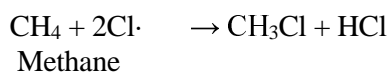
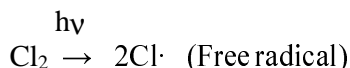


**b) Electrophilic substitution reaction (S<sub>E</sub>)**

When a substitution reaction involves an attack by an electrophile, the reaction is referred to as S<sub>E</sub> (S - stands for substitution and E for electrophile).

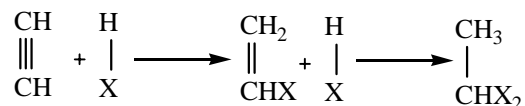
**c) Free radicals substitution reaction**

These reactions are initiated by free radicals.



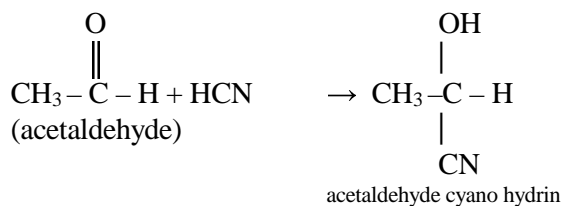
**Addition Reactions**

All organic compounds having double or triple bond adopt addition reactions in which two substances unite to form a single compound.

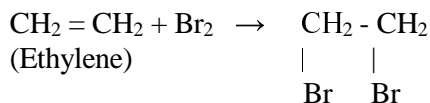


Depending on the type of reagent initiating these reactions, addition reactions are classified into three types.

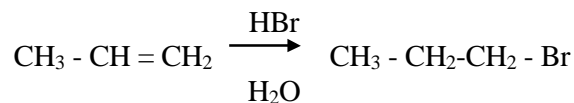
**(a) Nucleophilic addition**



**(b) Electrophilic addition**



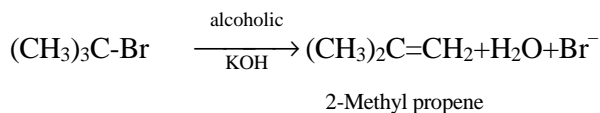
### (c) Free radical addition



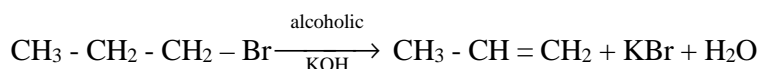
### Elimination reactions

In these reactions, two atoms or groups are removed from a molecule without being substituted by other atoms (or) groups. The reverse of addition reactions are eliminations. These reactions are classified into two types.

#### (a) Unimolecular elimination (E<sub>1</sub>)



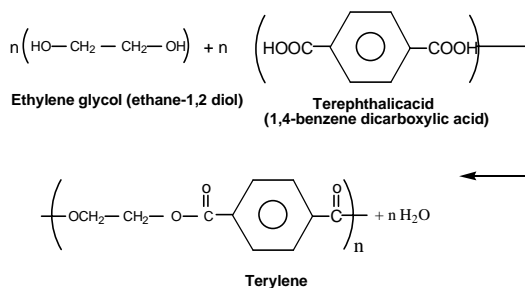
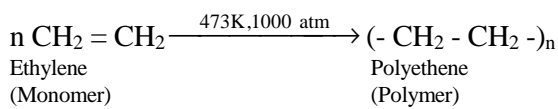
#### (b) Bimolecular elimination (E<sub>2</sub>)



### Polymerisation

The union of two or more molecules to form a large single molecule is called **polymerisation** and the product is a polymer.

#### Examples

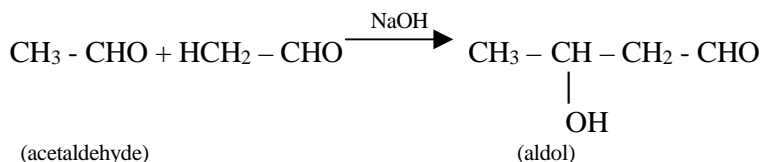


## Condensation reactions

When two molecules (similar or different) combine to form a single molecule with or without the elimination of simple molecules like  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{HCl}$ ,  $\text{CO}_2$ , it is called a **condensation** reaction.

### Example

#### Aldol condensation reaction

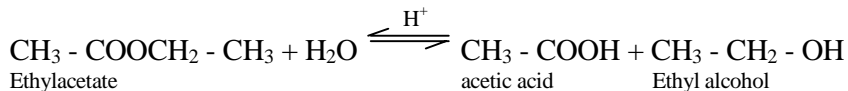


## Hydrolysis

Esters are hydrolysed by boiling with mineral acids or alkalis.

### a) Acid hydrolysis

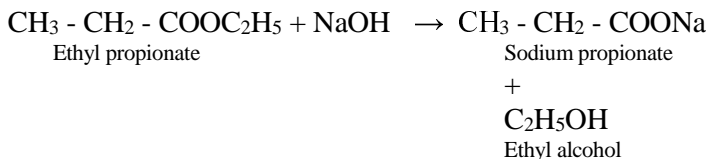
An ester can be hydrolysed to give the parent carboxylic acid and alcohol by using mineral acid ( $\text{H}_2\text{SO}_4$  or  $\text{HCl}$ ) as catalyst.



The above reaction is reversible and is exactly opposite of esterification. In order to hydrolyse most of the ester, the equilibrium must be pushed to the right by using large excess of water.

### b) Basic hydrolysis

When an ester is treated with an alkali ( $\text{NaOH}$  or  $\text{KOH}$ ) as catalyst, the hydrolysis yields the parent alcohol and sodium salt of the carboxylic acid.



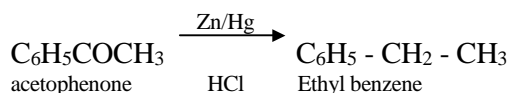
## Reduction and oxidation reactions

A reaction which proceeds by the addition of hydrogen is termed

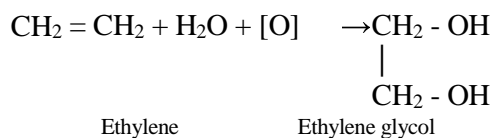
**Reduction** and the one that involves the addition of oxygen is called **Oxidation**. For example,

### 1) Clemmensen Reduction

Ketones can be reduced to their corresponding hydrocarbons by the mixture of Zn/Hg and conc. HCl.



2) Very mild oxidising agent such as  $\text{KMnO}_4$ , causes a splitting of the molecule at the double bond.



## 15.7.1 Types of Reagents

### Electrophilic reagents

These reagents are electron deficient. This deficiency accounts for their affinity for electrons (electro = electron, philic = loving). They are also called cationic reagents and may carry positive charge or have incomplete valence shells. These reagents can therefore, be of two types.

- (i) Positive electrophiles (or) Ionic electrophiles
- (ii) Neutral electrophiles

Some common electrophiles are given in the table

S. No.	Ionic electrophiles	Neutral electrophiles (Lewis acids)
1.	$\text{H}^+$ (proton)	$\text{AlCl}_3$
2.	$\text{Cl}^+$ (chloronium)	$\text{BF}_3$
3.	$\text{Br}^+$ (bromonium)	$\text{ZnCl}_2$
4.	$\text{NO}_2^+$ (Nitronium)	$\text{FeCl}_3$
5.	$>\text{C}^+$ carbonium	$\text{SO}_3$

### Nucleophilic reagents

Nucleophiles or nucleophilic reagents are electron rich substances containing atoms which have at least an unshared pair of electron. These reagents are nucleus loving (nucleo = nucleus, philic = loving). Nucleophiles can be (i) negatively charged (or) Ionic (ii) neutral species (Lewis bases). Some of the common nucleophiles are reported in table

S. No.	Neutral nucleophiles (Lewis bases)	Ionic nucleophiles
1.	NH <sub>3</sub>	X <sup>-</sup> (halide ions)
2.	H <sub>2</sub> O	OH <sup>-</sup> (hydroxide)
3.	R-OH	RO <sup>-</sup> (alkoxide)
4.	R-NH <sub>2</sub>	CN <sup>-</sup> (cyanide)
5.	R <sub>3</sub> -N	<C <sup>-</sup> (carbanion)

The differences between these reagents are summarised in the following table.

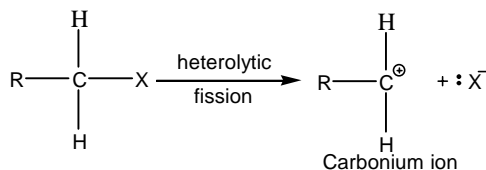
S. No.	Electrophiles	Nucleophiles
1.	are electron deficient	are electron rich
2.	are cations	are often anions
3.	are Lewis acids	are Lewis bases
4.	accept an electron pair	donate an electron pair
5.	attack on electron rich sites	attack on electron deficient sites
6.	possess an empty orbital to house the lone pair from the nucleophiles	possess a minimum of one lone pair of electron.

#### 15.7.2 Carbonium ions

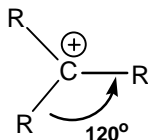
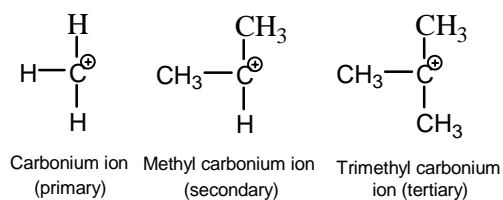
Let us consider the heterolytic fission of the bond C – X present in an organic molecule. If the atom X has greater electronegativity than the carbon atom, the former takes away the bonding electron pair and becomes negatively charged while the carbon will lose its electron and thus acquire a positive charge. Such cationic species carrying a positive charge on carbon

are known as carbonium ions.

For illustration



These carbonium ions are called primary, secondary and tertiary depending up on the nature of the carbon atom bearing the charge.



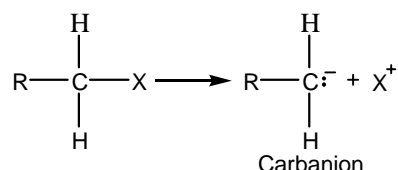
### The geometry of alkyl carbonium ion

Since the carbon of the carbonium ion is in  $sp^2$  hybridised state, the ion is planar with a vacant p orbital perpendicular to the plane of the three covalent bonds to carbon.

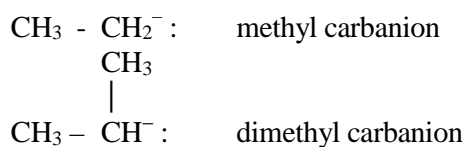
### Carbanion

Let us consider the heterolytic fission of the bond C - X present in an organic molecule. If the carbon atom has greater electronegativity than the atom X, the former takes away the bonding electron pair and acquires a negative charge. The resulting carbon anion is known as carbanion.

### For illustration



### Examples



## 15.8 Free Radicals

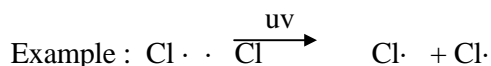
Free radicals are species with one or more unpaired electrons obtained by the homolytic fission of covalent bond. The free radicals themselves are electrically neutral. The free radicals are denoted by putting a dot against the atom or group of atoms.

*Few examples :*  $\text{Cl}\cdot$  ,  $\text{CH}_3\cdot$  ,  $\text{C}_6\text{H}_5\cdot$

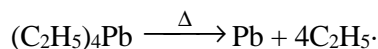
They are classified as short lived free radicals and long lived free radicals on the basis of their life time.

### Formation of free radicals

**(a) Photochemical fission :** When an organic compound is exposed to ultraviolet region it under goes bond fission.



**(b) Thermal fission :** All organic compounds on heating yield free radicals.



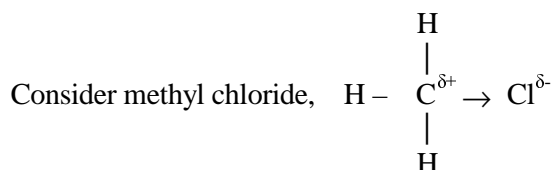
### Polar Effects

#### Inductive Effect

If a covalent bond is formed by two atoms differing much in electronegativity then the bond is said to be polarised. The electron pair

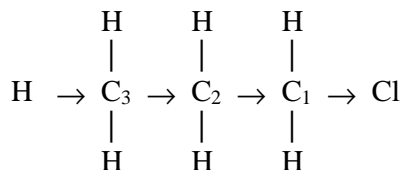


shifts towards the more electronegative atom resulting in the origin of fractional charges on the atoms.



In this molecule, chlorine atom is more electronegative than the carbon atom. Due to this, chlorine pulls the electron pair and acquires a small negative charge.

Let us consider, 1 - chloropropane



As  $\text{C}_1$  is positively charged, it attracts towards itself the electron pair shared between  $\text{C}_1$  and  $\text{C}_2$ . This causes  $\text{C}_2$  to acquire a small positive charge but the charge is smaller than the charge on  $\text{C}_1$ . This type of electron displacement occurring in saturated compounds along a carbon chain is termed, inductive effect.

It is a permanent effect and decreases rapidly as the distance from the electronegative atom increases. It is represented by  $\rightarrow$  the arrow head pointing towards the more electronegative atom. This effect operates in the case of  $\sigma$  - electrons only.

For measurements of relative inductive effect, atoms or groups having greater electron affinity than hydrogen are said to have - I effect. Similarly, atoms or groups having lesser electron affinity than hydrogen are said to have + I effect. Some of the atoms and groups arranged in the increasing order of inductive effect are given as

Groups having - I effect [electron - attracting].

-  $\text{C}_6\text{H}_5$ ,  $\text{OH}$ , -I, -Br, -Cl, -F

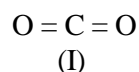
Groups having + I effect [electron pumping]

CH<sub>3</sub> -, CH<sub>3</sub> - CH<sub>2</sub> -, (CH<sub>3</sub>)<sub>2</sub>CH-, (CH<sub>3</sub>)<sub>3</sub>C -  
 (Methyl) (Ethyl) Isopropyl tertiarybutyl

### Resonance (Mesomeric) Effect

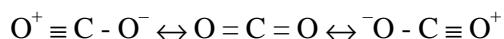
When several structures may be assumed to contribute to the true structure of a molecule but none of them can be said to represent it uniquely, then the molecule is referred to as a resonance hybrid and the phenomenon is termed as resonance.

It is somewhat abstract, but it can be better understood if we consider the structure of a simple molecule carbon dioxide.



The above structure does not account for all observed properties although it can explain many. The C-O bond length in CO<sub>2</sub> molecule is 1.15 Å where as it is expected to be 1.22 Å on the basis of the above structure.

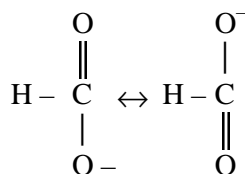
Again, the heat of formation of carbon dioxide is 1592 kJ.mol<sup>-1</sup> where as on the basis of the above structure it is expected to be approximately 1466 kJ.mol<sup>-1</sup>. These discrepancies can be explained only if we assume the following resonance hybrid for carbon dioxide.



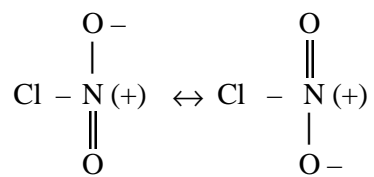
The difference in energy i.e. 126 KJ.mol<sup>-1</sup> is regarded as resonance energy.

Few other examples

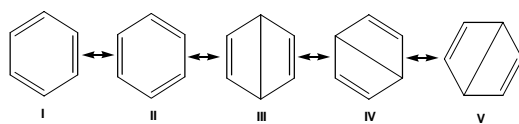
1. Formate ion, HCOO<sup>-</sup>



2. Nitryl chloride, NO<sub>2</sub>Cl



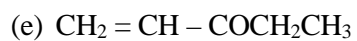
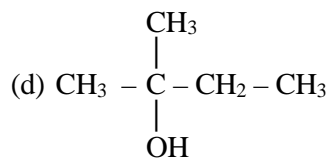
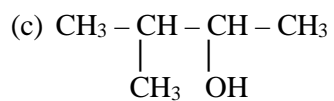
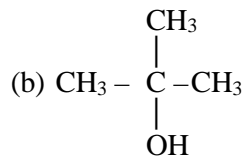
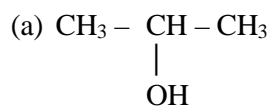
3.

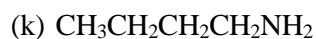
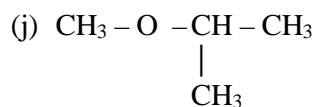
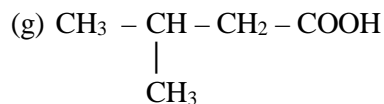


Benzene

### Questions

A. Write IUPAC name of the following





**B. Explain briefly on the following**

1. Homolytic and heterolytic fission.
2. Substitution reaction.
3. Addition reaction.
4. Elimination reaction.
5. Polymerisation reaction.
6. Condensation reaction.
7. Hydrolysis.
8. Reduction and oxidation reactions.
9. Electrophilic and Nucleophilic reagents.
10. Carbonium ions and carbanions.
11. Free radicals.
12. Inductive effect.
13. Resonance effect.

**SUMMARY**

- This chapter explains the ability of carbon atoms to form long chains held together by strong carbon-carbon bonds, catenation.
- Characteristics of homologous series and structural isomers are explained.

## 15. BASIC CONCEPTS OF ORGANIC CHEMISTRY

### OBJECTIVES

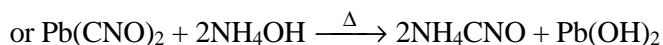
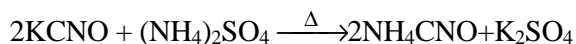
*This topic explains the nature of organic compounds and explores the possibilities of all basic concepts of organic chemistry.*

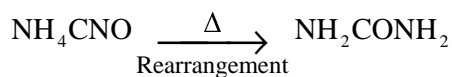
- *Catenation and the reason for innumerable number of organic compounds.*
- *Classification of organic compounds based on functional groups.*
- *IUPAC method of naming all types of organic compounds.*
- *Details about isomerism.*
- *Fission of bonds and types of organic reactions.*
- *Nature of reagents, electrophiles and Nucleophiles.*
- *Knowledge about carboniumion and carbanion and free radicals.*
- *Different types of electron displacements in organic chemistry.*

### Introduction

Initially (before 1828), the name organic chemistry was given for the chemistry of compounds obtained from plants and animals (i.e, from living organisms). The word organic signifies life. Lavoisier (who is considered as the father of chemistry) showed that the compounds obtained from plants are often made of C, H and O and the compounds obtained from animals contain C, H, O, N, S, P. .... etc.

Berzelius proposed vital force theory (a theory of life process) to deal with organic compounds. The vital force theory suffered blow in 1828 when Wohler synthesized the first organic compound urea in the laboratory from an inorganic compound, i.e, from ammonium cyanate ( $\text{NH}_4 \text{CNO}$ ).





Later on, a further blow to vital force theory was given by Kolbe (1845) who prepared acetic acid, the first organic compound, in laboratory from its elements.

Now a days organic chemistry is defined as **the chemistry of carbon compounds or the chemistry of hydrocarbons and their derivatives**. Organic compounds obey the same fundamental laws of chemistry as the inorganic compounds. However they are studied as a separate branch of chemistry because of two reasons:

- i. The total number of organic compounds known so far exceeds several times the total number of inorganic compounds known.
- ii. There are marked differences between the structure, composition and behaviour of organic and inorganic compounds. The phenomenon of **isomerism** and tendency of **catenation** are unique properties of organic compounds.

### 15.1 Catenation

1. The tendency of atoms of an element to unite with each other forming a chain of covalent bond is known as **catenation**.
2. Catenation may give rise to open chain or closed chain compounds.
3. Carbon possesses maximum tendency for catenation i.e. **Bond energy (kcal mol<sup>-1</sup>) for catenation of C is maximum.**

C-C,	Si-Si,	N-N,	P-P,	O-O,	S-S
85	54	39	50	35	54

4. Carbon also forms double as well as triple bonds.
5. A large number of compounds of carbon are known due to catenation.
6. The stability or strength of bond decreases as the bond energy decreases. Hence the catenation order among the following is C > Si ≈ S > P > N > O.

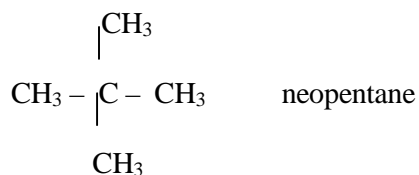
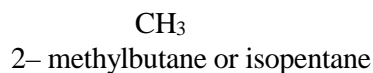
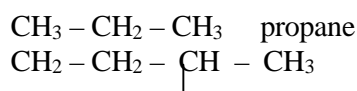
### 15.2 Classification into open chain and cyclic compounds

The organic compounds are classified into two main types, namely.

### (1) Open - chain or acyclic compounds or aliphatic compounds

The open chain or acyclic compounds are those in which carbon atoms are linked to each other either in linear or branched fashion such that the molecule is having open chain structure. These compounds are also called aliphatic compounds (Greek word : aliphar meaning fat).

Examples



### (2) Closed chain or cyclic compounds

Organic compounds with closed chain of atoms are called closed chain compounds or ring compounds.

These compounds are further classified into

- (a) Homocyclic or carbocyclic compounds
- (b) Heterocyclic compounds

**(a) Homocyclic compounds :** In these compounds the ring structure is made up of only carbon atoms.

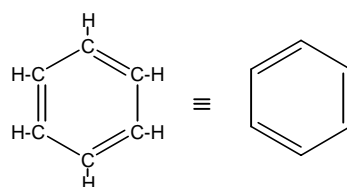
These compounds are further classified into

- (i) Aromatic compounds and
- (ii) Alicyclic compounds

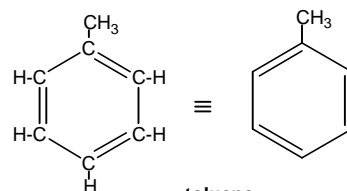
**(i) Aromatic compounds (Benzenoid) :** Compounds containing one or more benzene rings in their structure are classified as aromatic benzenoid compounds. Most of these compounds have pleasant odour (Greek : Aroma - sweet smell).

## Examples

### Monocyclic

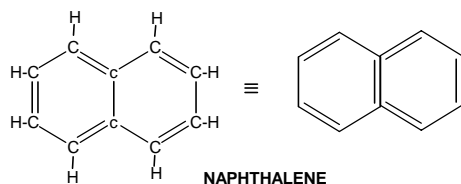


benzene

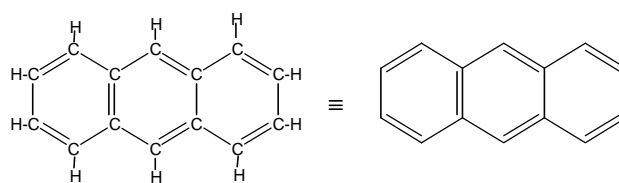


toluene

### Polycyclic



NAPHTHALENE

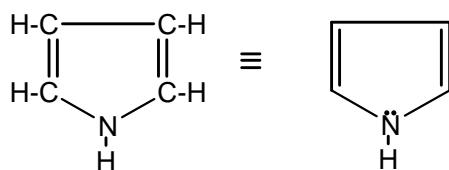


ANTHRACENE

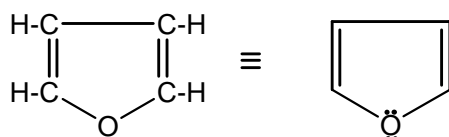
**Heterocyclic compounds** (Non - benzenoid aromatic) : Cyclic compounds in which the ring atoms are made up of hetero atoms like nitrogen, oxygen and sulphur in addition to carbon atoms are called heterocyclic compounds.



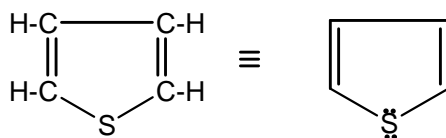
### Examples



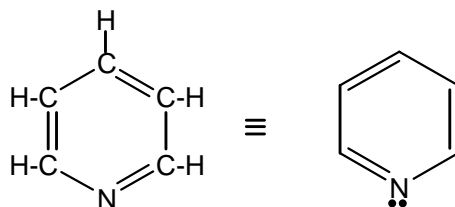
**pyrrole**



**furan**



**thiophene**

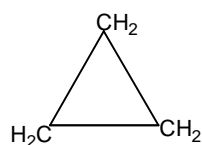


**pyridine**

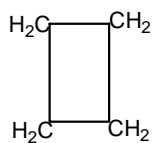
The above compounds are aromatic non-benzenoid compounds.

- (ii) **Alicyclic compounds** : Cyclic compounds with ring structure containing only carbon atoms are called alicyclic or carbocyclic compounds. Though these compounds possess a ring structure, they behave more like aliphatic compounds.

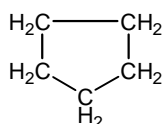
## Examples



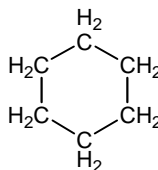
**cyclopropane**



**cyclobutane**

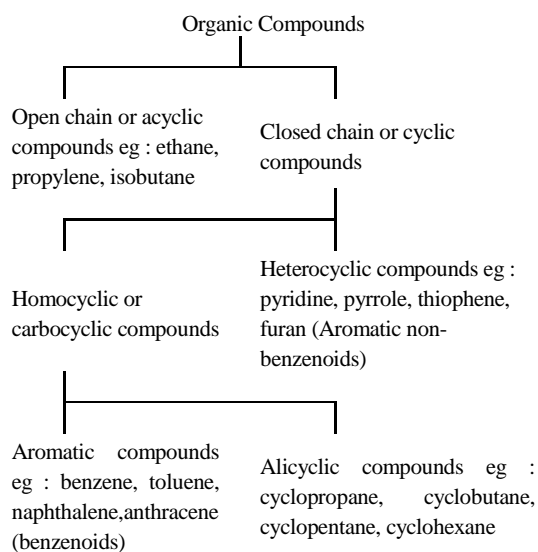


**cyclopentane**



**cyclohexane**

The above classification can be schematically represented as follows :



## Characteristics of organic compounds

All organic compounds have the following characteristic properties

- (1) Many organic compounds are inflammable
- (2) They are mostly covalent compounds

- (3) They are generally soluble in non - polar solvents like carbon tetrachloride, benzene etc.
- (4) They have generally low boiling point and melting point.
- (5) They exhibit isomerism

### **Homologous series**

A group or class of organic compounds related to each other by a general molecular formula constitutes homologous series.

### **Characteristics of homologous series**

Homologous series have the following characteristics :

- (1) All members of a series contain same elements and the same functional groups.
- (2) All the members of a homologous series can be represented by a general formula

### **Examples**

Alkanes	$C_nH_{2n+2}$
Alkenes	$C_nH_{2n}$
Alkynes	$C_nH_{2n-2}$

- (3) All the members of a homologous series can be prepared by similar methods.
- (4) All members of a homologous series usually undergo similar chemical reactions.
- (5) Successive members in a series differ by a  $-CH_2$  group
- (6) The physical properties of the members of a homologous series vary in a regular way down the series. For example, boiling point, melting point and density of the alkane series vary in a regular way with increasing number of carbon atoms.

### **15.3 Functional groups**

The chemical properties of all the members of a homologous series are characterised by a group called the functional group. It is characteristic of a particular series.

The following table gives a list of functional groups and names.

Halide	$-X$
Alcohol	$-OH$
Ether	$-O-$

Aldehyde	- CHO
Ketone	$\begin{array}{c} \text{---C---} \\    \\ \text{O} \end{array}$
Carboxylic acid	- COOH
Ester	- COOR
Amide	$\begin{array}{c} \text{---C---NH}_2 \\    \\ \text{O} \end{array}$
Acid halide	$\begin{array}{c} \text{---C---X} \\    \\ \text{O} \end{array}$ (X = -Cl, -Br, -I)
Acid anhydride	$\begin{array}{c} \text{---C---O---C---} \\    \qquad \qquad    \\ \text{O} \qquad \qquad \text{O} \end{array}$
Amine	- NH <sub>2</sub>
Nitro compounds	- NO <sub>2</sub>

#### 15.4 IUPAC system of nomenclature (1993)

The international union of pure and applied chemistry (abbreviated as IUPAC) has done a commendable job in framing set rules for naming organic compounds. Two commonly used systems of nomenclature are described below.

- (1) Common or Trivial system      (2) IUPAC system

#### IUPAC Nomenclature of Aliphatic Compounds

The IUPAC name of a compound essentially consists of three parts.

- (a) Root word   (b) Suffix   (c) Prefix

#### Root words for alkanes

The root words for the first four members are taken from their trivial or common names.

e.g.

Meth	-	for Methane
Eth	-	for Ethane
Prop	-	for Propane
But	-	for Butane

For the higher homologue, root words are derived from the Greek/Latin number indicating the total number of carbon atoms.

- e.g. Pent - is derived from penta for five  
 Hex - is derived from hexa for six  
 Hept - is derived from hepta for seven  
 Oct - is derived from octa for eight

### Suffix

There are two types of suffixes **Primary suffix** and secondary suffix.

### Primary suffix

A primary suffix is added to the **Root word** to indicate whether the parent chain is saturated or unsaturated. Some primary suffixes are given below.

Sl. No.	Nature of carbon chain (parent chain)	Primary suffix
1.	Saturated	ane
2.	Unsaturated with One double bond Two double bond Three double bond	ene diene triene
3.	Unsaturated with One triple bond Two triple bond	yne diyne

Sl. No.	Structural formula	No. of C atoms	Root word	Primary suffix	IUPAC name
1.	$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_3$	4	But	ane	Butane
2.	$\text{CH}_3\text{-CH=CH}_2$	3	Prop	ene	Propene
3.	$\text{CH}\equiv\text{CH}$	2	Eth	yne	Ethyne
4.	$\text{CH}_2\text{=CH-CH=CH}_2$	4	Buta <sup>*</sup>	diene	Butadiene
5.	$\text{HC}\equiv\text{C-C}\equiv\text{CH}$	4	Buta <sup>*</sup>	diyne	Butadiyne

\* extra 'a' has been added to the root word since the primary suffix, ie diene or diyne begins with a consonant (d).

### Secondary suffix

Secondary suffix is used to indicate the functional group in the organic compound secondary suffixes for various functional groups are given below.

Sl. No.	Class	Functional group	Secondary suffix	IUPAC name
1.	Alcohols (R-OH)	-OH	-ol	Alkanols
2.	Aldehyde (R-CHO)	-CHO	-al	Alkanals
3.	Ketones (RCOR')	$>C=O$	-one	Alkanones
4.	Carboxylic acids (R-COOH)	-COOH	-oic acid	Alkanoic acid
5.	Ester (RCOOR')	-COOR	-alkanoate	alkyl alkanoates

Secondary suffix is added to the primary suffix; ie written after the primary suffix. While adding the secondary suffix to the primary suffix following rules should be followed.

- If the secondary suffix begins with a vowel, then the terminal **e** of the primary suffix is dropped before adding the secondary suffix.
- If the secondary suffix begins with a consonant, then the last (terminal) **e** is retained and the secondary suffix is added after e.
- If the secondary suffix has some **numerical prefix**, such as, **di, tri etc.**, before it then the terminal **e** of the primary suffix is retained.

The addition of the secondary suffix to the primary suffix is illustrated below

Sl. No.	Structural formula	No. of C atoms	Root word	Primary suffix	Secondary suffix	IUPAC name	Remarks
1.	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_2\text{-OH} \end{array}$	2	Eth	ane	ol	Ethanol	'e' of prim suffix dropped

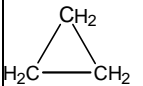
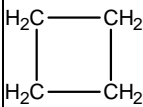
2.	$\begin{array}{c} \text{CH}_2\text{-OH} \\   \\ \text{CH}_2\text{-OH} \end{array}$	2	Eth	ane	diol	Ethane diol	'e' of prim suffix not dropped
3.	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_2 \\   \\ \text{CHO} \end{array}$	3	Prop	ane	al	Propanal	'e' of the prim suffix dropped
4.	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_2 \\   \\ \text{CH}_2 \\   \\ \text{COOH} \end{array}$	4	But	ane	oic acid	Butanoic acid	'e' of prim suffix dropped

### Prefix

Prefix is a part of the name which appears before the root word. There are two types of prefixes - primary prefix and secondary prefix.

#### Primary prefix

A primary prefix is used to distinguish alicyclic (aliphatic cyclic compounds) from acyclic (open chain) compounds. If the given compound is an alicyclic compound, then a prefix cyclo is used just before the root word. For example.

Structural formula	No. of C atoms	Root word	Primary suffix	Primary prefix	IUPAC name
	3	Prop	ane	Cyclo	Cyclo propane
	4	But	ane	Cyclo	Cyclo butane

### Secondary prefix

In the IUPAC system of nomenclature, certain characteristic groups are not considered as functional groups. Such characteristic groups are considered as the **substituents**. Each such group or substituent is denoted by a secondary prefix. Some typical secondary prefixes are listed below.

Substituent group	Secondary prefix
- F	Fluoro
- Cl	Chloro
- Br	Bromo
- I	Iodo
- CH <sub>3</sub>	Methyl
- C <sub>2</sub> H <sub>5</sub>	Ethyl
CH <sub>3</sub> - CH <sub>2</sub> - CH <sub>2</sub> -	n-propyl
(CH <sub>3</sub> ) <sub>2</sub> CH -	Iso propyl
(CH <sub>3</sub> ) <sub>3</sub> C -	t - Butyl
- NO <sub>2</sub>	Nitro
- NH <sub>2</sub>	Amino
- NO	Nitroso
N $\equiv$ N	Diazo
- OCH <sub>3</sub>	Methoxy
- OC <sub>2</sub> H <sub>5</sub>	Ethoxy

In the case of open chain compounds, the secondary prefix is added just before the root word in the **alphabetical** order. This is illustrated below.

Sl. No.	Structural formula	No. of C atoms	Root word	Suffix		Prefix		IUPAC Name
				Primary	Sec	Pri	Sec	
1.	CH <sub>3</sub> -CH <sub>2</sub> -Cl	2	Eth	ane	-	-	Chloro	Chloro ethane
2.	CH <sub>3</sub> -NO <sub>2</sub>	1	Meth	ane	-	-	Nitro	Nitro methane



### Saturated Hydrocarbons : Alkanes

**General formula :**  $C_nH_{2n+2}$       **Suffix :** ane

Sl. No.	Structural formula	Common Name	IUPAC name
1.	CH <sub>4</sub>	Methane	Methane
2.	H <sub>3</sub> C - CH <sub>3</sub>	Ethane	Ethane
3.	H <sub>3</sub> C - CH <sub>2</sub> - CH <sub>3</sub>	Propane	Propane
4.	H <sub>3</sub> C - CH <sub>2</sub> - CH <sub>2</sub> - CH <sub>3</sub>	n-butane	Butane

### Alkyl groups

The univalent hydrocarbon unit derived from an alkane by the loss of one hydrogen atom is termed as alkyl group.

The alkyl groups are named after their parent alkanes by replacing the suffix-**ane** by- **yl**.

### Continuous straight chain alkyl groups (or, normal alkyl (n-) groups)

Sl. No.	Alkane		Alkyl group	
	Formula	Name	Formula	Name
1.	CH <sub>4</sub>	Methane	CH <sub>3</sub> -	Methyl
2.	CH <sub>3</sub> - CH <sub>3</sub>	Ethane	CH <sub>3</sub> - CH <sub>2</sub> -	Ethyl
3.	CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>3</sub>	Propane	CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -	Propyl

### Branched chain alkyl groups

When a hydrogen atom from a secondary or tertiary carbon atom in any carbon chain is removed, a branched chain alkyl group is obtained. The common prefixes used are,

a) iso - b) sec - c) tert - d) neo –

a) **iso** – The alkyl group in which a - CH<sub>3</sub> branch is present at the end of the chain is designated as isoalkyl group. In other words, the alkyl group in which the second last carbon atom in the chain is branched to one - CH<sub>3</sub> group is called on isoalkyl group.

Sl.No.	Structure	IUPAC name
1.	$\begin{array}{c} \text{CH}_3 - \text{CH} - \\   \\ \text{CH}_3 \end{array}$	1-methyl ethyl (iso-propyl)
2.	$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 - \\   \\ \text{CH}_3 \end{array}$	2-methyl propyl (iso-butyl)
3.	$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_2 - \\   \\ \text{CH}_3 \end{array}$	3-methyl butyl (iso-pentyl)

**b) Sec -** The prefix sec - before the name of the alkyl group indicates that the H-atom was removed from a secondary carbon atom.

Sl.No.	Structure	IUPAC name
1.	$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_3 \\   \\ \text{CH}_3 \end{array}$	1 - Methyl ethyl (Sec - propyl)
2.	$\begin{array}{c} \text{CH}_3 - \text{CH}_2 - \text{CH} - \\   \\ \text{CH}_3 \end{array}$	1 - methyl propyl (Sec - butyl)
3.	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH} - \end{array}$	1 - methyl butyl (Sec - pentyl)

**c) Tert - (or) t -**

The prefix tert - before the name of the alkyl group indicates that the H - atom has been removed from a tertiary carbon atom.

Sl. No.	Structure	IUPAC name
1.	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3 - \text{C} - \\   \\ \text{CH}_3 \end{array}$	1,1 - dimethyl ethyl (tert - butyl)
2.	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3 - \text{CH}_2 - \text{C} - \\   \\ \text{CH}_3 \end{array}$	1,1 - dimethyl propyl (tert - pentyl)

## Alkenes

**General formula :**  $C_nH_{2n}$  **Suffix : ene**

The common name of alkene is obtained by replacing the ending - **ane** from the name of its parent alkane with - **ylene**.

The IUPAC name of an alkene is obtained by replacing - **ane** of the alkane by - **ene**.

Structural formula	Common Name	IUPAC name
$CH_2 = CH_2$	Ethylene	Ethene
$CH_3 - CH = CH_2$	Propylene	Propene
$CH_3-CH_2-CH=CH_2$ (double bond starts at $C_1$ )	1- Butylene	But-1-ene
$CH_3-CH=CH-CH_3$ (double bond starts at $C_2$ )	2- Butylene	But-2-ene

## Alkenyl group

The group obtained by removing a hydrogen atom from an alkene molecule, are called **alkenyl** group.

The IUPAC name of alkenyl group is obtained by replacing - **e** of the alkene by the suffix - **yl**.

Sl. No.	Structure	Common name	IUPAC name
1.	$CH_2 = CH_2$	vinyl	ethenyl
2.	$CH_2=CH-CH_2-$	allyl	Prop - 2 - enyl

## Alkynes

**General formula :**  $C_nH_{2n-2}$  **Suffix : - yne**

The IUPAC name of an alkyne is obtained by replacing the ending - **ane** from the name of the parent alkane with - **yne**.

Sl. No.	Structural formula	Common Name	IUPAC name
1.	$\text{HC} \equiv \text{CH}$	Acetylene	Ethyne
2.	$\text{CH}_3 - \text{C} \equiv \text{CH}$	Methyl acetylene	Propyne
3.	$\text{CH}_3 - \text{C} \equiv \text{C} - \text{CH}_3$	Dimethyl acetylene	But-2-yne

### Alkyl halides

The general formula of alkyl halides is  $\text{R-X}$  where R stands for alkyl group and "X" stands for halogen (F, Cl, Br, I). They are named by introducing the prefix halo (chloro, bromo, iodo, fluoro) to the name of the parent alkane.

Formula	Common name	IUPAC name
$\text{CH}_3\text{-Cl}$	Methyl chloride	Chloromethane
$\text{CH}_3\text{-CH}_2\text{-Br}$	Ethyl bromide	Bromoethane
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-Br}$	n-propyl bromide	1-bromopropane
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_3 \\   \\ \text{I} \end{array}$	Iso-propyl iodide	2-iodopropane
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-Cl}$	n-butyl chloride	1-chlorobutane
$\begin{array}{c} \text{CH}_3\text{-CH}_2\text{-CH-CH}_3 \\   \\ \text{Br} \end{array}$	Sec-butyl bromide	2-bromobutane
$\begin{array}{c} \text{CH}_3\text{-CH-CH}_2\text{-Cl} \\   \\ \text{CH}_3 \end{array}$	Isobutyl chloride	1-chloro-2-methyl propane
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3 - \text{C} - \text{I} \\   \\ \text{CH}_3 \end{array}$	ter-butyl iodide	2-iodo-2-methyl propane
$\text{CH}_2=\text{CH-Cl}$	Vinyl chloride	Chloroethene
$\text{CH}_2=\text{CH-CH}_2\text{-Cl}$	Allyl chloride	3-Chloro-1-propene

## Alcohols

The term alcohol is applied to all organic compounds obtained by replacing one or more hydrogen atoms of an open-chain hydrocarbon by hydroxyl groups. The alcohols are further classified into **mono-**, **di-**, **tri-**hydric alcohols according to the number of hydroxyl groups which they may contain.

In IUPAC nomenclature, the terminal "e" of the alkane is replaced by "ol".

### Monohydric alcohols

Alcohols which contain only one hydroxyl group per molecule are called monohydric alcohols.

Formula	Common name	IUPAC name
CH <sub>3</sub> -OH	Methyl alcohol	methanol
CH <sub>3</sub> -CH <sub>2</sub> -OH	Ethyl alcohol	ethanol
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -OH	n-propyl alcohol	1-propanol
CH <sub>3</sub> -CH - CH <sub>3</sub>   OH	Isopropyl alcohol	2-propanol
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -OH	n-butyl alcohol	1-butanol
CH <sub>3</sub> - CH <sub>2</sub> -CH - CH <sub>3</sub>   OH	sec-butyl alcohol	2-butanol
CH <sub>3</sub> -CH - CH <sub>2</sub> - OH   CH <sub>3</sub>	Isobutyl alcohol	2-methyl-1-propanol
CH <sub>3</sub> - C - OH   CH <sub>3</sub>	tert-butyl alcohol	2-methyl-2-propanol
CH <sub>2</sub> =CH-CH <sub>2</sub> -OH	Allyl alcohol	2-propene-1-ol

### Dihydric alcohols

Alcohols which contain two -OH groups per molecule are called dihydric alcohols.

Structural formula	Common name	IUPAC name
$\begin{array}{c} \text{CH}_2\text{-OH} \\   \\ \text{CH}_2\text{-OH} \end{array}$	Ethylene glycol	1,2-Ethanediol

### Trihydric alcohols

Alcohols which contain three -OH groups per molecule are called trihydric alcohols.

Structural formula	Common name	IUPAC name
$\begin{array}{c} \text{CH}_2\text{ - OH} \\   \\ \text{CH - OH} \\   \\ \text{CH}_2\text{ - OH} \end{array}$	Glycerol	1,2,3-propanetriol

### Ethers

An ether is a substance that has two organic groups bonded to the same oxygen atom, **R-O-R'**. The organic group may be alkyl or aryl. When the groups attached to the oxygen atom are the same, they are termed as simple ethers. When the groups attached to the oxygen atom are different, they are termed as mixed ethers.

In IUPAC system, ethers are considered to be alkoxy derivatives of hydrocarbons.

Structural formula	Common name	IUPAC name
<b>Simple ethers</b>		
$\text{CH}_3\text{-O-CH}_3$	Dimethyl ether	Methoxymethane
$\text{CH}_3\text{-CH}_2\text{-O-CH}_2\text{-CH}_3$	Diethyl ether	Ethoxyethane
<b>Mixed ethers</b>		
$\text{CH}_3\text{-O-CH}_2\text{-CH}_3$	Ethyl methyl ether	Methoxyethane
$\text{CH}_3\text{-O-CH}_2\text{-CH}_2\text{-CH}_3$	Methyl n-propyl ether	1-methoxypropane
$\begin{array}{c} \text{CH}_3\text{ - O - CH - CH}_3 \\   \\ \text{CH}_3 \end{array}$	Isopropyl methyl ether	2-methoxypropane

## Aldehydes

Aldehydes and ketones are two important classes of compounds containing the carbonyl group  $\text{—}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\text{—}$ . In aldehydes the  $\text{—}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\text{—}$  group is

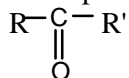
linked to an alkyl group and a hydrogen or two hydrogens. Aldehydes are represented by the general formula  $\text{R-CHO}$ .

IUPAC names of aldehydes are obtained by replacing the terminal "e" of alkane with "al".

Structural formula	Common name	IUPAC name
$\text{H-CHO}$	Formaldehyde	Methanal
$\text{CH}_3\text{-CHO}$	Acetaldehyde	Ethanal
$\text{CH}_3\text{-CH}_2\text{-CHO}$	Propionaldehyde	Propanal
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CHO}$	Butyraldehyde	1-Butanal
$\begin{array}{c} \text{CH}_3\text{-CH-CHO} \\   \\ \text{CH}_3 \end{array}$	Isobutyraldehyde	2-Methylpropanal

## Ketones

In ketones  $\text{—}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\text{—}$  group is united with 2 alkyl groups. These compounds are represented by the general formula.



Ketones are named by replacing the terminal "e" of the corresponding alkane name with "one".

Structural formula	Common name	IUPAC name
$\begin{array}{c} \text{CH}_3-\overset{\text{O}}{\underset{\text{  }}{\text{C}}}-\text{CH}_3 \end{array}$	Acetone (Dimethyl ketone)	Propanone
$\text{CH}_3\text{-CH}_2-\overset{\text{O}}{\underset{\text{  }}{\text{C}}}-\text{CH}_3$	Ethylmethyl ketone	Butanone
$\text{CH}_3\text{-CH}_2-\overset{\text{O}}{\underset{\text{  }}{\text{C}}}-\text{CH}_2\text{-CH}_3$	Diethyl ketone	3-pentanone

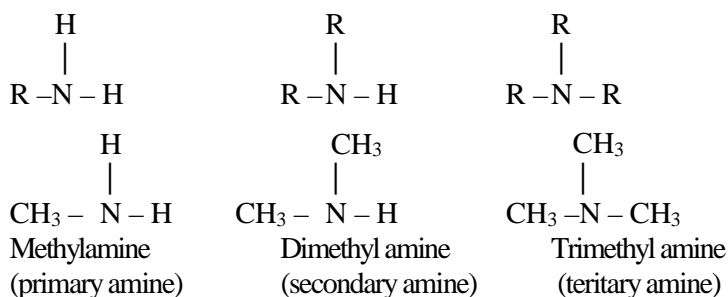
## Carboxylic acids

These are represented by the general formula  $R\text{-COOH}$ . IUPAC name is derived by replacing the terminal "e" of the alkane name with "**oic acid**". These compounds are further classified into **mono-** and **di-**carboxylic acids.

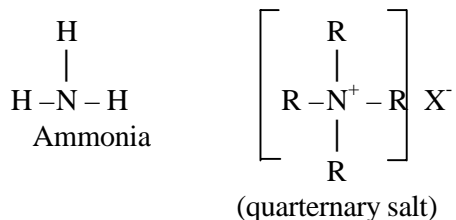
Structural formula	Common name	IUPAC name
<b>Monocarboxylic acids</b>		
$\text{H-COOH}$	Formic acid	Methanoic acid
$\text{CH}_3\text{-COOH}$	Acetic acid	Ethanoic acid
$\text{CH}_3\text{-CH}_2\text{-COOH}$	Propionic acid	Propanoic acid
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-COOH}$	Butyric acid	Butanoic acid
<b>Dicarboxylic acids</b>		
$\begin{array}{c} \text{COOH} \\   \\ \text{COOH} \end{array}$	Oxalic acid	Ethanedioic acid
$\begin{array}{c} \text{COOH} \\ / \quad \backslash \\ \text{CH}_2 \\ \backslash \quad / \\ \text{COOH} \end{array}$	Malonic acid	Propanedioic acid
$\begin{array}{c} \text{CH}_2\text{-COOH} \\   \\ \text{CH}_2\text{-COOH} \end{array}$	Succinic acid	Butanedioic acid

## Amines

Amines are the derivatives of ammonia in which one or more H-atoms have been replaced by alkyl groups. They are designated as primary, secondary and tertiary amines according as one, two or three hydrogen atoms in ammonia molecule have been replaced by alkyl groups.







When one alkyl group is attached to N-atom, it is called primary amine, when two alkyl groups are attached to nitrogen atom, then it is called secondary amine. When three alkyl groups are attached to nitrogen atom it is called tertiary amine. When four alkyl groups are attached to nitrogen atom it is called quarternary salt.

Structural formula	Common	IUPAC name
<b>Primary Amines</b>		
$\text{CH}_3\text{-NH}_2$	Methyl amine	aminomethane
$\text{CH}_3\text{-CH}_2\text{-NH}_2$	Ethyl amine	aminoethane
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-NH}_2$	n-propyl amine	1-aminopropane
$  \begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_3 \\   \\ \text{NH}_2 \end{array}  $	Isopropyl amine	2-aminopropane
<b>Secondary Amines</b>		
$\text{CH}_3\text{-NH-CH}_3$	Dimethyl amine	(N-methylamino) methane
$\text{CH}_3\text{-CH}_2\text{-NH-CH}_2\text{-CH}_3$	Diethyl amine	(N-ethylamino) ethane
$\text{CH}_3\text{-NH-CH}_2\text{-CH}_3$	Ethylmethyl amine	(N-methylamino) ethane

Structural formula	Common name	IUPAC name
<b>Tertiary Amines</b>		
$  \begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3 - \text{N} \\   \\ \text{CH}_3 \end{array}  $	Trimethyl amine	(N,N - dimethyl amino) methane
$  \begin{array}{c} \text{CH}_3 \\   \\ \text{C}_2\text{H}_5 - \text{N} \\   \\ \text{CH}_3 \end{array}  $	Ethyldimethyl amine	(N,N - dimethyl amino) ethane

## Nitro compounds

These compounds are represented by the general formula  $RNO_2$ . IUPAC names are obtained by adding the prefix "**nitro**" to the alkane.

Structural formula	Common/IUPAC name
1. $CH_3 - NO_2$	Nitromethane
2. $CH_3 - CH_2 - NO_2$	Nitroethane
3. $CH_3 - CH_2 - CH_2 - NO_2$	1-Nitropropane
4. $\begin{array}{c} CH_3 - CH - CH_3 \\   \\ NO_2 \end{array}$	2-Nitropropane

## 15.5 Isomerism

The molecular formula of an organic compound represents only the number of different atoms present in a molecule. But the molecular formula does not tell about the arrangement of atoms. A given molecular formula may lead to more than one arrangement of atoms such that there are many compounds which may have same molecular formula but with different physical and chemical properties. This phenomenon in which the same molecular formula may exhibit different structural arrangement is called isomerism.

Compounds that have the same molecular formula but different structural formulae are called isomers (from the Greek word isos + meros, "made of the same parts").

There are two types of isomerism, namely,

1. Structural isomerism
2. Stereoisomerism

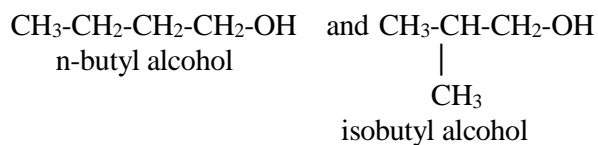
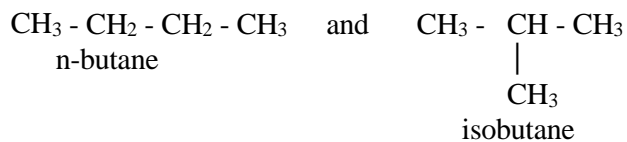
### Structural isomerism

When two or more compounds possess the same molecular formula but different structural formulae, they are said to exhibit structural isomerism. Structural isomerism is divided into.

#### 1. Chain isomerism or Nuclear isomerism

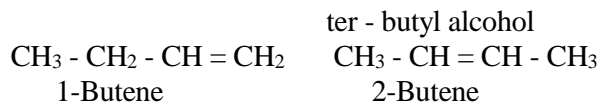
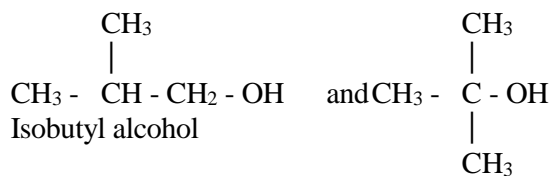
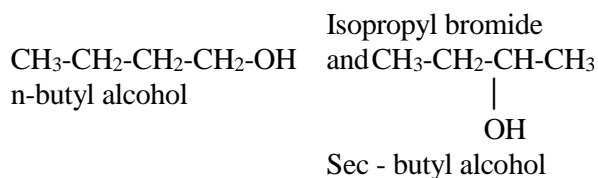
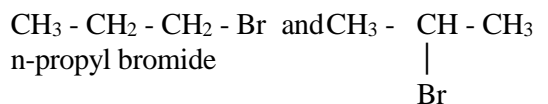
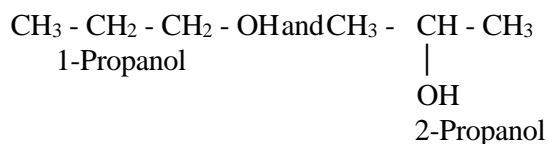
Chain isomers are compounds that have the same molecular formula but have different carbon skeletons.

## Examples



## 2. Position Isomerism

Position isomers are compounds that have the same formula, carbon skeleton and functional groups but have the functional groups located at different positions along the carbon skeleton.



## Functional isomerism

Functional isomers are compounds that have the same molecular formula but have different functional groups.

### Examples

- $\text{CH}_3 - \text{CH}_2 - \text{OH}$  and  $\text{CH}_3 - \text{O} - \text{CH}_3$   
Ethyl alcohol                  Dimethyl ether
- $\text{CH}_3 - \underset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{CH}_3$  and  $\text{CH}_3 - \text{CH}_2 - \text{CHO}$   
Acetone                  Propionaldehyde
- $\text{CH}_3 - \text{CH}_2 - \text{COOH}$  and  $\text{CH}_3 - \text{COO} - \text{CH}_3$   
Propionic acid                  Methyl acetate

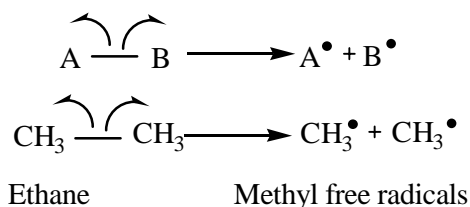
## 15.6 Fission of bonds

### How bond fission occurs?

A covalent bond ( $\sigma$  bond) joining two atoms exist because of the shared pair of electrons. When two atoms are separated from each other, bond fission is said to have taken place. The fission process can take place in two ways.

### Homolytic fission

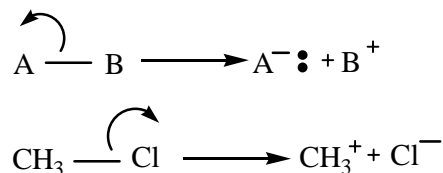
A covalent bond between two atoms A and B may be shown as  $\text{A} \cdot \cdot \text{B}$  or  $\text{A}-\text{B}$ . This bond may undergo fission in such a way that each atom retains the electrons of the shared pair. Such species are known as **free radicals** or odd electron molecules.



### Heterolytic fission

A covalent bond breaks in such a way that the shared pair of electron

stay on any one of the atoms. Breaking of the bond in this manner is known as heterolytic fission or heterolysis.



The atom or group which carries the unshared pair of electrons are represented with a negative sign as  $\text{A}^-$  is known as anions. The carbonium ion carries the positive charge which lacks a pair of electrons. Heterolysis occurs only when the initially bonded atoms are of different electronegativities and in that the electron pair becomes attached to the more electronegative atom.

An organic reaction may be represented as :

Reactants + attacking agent  $\rightarrow$  [intermediate]  $\rightarrow$  product

Depending upon the nature of the reaction which the intermediate species undergo, the reactions of the organic compounds are classified as substitution reactions, addition reactions, elimination reactions, polymerisation reactions, condensation reaction, hydrolysis, oxidation and reduction reactions.

## 15.7 Types of Reactions

### Substitution or Displacement reactions

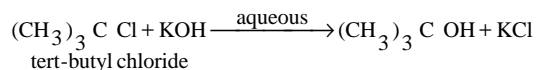
Displacement reaction is one in which an atom or group linked to a carbon atom is removed and in its place another atom or group is attached.

The substitution reactions are classified into three types.

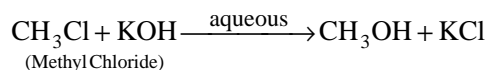
#### a) Nucleophilic substitution reaction ( $\text{S}_\text{N}$ )

When a substitution reaction is brought about by a nucleophile, the reaction is termed as  $\text{S}_\text{N}$  (S stands for substitution and N for nucleophile). These reactions are divided into two classes :

(1)  $\text{S}_\text{N}^1$  (substitution, nucleophilic, unimolecular)



(2)  $S_N^2$  (Substitution, nucleophilic, bimolecular)

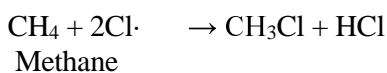
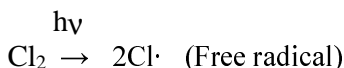


**b) Electrophilic substitution reaction ( $S_E$ )**

When a substitution reaction involves an attack by an electrophile, the reaction is referred to as  $S_E$  (S - stands for substitution and E for electrophile).

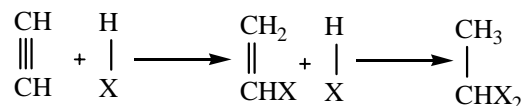
**c) Free radicals substitution reaction**

These reactions are initiated by free radicals.



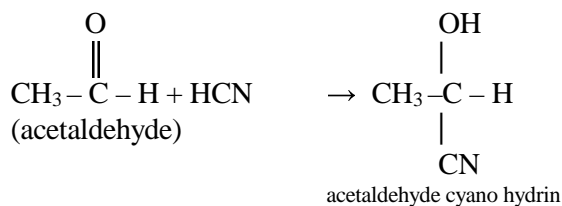
**Addition Reactions**

All organic compounds having double or triple bond adopt addition reactions in which two substances unite to form a single compound.

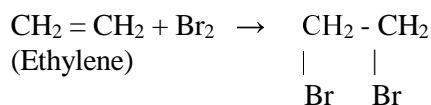


Depending on the type of reagent initiating these reactions, addition reactions are classified into three types.

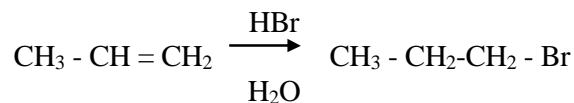
**(a) Nucleophilic addition**



**(b) Electrophilic addition**



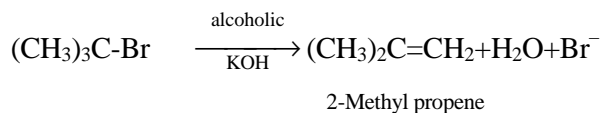
### (c) Free radical addition



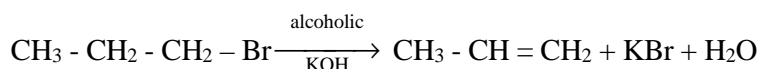
## Elimination reactions

In these reactions, two atoms or groups are removed from a molecule without being substituted by other atoms (or) groups. The reverse of addition reactions are eliminations. These reactions are classified into two types.

### (a) Unimolecular elimination ( $E_1$ )



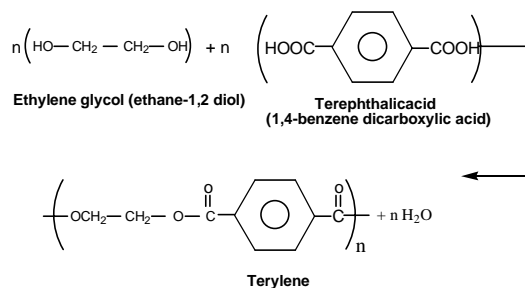
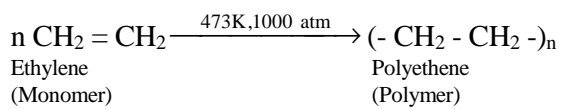
**(b) Bimolecular elimination (E<sub>2</sub>)**



## Polymerisation

The union of two or more molecules to form a large single molecule is called **polymerisation** and the product is a polymer.

## Examples

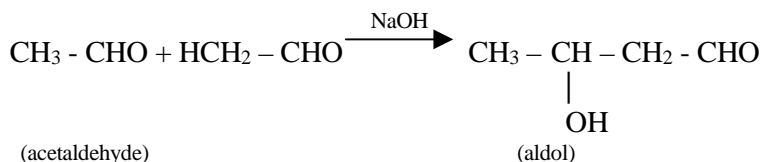


## Condensation reactions

When two molecules (similar or different) combine to form a single molecule with or without the elimination of simple molecules like  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{HCl}$ ,  $\text{CO}_2$ , it is called a **condensation** reaction.

### Example

#### Aldol condensation reaction

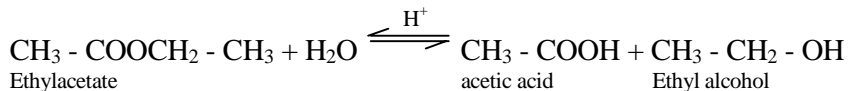


## Hydrolysis

Esters are hydrolysed by boiling with mineral acids or alkalis.

### a) Acid hydrolysis

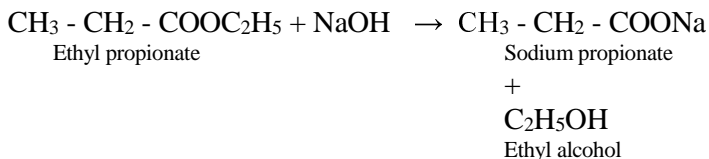
An ester can be hydrolysed to give the parent carboxylic acid and alcohol by using mineral acid ( $\text{H}_2\text{SO}_4$  or  $\text{HCl}$ ) as catalyst.



The above reaction is reversible and is exactly opposite of esterification. In order to hydrolyse most of the ester, the equilibrium must be pushed to the right by using large excess of water.

### b) Basic hydrolysis

When an ester is treated with an alkali ( $\text{NaOH}$  or  $\text{KOH}$ ) as catalyst, the hydrolysis yields the parent alcohol and sodium salt of the carboxylic acid.



## Reduction and oxidation reactions

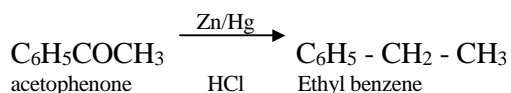
A reaction which proceeds by the addition of hydrogen is termed



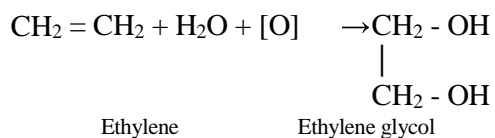
**Reduction** and the one that involves the addition of oxygen is called **Oxidation**. For example,

### 1) Clemmensen Reduction

Ketones can be reduced to their corresponding hydrocarbons by the mixture of Zn/Hg and conc. HCl.



2) Very mild oxidising agent such as  $\text{KMnO}_4$ , causes a splitting of the molecule at the double bond.



## 15.7.1 Types of Reagents

### Electrophilic reagents

These reagents are electron deficient. This deficiency accounts for their affinity for electrons (electro = electron, philic = loving). They are also called cationic reagents and may carry positive charge or have incomplete valence shells. These reagents can therefore, be of two types.

- (i) Positive electrophiles (or) Ionic electrophiles
- (ii) Neutral electrophiles

Some common electrophiles are given in the table

S. No.	Ionic electrophiles	Neutral electrophiles (Lewis acids)
1.	$\text{H}^+$ (proton)	$\text{AlCl}_3$
2.	$\text{Cl}^+$ (chloronium)	$\text{BF}_3$
3.	$\text{Br}^+$ (bromonium)	$\text{ZnCl}_2$
4.	$\text{NO}_2^+$ (Nitronium)	$\text{FeCl}_3$
5.	$>\text{C}^+$ carbonium	$\text{SO}_3$

### Nucleophilic reagents

Nucleophiles or nucleophilic reagents are electron rich substances containing atoms which have at least an unshared pair of electron. These reagents are nucleus loving (nucleo = nucleus, philic = loving). Nucleophiles can be (i) negatively charged (or) Ionic (ii) neutral species (Lewis bases). Some of the common nucleophiles are reported in table

S. No.	Neutral nucleophiles (Lewis bases)	Ionic nucleophiles
1.	NH <sub>3</sub>	X <sup>-</sup> (halide ions)
2.	H <sub>2</sub> O	OH <sup>-</sup> (hydroxide)
3.	R-OH	RO <sup>-</sup> (alkoxide)
4.	R-NH <sub>2</sub>	CN <sup>-</sup> (cyanide)
5.	R <sub>3</sub> -N	< C <sup>-</sup> (carbanion)

The differences between these reagents are summarised in the following table.

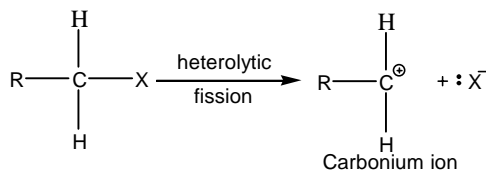
S. No.	Electrophiles	Nucleophiles
1.	are electron deficient	are electron rich
2.	are cations	are often anions
3.	are Lewis acids	are Lewis bases
4.	accept an electron pair	donate an electron pair
5.	attack on electron rich sites	attack on electron deficient sites
6.	possess an empty orbital to house the lone pair from the nucleophiles	possess a minimum of one lone pair of electron.

#### 15.7.2 Carbonium ions

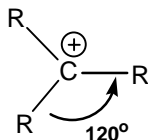
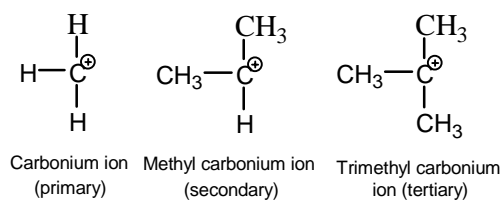
Let us consider the heterolytic fission of the bond C – X present in an organic molecule. If the atom X has greater electronegativity than the carbon atom, the former takes away the bonding electron pair and becomes negatively charged while the carbon will lose its electron and thus acquire a positive charge. Such cationic species carrying a positive charge on carbon

are known as carbonium ions.

For illustration



These carbonium ions are called primary, secondary and tertiary depending up on the nature of the carbon atom bearing the charge.



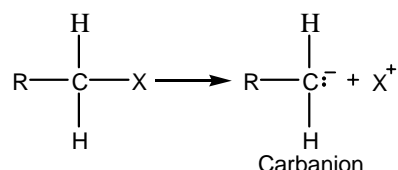
### The geometry of alkyl carbonium ion

Since the carbon of the carbonium ion is in  $sp^2$  hybridised state, the ion is planar with a vacant p orbital perpendicular to the plane of the three covalent bonds to carbon.

### Carbanion

Let us consider the heterolytic fission of the bond C - X present in an organic molecule. If the carbon atom has greater electronegativity than the atom X, the former takes away the bonding electron pair and acquires a negative charge. The resulting carbon anion is known as carbanion.

### For illustration



### Examples

$\text{CH}_3 - \text{CH}_2^-$  : methyl carbanion

$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 - \text{CH}^- \end{array}$  : dimethyl carbanion

## 15.8 Free Radicals

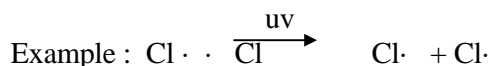
Free radicals are species with one or more unpaired electrons obtained by the homolytic fission of covalent bond. The free radicals themselves are electrically neutral. The free radicals are denoted by putting a dot against the atom or group of atoms.

*Few examples :*  $\text{Cl}\cdot$  ,  $\text{CH}_3\cdot$  ,  $\text{C}_6\text{H}_5\cdot$

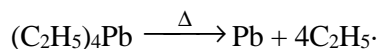
They are classified as short lived free radicals and long lived free radicals on the basis of their life time.

### Formation of free radicals

**(a) Photochemical fission :** When an organic compound is exposed to ultraviolet region it under goes bond fission.



**(b) Thermal fission :** All organic compounds on heating yield free radicals.

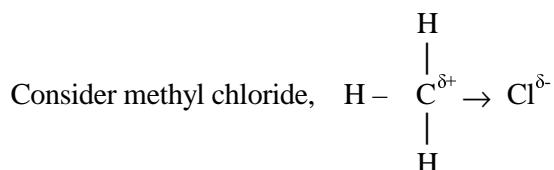


### Polar Effects

#### Inductive Effect

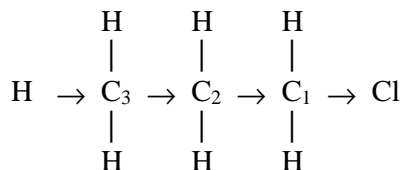
If a covalent bond is formed by two atoms differing much in electronegativity then the bond is said to be polarised. The electron pair

shifts towards the more electronegative atom resulting in the origin of fractional charges on the atoms.



In this molecule, chlorine atom is more electronegative than the carbon atom. Due to this, chlorine pulls the electron pair and acquires a small negative charge.

Let us consider, 1 - chloropropane



As  $\text{C}_1$  is positively charged, it attracts towards itself the electron pair shared between  $\text{C}_1$  and  $\text{C}_2$ . This causes  $\text{C}_2$  to acquire a small positive charge but the charge is smaller than the charge on  $\text{C}_1$ . This type of electron displacement occurring in saturated compounds along a carbon chain is termed, inductive effect.

It is a permanent effect and decreases rapidly as the distance from the electronegative atom increases. It is represented by  $\rightarrow$  the arrow head pointing towards the more electronegative atom. This effect operates in the case of  $\sigma$  - electrons only.

For measurements of relative inductive effect, atoms or groups having greater electron affinity than hydrogen are said to have - I effect. Similarly, atoms or groups having lesser electron affinity than hydrogen are said to have + I effect. Some of the atoms and groups arranged in the increasing order of inductive effect are given as

Groups having - I effect [electron - attracting].

-  $\text{C}_6\text{H}_5$ ,  $\text{OH}$ , -I, -Br, -Cl, -F

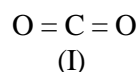
Groups having + I effect [electron pumping]

CH<sub>3</sub> -, CH<sub>3</sub> - CH<sub>2</sub> -, (CH<sub>3</sub>)<sub>2</sub>CH-, (CH<sub>3</sub>)<sub>3</sub>C -  
 (Methyl) (Ethyl) Isopropyl tertiarybutyl

### Resonance (Mesomeric) Effect

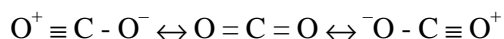
When several structures may be assumed to contribute to the true structure of a molecule but none of them can be said to represent it uniquely, then the molecule is referred to as a resonance hybrid and the phenomenon is termed as resonance.

It is somewhat abstract, but it can be better understood if we consider the structure of a simple molecule carbon dioxide.



The above structure does not account for all observed properties although it can explain many. The C-O bond length in CO<sub>2</sub> molecule is 1.15 Å where as it is expected to be 1.22 Å on the basis of the above structure.

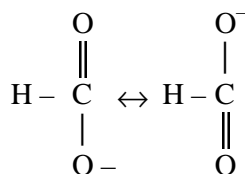
Again, the heat of formation of carbon dioxide is 1592 kJ.mol<sup>-1</sup> where as on the basis of the above structure it is expected to be approximately 1466 kJ.mol<sup>-1</sup>. These discrepancies can be explained only if we assume the following resonance hybrid for carbon dioxide.



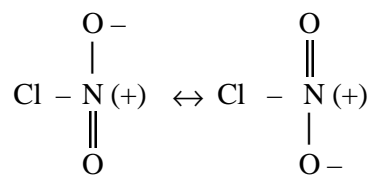
The difference in energy i.e. 126 KJ.mol<sup>-1</sup> is regarded as resonance energy.

Few other examples

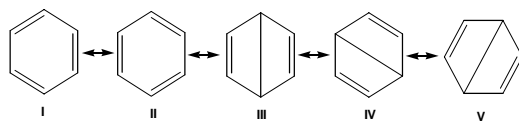
1. Formate ion, HCOO<sup>-</sup>



2. Nitryl chloride, NO<sub>2</sub>Cl



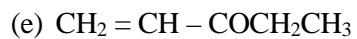
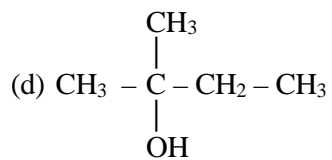
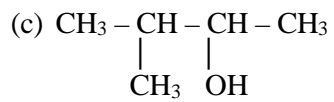
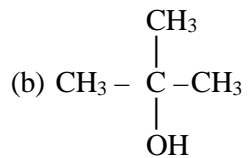
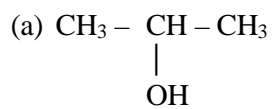
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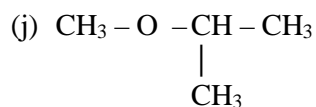
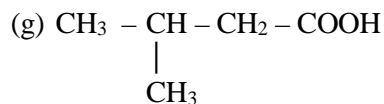


Benzene

### Questions

A. Write IUPAC name of the following





**B. Explain briefly on the following**

1. Homolytic and heterolytic fission.
2. Substitution reaction.
3. Addition reaction.
4. Elimination reaction.
5. Polymerisation reaction.
6. Condensation reaction.
7. Hydrolysis.
8. Reduction and oxidation reactions.
9. Electrophilic and Nucleophilic reagents.
10. Carbonium ions and carbanions.
11. Free radicals.
12. Inductive effect.
13. Resonance effect.

**SUMMARY**

- This chapter explains the ability of carbon atoms to form long chains held together by strong carbon-carbon bonds, catenation.
- Characteristics of homologous series and structural isomers are explained.



- Method of writing IUPAC names of different organic compounds are explained with suitable examples.
- All types of organic reactions, like substitution, addition, elimination, condensation, polymerisation, hydrolysis, oxidation and reduction reactions are explained with suitable examples.
- Different types of isomerism and the representations are explained.
- Nature of fission of bonds, reagents, carbonium ions carbanions and free radicals are structurally explained with suitable examples.
- Notable electron displacements in organic chemistry like inductive and mesomeric effect in covalent bond are explained.

#### **REFERENCES**

1. Advanced Organic Chemistry by I.L.Finar.
2. Organic Chemistry by Bahl and Arun Bahl.

## 16. PURIFICATION OF ORGANIC COMPOUNDS

### OBJECTIVES

*The main objectives of this chapter are to provide*

- \* *Characteristics of organic compounds*
- \* *Need for purification*
- \* *Methods of purifying organic substances like crystallisation, distillation, fractional distillation, steam distillation, distillation under reduced pressure and various methods of chromatography.*

### 16.1 Characteristics of organic compounds

Organic compounds have the following general characteristics.

- i) Organic compounds are generally covalent and hence they do not dissolve in water (polar solvents) but dissolve in organic solvents (non-polar solvents) such as ether, alcohol, benzene etc.
- ii) Due to maximum catenation and tetravalency of carbon, they have tendency to form long open and closed chain compounds.
- iii) They are volatile, inflammable and possess low boiling points and melting points.
- iv) Some organic compounds exhibit the phenomenon of polymerisation. For example, ethylene polymerises to poly ethylene.
- v) They exhibit isomerism.
- vi) They contribute homologous series.
- vii) They are non-conductors of electricity.

### Need for purification of organic compounds

The organic compounds obtained from natural sources are not pure. They contain a number of other compounds which occur with them. Similarly, the organic compounds prepared in the laboratory are also not pure. They are found to contain other products formed during the reaction. In order to investigate the structure and properties of an organic compound, it should be in the purest form. Hence purification of organic compounds become essential.

Various methods used for purification and separation of organic compounds are:

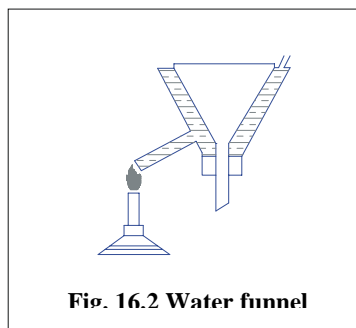
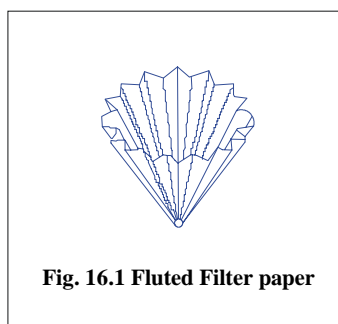
- i) Crystallisation
- ii) Fractional Crystallisation
- iii) Sublimation
- iv) Distillation
- v) Extraction with solvents
- vi) Chromatography

## 16.2 Crystallisation

Crystallisation is carried out in four stages (a) preparation of the solution of the substance in a suitable solvent (b) filtration of the hot solution (c) crystallisation by cooling the hot filtrate (d) isolation and drying of the purified substance.

**a) Preparation of the solution :** The powdered organic substance is taken in a semi-micro round bottom flask and the solvent is added little by little with constant stirring and heating till the amount added is just sufficient to dissolve the solute, when the solution is just boiled. If the solvent is non-inflammable, heating may be done on the wire gauze, while in the case of inflammable solvents, heating should be done on a water bath.

**b) Filtration of the Solution :** The hot saturated solution obtained is filtrated through a fluted filter paper placed in a hot water funnel.



**c) Crystallisation** : When the filtration is over, the beaker containing the solution is allowed to cool when pure crystals separate. Sometimes the crystals do not separate due to super cooling of the solution. Crystallisation can be started in such cases by scratching the sides of the vessel containing the solution with a glass rod or seeding with a tiny crystal of the substances.

**d) Isolation and drying of the purified crystals** : The purified crystals are separated from the mother liquor by filtration using Buchner funnel and a suction pump.

When the whole of the mother liquor has been drained off, the crystals are washed with small amounts of cold solvent thrice. The crystals are then transferred to a porous plate, pressed by using filter paper and then dried by using infra-red light or by keeping in sunlight. If the crystals are coloured, decolourisation is effected by using animal charcoal.

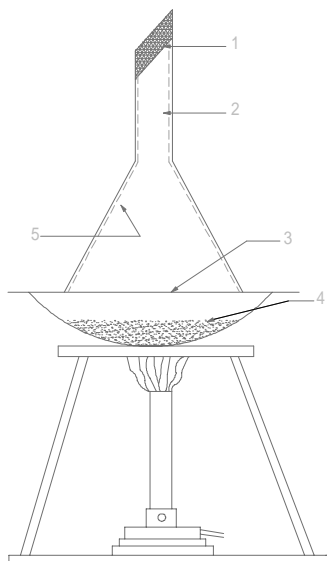
### **Fractional Crystallisation**

When the solubility of two substances in any solvent is not much different from one another, then the two compounds can be separated by fractional crystallisation, involving a series of repeated crystallisations. For example, when a solution containing two substances A and B is subjected to crystallisation, the slightly less soluble substances (say A) containing a small amount of the other substance (B) crystallises out. The mother liquor when subjected to crystallisation gives crystals of B containing a small amount of A.

Now, if these crystals are subjected to recrystallisation separately and the process is repeated number of times to get pure A and pure B.

### **16.3 Sublimation**

Certain solid substances like Naphthalene or camphor when heated pass directly from solid to the vapour state without melting. The vapours when cooled give back the solid substance. This process is known as sublimation.



- |                              |                    |
|------------------------------|--------------------|
| 1. Cotton                    | 2. Inverted funnel |
| 3. Perforated asbestos sheet | 4. Mixture         |
|                              | 5. Sublimate       |

**Fig. 16.3**

This process is very helpful in separating a volatile solid from a non-volatile solid. The powdered substance is taken in a China dish and covered with a perforated filter paper and an inverted funnel. The dish is carefully heated on a sand bath.

The vapours passing through the holes in the paper condense on the inner sides of the funnel. The non-volatile impurities remain in the dish.

#### **16.4 Methods for the purification of liquids Distillation**

Distillation is used for separating the constituents of a liquid mixture which differ in their boiling points. Depending upon the difference in the boiling points of the constituents, different types of distillation are employed. These are described below.

##### **i) Simple Distillation**

Liquids with boiling points widely apart (about 40K and above) can be purified by simple distillation if they do not decompose under ordinary pressure. Simple distillation involves conversion of a liquid into its vapour

by heating in a distilling flask and then condensation of the vapour into a liquid in the receiver.

Mixtures like the following can be separated by this simple distillation.

- a Nitro benzene (b.p 484K) and benzene (b.p.354K)
- b. Diethyl ether (b.p.308K) and ethyl alcohol (b.p.351K)

Note : Simple distillation is also helpful in separating non-volatile impurities from liquids.

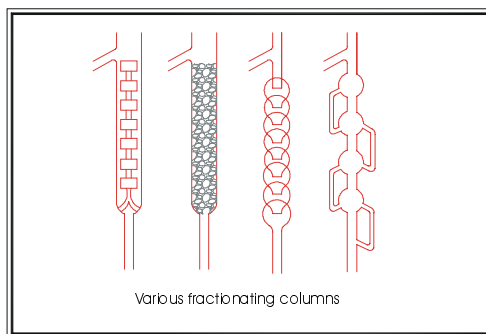
#### 16.4.1 Fractional Distillation

This method is applicable for the separation and purification of a mixture of two or more miscible liquids whose boiling points lie very close to each other.

This is similar to the ordinary distillation method with the only exception that a fractionating column is introduced in-between the distillation flask and 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 fractionating columns used for the purpose are of different shapes.

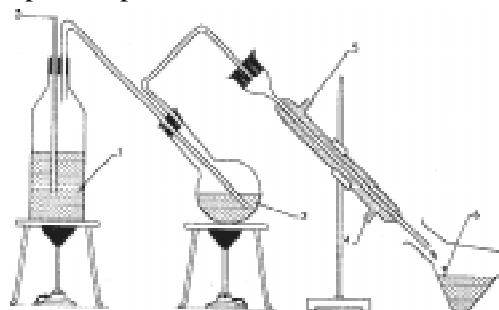


**Fig. 16.4**

#### 16.4.2 Steam Distillation

In steam distillation impure compounds are distilled in a current of steam. This method is applicable to solids as well as liquids. For purification by steam distillation, an impure compound must satisfy the following conditions:

- i) It should not decompose at the steam temperature.
- ii) It should have a fairly high vapour pressure at 373 K.
- iii) It should be insoluble in water.
- iv) The impurities present should be non-volatile



**Fig. 16.5**

- |                     |                    |          |                    |
|---------------------|--------------------|----------|--------------------|
| 1. Water            | 2. Protective tube | 3. Flask | 4. Inlet for water |
| 5. Outlet for water | 6. Pure liquid     |          |                    |

The apparatus used for steam distillation is shown in the figure (16.5). The impure compound is taken in the round bottomed flask and a small quantity of water is added. The flask is then heated gently. Now steam is bubbled through the contents in the flask. The vapours of the compound mix up with steam and escape into the condenser. The condensate thus obtained is a mixture of water and the organic compound which can be separated.

### Theory of steam distillation

Let  $p_1$  represent the vapour pressure of water and  $p_2$  the vapour pressure of the organic liquid. In steam distillation the liquid boils at a temperature at which

$$p_1 + p_2 = \text{Atmospheric Pressure}$$

This temperature must be lower than the normal boiling point of water or the organic liquid. The reason that  $p_1 + p_2$  becomes equal to the atmospheric pressure must earlier than  $p_1$  or  $p_2$  alone. Thus in steam distillation, the impure liquid boils at a temperature which is lower than its normal boiling point. Hence, steam distillation serves the same purpose as

distillation under reduced pressure. However, the former is cheaper but less useful than the latter.

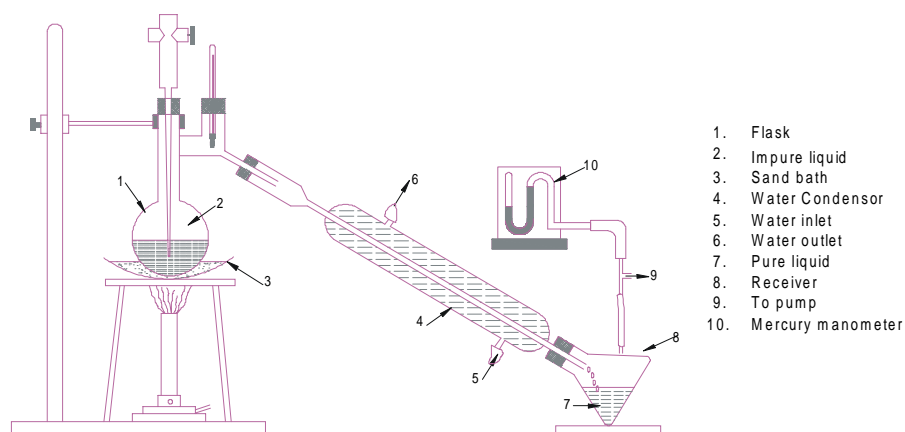
### 16.4.3 Distillation under reduced pressure

This technique is used for purifying or separating thermally unstable liquid compounds which decompose at their normal boiling points.

**Principle :** Lowering of pressure on the surface of a liquid lowers its boiling point. As a result, a liquid can be boiled and distilled at a temperature much below the normal boiling point without any decomposition.

**Procedure :** Distillation under reduced pressure or vacuum is carried out in a specially designed glass apparatus as shown in (Fig.17.6).

The receiver is attached to a vacuum pump to reduce pressure. The pressure is measured with the help of a manometer.



**Fig.16.6 Distillation under reduced pressure**

### Advantages of distillation under reduced pressure

Distillation under reduced pressure has the following advantages:



- i) The compounds which decompose on heating to their boiling points under normal pressure can be purified by distillation under reduced pressure. This is because at a reduced pressure, a liquid would boil at temperature much below its normal boiling point.
- ii) In distillation under reduced pressure, a liquid boils at temperature well below the normal boiling point. So, the distillation under reduced pressure is more fuel-economical.

#### **16.4.4 Extraction with solvents**

This method is based on the fact that organic substances are more soluble in organic solvents than in water.

The organic substance is extracted from its aqueous solution adopting the following procedure.

- a. The aqueous solution containing organic substance is shaken with a suitable organic solvent which dissolves the substance but is immiscible with water. Two layers are formed; the organic layer and aqueous layer.
- b. The solvent layer containing the organic substance (organic layer) is separated using a 'separating funnel'. The impurities remain in the aqueous layer removed by distillation to obtain the organic substance.
- c. The organic solvent is removed by distillation to obtain the organic substance.

#### **16.5 Chromatography**

This technique was introduced by M.S.Tswett, a Russian botanist in 1906 when he reported the separation of different coloured constituents of chlorophyll. He achieved it by passing a petroleum ether solution of the chlorophyll present in leaves through a column of calcium carbonate firmly packed into a narrow glass tube. Different components of the pigment got separated into band or zones of different colours.

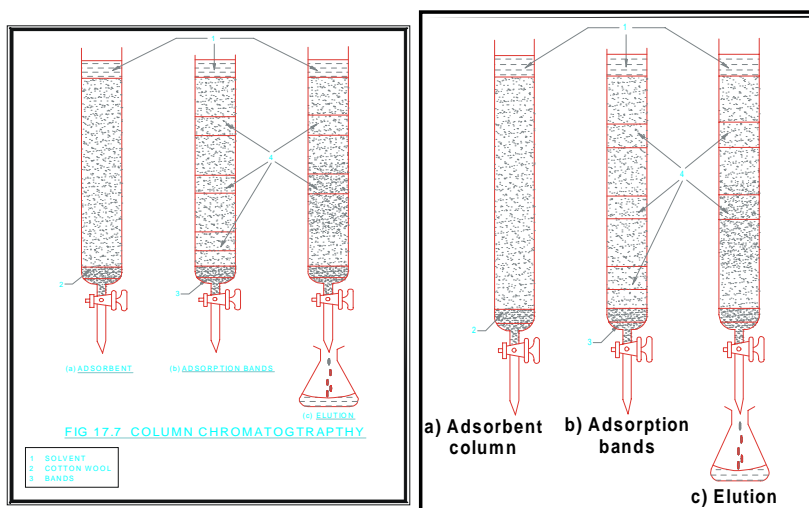
Chromatography is based on the general principle of distributing the components of a mixture of organic compounds between two phases - a stationary phase and a moving phase. The stationary phase can be a solid or liquid supported on a solid, while the moving phase is a liquid or a gas. When the stationary phase is a solid, the basis of separation is adsorption; when it is a liquid, the basis is partition.

Hence, chromatography can be defined as the technique for the separation of a mixture of compounds where the separation is brought about by the differential movement of the individual compounds through a porous medium under the influence of a moving solvent. The technique has now a days undergone tremendous modification and is widely used for the separation and purification of different types of organic compounds.

The different chromatographic techniques used are : column chromatography (CC), thin-layer chromatography (TLC), paper chromatography (PC), gas-liquid chromatography (GLC) and ion-exchange chromatography.

#### a) Column Chromatography

The simplest chromatographic method is column chromatography. It is carried out in a long glass column having a stop-cock near the bottom. To start the operation, a plug of cotton or glass wool is placed at the bottom of the column to support the adsorbent powder. The tube is packed uniformly with suitable adsorbent. This constitutes what is known as the stationary phase. The commonly employed adsorbents are activated aluminium oxide (alumina), magnesium oxide, silica gel and starch. A loose plug of cotton or glass wool is then placed at the top of the adsorbent column.



**Fig. 16.7 Column chromatography**

The substance to be purified is added, as such if it is a liquid or in the form of its solution in some suitable solvent if it is a solid, at the top of the column and allowed to pass slowly through it. As it passes through the column, the different components of a mixture (Say A, B and C) get adsorbed to different extent and are thus retained by the adsorbent at different levels of the column. The components which are adsorbed very strongly are retained at the top while others are retained at lower levels. In this way different zones or bands are formed in the column which contain different components of a mixture. As soon as the last portion of the substances enter the column, a selected solvent, known as eluent, is added to the column. This acts as moving phase. The elements dissolve out the different components from the various zones selectively and thus 'take out' the different bands in the form of fractions which are collected separately.

#### **b) Thin Layer Chromatography (TLC)**

Thin layer chromatography (TLC) is another type of adsorption chromatography, which involves separation of the substances of a mixture over a thin layer of an adsorbent. A thin layer (about 0.2mm thick) of an adsorbent (Silica gel or alumina) is spread over a glass plate of suitable size. The plate is known as thin layer chromatography plate. The solution of the mixture to be separated is applied as a small spot about 2 cm above one end of the TLC plate. The glass plate is then placed in a closed jar containing the solvent (Below 2cm height). As the solvent moves up the plate, the components of mixture move up along the plate to different distances depending on this degree of adsorption and separation takes place. The relative adsorption of each component of the mixture is expressed in terms of its retention factor i.e.,  $R_f$  Value.

$$R_f = \frac{\text{Distance moved by the substance from base line (x)}}{\text{Distance moved by the solvent from base line (y)}}$$

#### **c) Paper Chromatography**

It is an important and useful class of partition chromatography. In this technique, the stationary phase is considered to be made up of water molecules bound to the cellulose network (inert support) of the paper. The mobile phase, known as the developing solvent consists of either one solvent or a mixture of different solvents. Separation of the mixture into pure compounds takes place by the partitioning of different compounds

between these two liquid phases. The mobile phase travels by capillary action through the paper. Depending upon the way the solvent travels on the paper, there are three types of paper chromatography.

- i) Ascending Paper Chromatography : The mobile phase moves upwards on the paper strip in this case.
- ii) Descending Paper Chromatography : The mobile phase in this case moves downward on the paper strip.
- iii) Circular or radial paper chromatography: The mobile phase moves horizontally along a circular sheet of paper in this case.

In the ascending paper chromatography, the mixture of compounds is applied on the paper as a spot little above the lower end and then this end is dipped in the solvent. When the solvent has risen more than two third length of the paper, then it is removed from the solvent. The paper is dried and is known as chromatogram.

Now the spots for different compounds can be visualised using some suitable chemicals. The ratio of the distance travelled by the compound in a particular solvent to that the distance travelled by the solvent is a constant and is known as retention factor ( $R_f$ ). This value is used in identifying the compounds.

$$R_f = \frac{\text{Distance travelled by the compound}}{\text{Distance travelled by the solvent}}$$

Type of Chromatography	Stationary Phase	Mobile Phase
1. Column Chromatography	Solid	Liquid
2. Thin Layer Chromatography (TLC)	Solid	Liquid
3. Paper Chromatography	Liquid	Liquid
4. Gas Liquid Phase Chromatography	Liquid	Gas

**Difference between paper chromatography and thin layer chromatography**

Paper Chromatography	Thin Layer Chromatography
(i) Separation based on partition	Separation is based on partition, adsorption and ion exchange.
(ii) Stationary phase is the water molecules bound on the paper.	Stationary phase is a layer of silica gel or alumina on glass plate.

**Questions****A. Choose the best answer**

- Organic compounds are soluble in
  - Non-polar Solvents
  - Polar solvents
  - Water
  - HCl
- Decolourisation of coloured compounds can be effected by using
  - Animal charcoal
  - Carbon
  - Coke
  - Infra-red rays
- Compounds having boiling points widely apart 40 K and above can be purified by
  - Crystallisation
  - Simple distillation
  - Fractional distillation
  - Sublimation
- Nitrobenzene and benzene can be separated by the method of
  - Steam distillation
  - Crystallisation
  - Fractional crystallisation
  - Chromatography
- Purification of two miscible liquids possessing very close boiling points can be separated using
  - Fractional distillation
  - Sublimation
  - Simple distillation
  - Steam distillation
- Purification of mixture of compounds can be done by steam distillation only if the impurities are
  - Non-volatile
  - Volatile
  - Insoluble in Water
  - both a & c
- When the stationary phase is solid, then the compounds can be separated on the basis of
  - Adsorption
  - Partition
  - Both partition and adsorption
  - Either
- Column Chromatography is based on the principle of
  - Adsorption
  - Partition
  - Absorption
  - Distribution
- In Ascending paper Chromatography, the solvent moves
  - Upwards
  - Downwards
  - Horizontally
  - None
- The existence of wide range of organic compounds is due to their, property of
  - Extensive catenation
  - Lower boiling points
  - Polymerisation
  - Isomerism

**B. Fill in the blanks**

1. The Compounds separated and purified by crystallisation can be dried over \_\_\_\_\_.
2. Camphor can be purified by the process of \_\_\_\_\_.
3. In simple distillation the compounds should not decompose at \_\_\_\_\_.
4. Water insoluble compounds can be purified by \_\_\_\_\_.
5. In T.L.C the stationary phase is a \_\_\_\_\_.
6. Chromatographic technique was first introduced by \_\_\_\_\_.
7. In paper chromatography, the mobile phase travels by \_\_\_\_\_ action through the paper.
8. The adsorbent used in column Chromatography method is \_\_\_\_\_.
9. In Chromatographic technique, the separation of compounds are brought about by \_\_\_\_\_ movement of the compounds.
10. Paper Chromatography is \_\_\_\_\_ Chromatography.

**C. Write in one or two sentence**

1. What are the different stages followed during Crystallisation?
2. Define steam distillation.
3. What are different types of distillation?
4. Give the advantages of distillation under reduced pressure.
5. What are the types of paper chromatography?

**D. Explain briefly on the following**

1. Explain the method of purifying a solid organic compound.
2. Write short notes on
  - a) Fractional crystallisation
  - b) Solvent extraction
3. Explain the purification of compounds by using thin layer chromatography.
4. What are the various principles used in chromatographic separation?
5. Write down the general characteristics of organic compounds.

**SUMMARY**

All organic compounds must be purified before study. There are various purification methods adopted. Depending on the physical and chemical properties of the organic compounds, purification methods are done. Methods like crystallization, sublimation, distillation, solvent extraction and chromatographic techniques are dealt in detail in this chapter.

**REFERENCES**

1. Organic Chemistry by Bahl and Arun Bahl.
2. Organic Quantitative Analysis by Arthur I Vogel, ELBS edition.

## 17. DETECTION AND ESTIMATION OF ELEMENTS

### OBJECTIVES

*The main objectives of the chart are to provide*

- \* *Detection and estimation of carbon, hydrogen, nitrogen, sulphur and halogens.*
- \* *The various methods for the detection and estimations are discussed in detail.*

### 17.1 Qualitative Analysis

Qualitative analysis of an organic compound involves the detection of various elements present in it. The elements commonly present in organic compounds are carbon, hydrogen, oxygen, nitrogen, halogens and sulphur and sometimes phosphorous. The carbon and hydrogen are present in almost all the organic compounds.

#### A) Detection of carbon and hydrogen

The detection of carbon and hydrogen in an organic compound is done by a single experiment.

A small quantity of pure and dry compound is mixed with about ten times its weight of copper oxide (CuO). The mixture is taken in a hard glass test tube fitted with a delivery tube having a small bulb. The other end of the tube is immersed in freshly prepared lime water. In the bulb of delivery tube, a small amount of anhydrous copper sulphate (white) is placed. The mixture is heated strongly when carbon and hydrogen present are oxidised to carbon dioxide and water respectively.

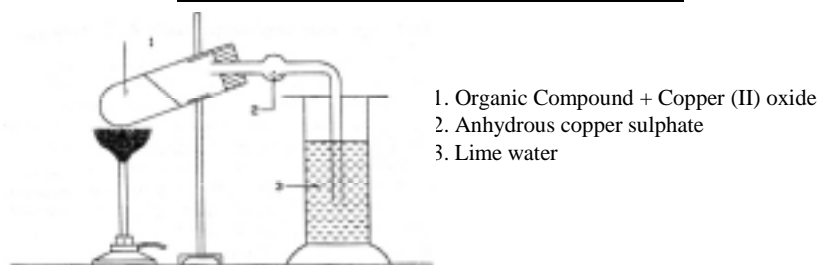
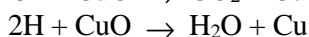
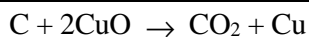
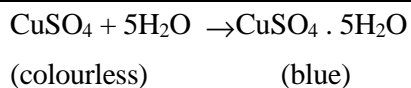
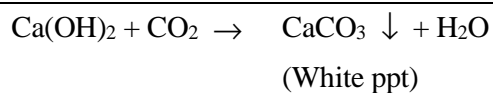


Fig. 17.1

Carbon dioxide turns **lime water milky** and the water vapour turns colourless copper sulphate, blue.



**Turning of lime water milky** and of colourless copper sulphate blue shows the **presence of carbon and hydrogen** respectively.

### B. Detection of Oxygen

There is no direct method for the detection of oxygen in organic compounds. It is detected indirectly. For example,

- If any organic compound on heating in a dry test tube, gives out water vapour, then the presence of oxygen in the organic compound is indicated.
- If any organic compound is found to contain any oxygen containing functional groups such as - OH, -CHO, -COOH, -NO<sub>2</sub> etc., then the compound contains oxygen.
- If the sum of the percentages of various elements present in the compound is less than 100, then the compound contains oxygen.

### C) Detection of nitrogen, sulphur and halogens

All these can be detected by **Lassaigne's Test**.

**Lassaigne's Test** : The organic compound is taken in an ignition tube. A pea-size sodium metal is added to it and heated to red hot. The hot tube is crushed to powder under a few ml of water in a mortar. The solution is filtered and the filtrate is known as 'sodium extract' or '**lassaigne's filtrate**'. The filtrate is used for the detection of the elements.

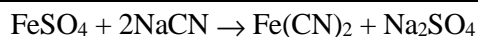
**Nitrogen** : During fusion, the carbon and nitrogen of the organic compound combine with sodium metal forming sodium cyanide.





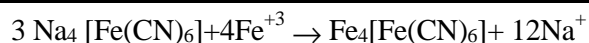
The unreacted sodium combines with water forming caustic soda, so the solution becomes alkaline.

**Test :** To the extract, ferrous sulphate solution is added and warmed. Sodium ferrocyanide is formed.



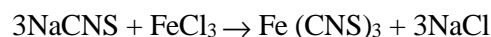
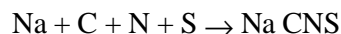
sodiumferrocyanide

A few drops of **ferric chloride** are added to it and the solution is **acidified with dilute sulphuric acid**. The ferric ions react with sodium ferrocyanide giving a bright blue (prussion blue) coloration



ferric ferrocyanide  
(prussion blue)

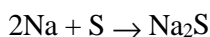
**Test :** If an organic compound contains nitrogen along with sulphur, a blood red colour will be obtained in the above test.



(Ferric sulphocyanide)  
(blood red colour)

## Sulphur

Organic compounds containing sulphur give sulphide on fusion with sodium.

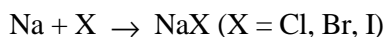


**Test :** To the Lassaigne's filtrate, sodium nitroprusside is added. **Purple colour** is developed.

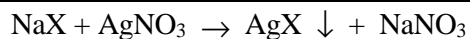


sodium nitroprusside                      purple

**Halogens** : In sodium extract, the halogen is present as sodium halide.



**Test** : The extract is acidified with dilute nitric acid and silver nitrate solution is added. Formation of precipitate indicates the presence of halogen.



The halogen is identified from the **colour** and the **solubility** of the precipitate in ammonium hydroxide.

Sl. No.	Colour of the precipitate	Halogen present	Solubility in ammonium hydroxide
1.	White	chlorine	Easily soluble
2.	Pale yellow	bromine	Sparingly soluble
3.	Yellow	iodine	Insoluble

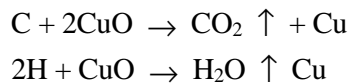
## 17.2 Quantitative analysis of organic compounds

Once we have known the various elements present in any organic compound, the next point of interest is to know how much of each element is present in the compound. Determination of the relative proportions (generally as percentages) of various elements present in an organic compound is called **quantitative analysis of that compound**. For quantitative analysis, the percentages of the various elements present in any compound are estimated by suitable chemical methods.

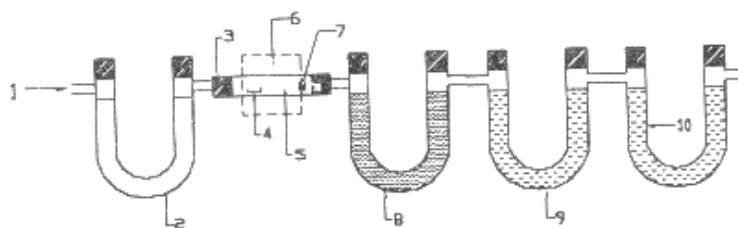
### (a) Estimation of carbon and hydrogen (liebig's combustion method)

The estimation of carbon and hydrogen is carried out in one experiment.

A known weight of the organic compound is strongly heated with excess of dry copper oxide in an atmosphere of dry and pure oxygen or air. Carbon of the compound is oxidised to carbon dioxide and hydrogen to water.



The  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are absorbed by a strong solution of **caustic potash** and **anhydrous calcium chloride** respectively. The percentage of carbon and hydrogen is calculated from the weights of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  obtained. These weights are obtained by finding the weights of caustic potash and calcium chloride tubes before and after the experiment.



**Fig.17.2**

- |  |   |  |
|--|---|--|
| 1. Oxygen supply                       | 2. Drying tube                          | 3. Glass joints  |
| 4. Platinum boat with organic compound | 5. CuO                                  |  |
| 6. Combustion tube                     | 7. Copper coil to remove nitrogen oxide |  |
| 8. $\text{CaCl}_2$ guard tube          | 9. KOH tube                             | 10. To prevent the incoming $\text{CO}_2$ and $\text{H}_2\text{O}$ |

### Calculation

Let, weight of organic compound =  $w_g$

Increase in weight of  $\text{CaCl}_2$  tube  
(weight of water formed) =  $w_1g$

Increase in weight of potash bulbs  
(weight of carbon dioxide formed) =  $w_2g$

### Percentage of carbon

Molecular weight of  $\text{CO}_2 = (12 + 32) = 44$

44 g of carbon dioxide contains, carbon = 12 g

$w_2g$  of carbon dioxide contains,

$$= \frac{12}{44} \times w_2g \text{ carbon}$$

$w_g$  of compound contains

$$= \frac{12}{44} \times w_2 \text{ g of carbon}$$

∴ 100 g of compound contains

$$= \frac{12}{44} \times \frac{w_2}{w} \times 100 \text{ g of carbon}$$

$$\text{Percentage of carbon in the compound} = \frac{12}{44} \times \frac{w_2}{w} \times 100$$

### Percentage of hydrogen

$$\text{Molecular weight of H}_2\text{O} = (2 + 16) = 18$$

$$18 \text{ g of water contains, hydrogen} = 2 \text{ g}$$

$$w_1 \text{ g of water contains, hydrogen} = \frac{2}{18} \times w_1 \text{ g}$$

wg of compound contains

$$= \frac{2}{18} \times w_1 \text{ g of hydrogen.}$$

∴ 100 g of compound contains

$$= \frac{2}{18} \times \frac{w_1}{w} \times 100$$

### Example 1

0.30 g of a substance gives 0.88 g of carbon dioxide and 0.54 g water. Calculate the percentage of carbon and hydrogen in it.

### Solution

$$\text{Weight of organic compound} = 0.30 \text{ g}$$

$$\text{Weight of carbon dioxide} = 0.88 \text{ g}$$

$$\text{Weight of water} = 0.54 \text{ g}$$

### Percentage of carbon

$$44 \text{ g of carbondioxide contains, carbon} = 12 \text{ g}$$

$$0.88 \text{ g of carbon dioxide contains, carbon} = \frac{12 \times 0.88}{44} \text{ g}$$

$$0.30 \text{ g substance contains, carbon} = \frac{12 \times 0.88}{44} \text{ g}$$

100 g substance contains

$$= \frac{12 \times 0.88}{44} \times \frac{100}{0.30} = 80 \text{ g of carbon}$$

Percentage of carbon = 80

**Percentage of hydrogen**

$$18 \text{ g of water contains, hydrogen} = 2 \text{ g}$$

$$0.54 \text{ g of water contains, hydrogen} = \frac{2 \times 0.54}{18} \text{ g}$$

$$0.30 \text{ g of substance contains hydrogen} = \frac{2 \times 0.54}{18 \times 0.30} \text{ g}$$

$$100 \text{ g of substance contains} = \frac{2 \times 0.54}{18 \times 0.30} \times 100 \text{ g}$$

$$= 20 \text{ g of hydrogen}$$

$$\text{Percentage of hydrogen} = 20$$

**(b) Estimation of oxygen**

Oxygen is commonly estimated by the method of difference. The percentage of all other elements are added together and then subtracted from 100. The balance is the percentage of oxygen.

**Example 2**

0.2004 g of glucose gave on combustion 0.2940 g of  $\text{CO}_2$  and 0.1202 g of  $\text{H}_2\text{O}$ . Find the percentage composition.

**Solution**

$$\text{Weight of organic compound} = 0.2004 \text{ g}$$

$$\text{Weight of carbon dioxide} = 0.2940 \text{ g}$$

$$\text{Weight of water} = 0.1202 \text{ g}$$

**Percentage of carbon**

$$44 \text{ g of } \text{CO}_2 \text{ contains, carbon} = 12 \text{ g}$$

$$0.2940 \text{ g of CO}_2 \text{ contains, carbon} = \frac{12 \times 0.2940}{44} \text{ g}$$

$$\text{Percentage of carbon} = \frac{12 \times 0.2940}{44} \times \frac{100}{0.2004} = 40.01$$

#### Percentage of hydrogen

$$18 \text{ g of H}_2\text{O contains, hydrogen} = 2 \text{ g}$$

$$0.1202 \text{ of H}_2\text{O contains, hydrogen} = \frac{2 \times 0.1202}{18}$$

$$\text{Percentage of hydrogen} = \frac{2 \times 0.1202}{18} \times \frac{100}{0.2004} = 6.66$$

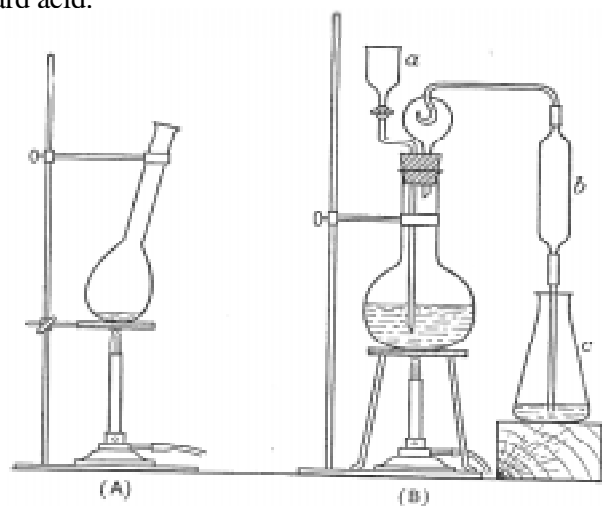
Percentage of oxygen is therefore by difference,

$$= [100 - (40.01 + 6.66)] = 53.33$$

#### Estimation of nitrogen

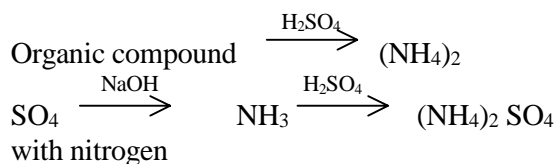
##### c) Kjeldahl Method

This method is based on the fact that many nitrogenous organic compounds when heated with con.  $\text{H}_2\text{SO}_4$ , are quantitatively converted into ammonium sulphate. The ammonium sulphate so obtained is heated with excess  $\text{NaOH}$  and the ammonia liberated is absorbed in a known volume of standard acid.



**Fig. 17.3 Kjeldahl's method**

From the volume of standard acid used by ammonia and the mass of organic compound taken for the experiment, we can calculate the mass of nitrogen in the compound.



Note : 1000 ml 1N acid  $\equiv$  17 g  $\text{NH}_3 \equiv$  14 g nitrogen.

### Calculation

$$\begin{array}{ll}
 \text{Mass of the nitrogenous substance} & = W \text{ g} \\
 \text{Volume of acid used up by } \text{NH}_3 & = V_1 \text{ ml} \\
 \text{Normality of acid} & = N_1 \\
 \text{Volume of 1 N acid} & = V_1 N
 \end{array}$$

$$\begin{aligned}
 \text{Mass of nitrogen} &= \frac{14 \times V_1 N_1}{1000} \\
 \% \text{ of nitrogen} &= \frac{14 \times V_1 N_1 \times 100}{1000 \times w}
 \end{aligned}$$

### Example 1

The ammonia evolved from 0.21 g of an organic compound by Kjeldahl method neutralised 15 ml of N/20 sulphuric acid solution. Calculate the percentage of nitrogen.

$$\text{Weight of organic compound} = 0.21 \text{ g}$$

$$\text{Normality of acid} = \frac{N}{20}$$

$$\text{Volume of standard acid neutralised by ammonia} = 15 \text{ ml}$$

1000 ml of 1N ammonia contains = 14 g of nitrogen

15 ml of ammonia of normality

$$\frac{N}{20} \text{ contains nitrogen} = \frac{14 \times 15 \times 1}{1000 \times 20}$$

0.21 g of compound contains nitrogen

$$= \frac{14 \times 15}{1000 \times 20}$$

100 g of compound contains nitrogen

$$= \frac{14 \times 15 \times 100}{1000 \times 20 \times 0.21} = 5\text{g}$$

$$\therefore \text{Percentage of nitrogen} = 5$$

### **Example 2**

0.35 g of an organic substance was Kjeldahlised and the ammonia obtained was passed into 100 ml of N/5 H<sub>2</sub>SO<sub>4</sub>. The excess acid required 154 ml of N/10 NaOH for neutralisation. Calculate the percentage of nitrogen in the compound.

### **Solution**

Volume of N/5 H<sub>2</sub>SO<sub>4</sub> solution taken = 100 mL

The volume of N/5 H<sub>2</sub>SO<sub>4</sub> neutralised by N/10

NaOH can be obtained as follows :

$$\begin{aligned} N_{\text{acid}} \times V_{\text{acid}} &= N_{\text{alkali}} \times V_{\text{alkali}} \\ \frac{N}{5} \times V_{\text{acid}} &= \frac{N}{10} \times 154 \text{ mL} \\ V_{\text{acid}} &= \frac{154}{10} \times 5 \text{ mL} \end{aligned}$$



$$= 77 \text{ mL}$$

Therefore,

Volume of N/5  $\text{H}_2\text{SO}_4$  used for

$$\begin{aligned} \text{neutralising ammonia} &= (100 - 77) \text{ mL} \\ &= 23 \text{ mL} \end{aligned}$$

Then,

Percentage of nitrogen in the sample

$$= \frac{1.4 \times \text{Normality volume of acid used for neutralising } \text{NH}_3}{\text{Mass of the compound taken}}$$

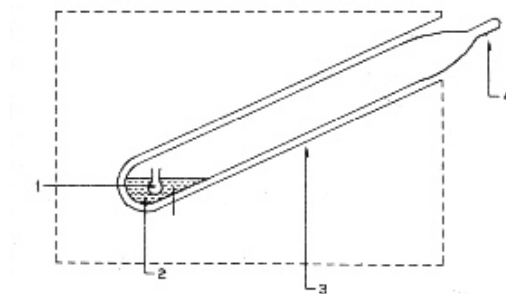
Percentage of nitrogen in the sample

$$= \frac{1.4 \times \frac{1}{5} \times 23}{0.35} = 18.4$$

#### d) Estimation of sulphur

##### Carius method

A known mass of the organic compound is heated in a sealed tube with fuming nitric acid. The sulphur present in the organic compound will be oxidised to sulphuric acid. The tube is cooled and broken in dilute hydrochloric acid. Then excess of barium chloride solution is added. The precipitate of barium sulphate obtained is filtered, washed, dried and weighed accurately.



**Fig.17.4**

1. Organic compound 2. Nitric acid 3. Iron tube 4. Carius tube

### Calculations

Mass of the organic compound =  $w$  g

Mass of barium sulphate =  $w_1$  g

233.4 g  $\text{BaSO}_4$  contains 32 g sulphur

$\therefore w_1$  g  $\text{BaSO}_4$  will contain  $\frac{32 \times w_1}{233.4}$  g sulphur

Percentage of sulphur

$$= \frac{32 \times w_1}{233.4 \times w} \times 100$$

### Example

0.316 g of an organic compound, after heating with fuming nitric acid and barium nitrate crystals in a sealed tube gave 0.466 g of the precipitate of barium sulphate. Determine the percentage of sulphur in the compound.

(Atomic masses : Ba = 137, S = 32, O = 16, C = 12, H = 1).

### Solution

Mass of the substance taken = 0.316 g

Mass of  $\text{BaSO}_4$  formed = 0.466 g

Molecular mass of  $\text{BaSO}_4$  =  $137 + 32 + 64 = 233$

Then, mass of S in 0.466 g of  $\text{BaSO}_4$

$$= \frac{0.466 \times 32}{233} \text{ g}$$

Percentage of S in compound

$$\begin{aligned} &= \frac{0.466 \times 32 \times 100}{233 \times 0.316} \\ &= 20.25 \end{aligned}$$

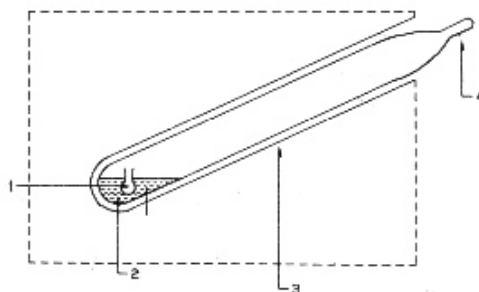
### e) Estimation of halogens

#### Carius Method

**Principle :** The organic compound is heated with silver nitrate and fuming nitric acid. The halogen in the organic compound becomes the halide ion and this reacts with silver ion of the silver nitrate solution. The silver halide is precipitated. The precipitate is filtered, washed, dried and then weighed accurately.

#### Procedure

About 0.2 g of the organic compound is weighed accurately in a small glass tube. The tube is introduced into the Carius tube containing fuming nitric acid and silver nitrate crystals. The upper end of the tube is sealed. The tube is then heated in a furnace for 5 to 6 hours. The organic compound breaks up and the halogen present gives a precipitate of silver halide. The Carius tube is cooled and then broken. The precipitate of silver halide is washed, dried and weighed accurately.



**Fig.17.5**

- |                     |                                 |
|---------------------|---------------------------------|
| 1. Organic compound | 2. Nitric acid + Silver nitrate |
| 3. Iron tube        | 4. Carius tube                  |

#### Calculation

Mass of organic compound =  $w$  g

Let the mass of silver halide be  $w_1$  g

143.5 g of silver chloride contains

35.5 g  $\text{Cl}_2$

$w_1$  g of  $\text{AgCl}$  contains  $\frac{35.5 \times w_1}{143.5}$  g of  $\text{Cl}_2$

$$\text{Percentage of chlorine} = \frac{35.5 \times w_1 \times 100}{143.5 \times w}$$

similarly,

Percentage of bromine

$$= \frac{80}{188} \times \frac{w_1}{w} \times 100$$

Percentage of iodine

$$= \frac{127}{235} \times \frac{w_1}{w} \times 100$$

### Example

0.15 g of iodoform gave 0.2682 g of AgI. Calculate the percentage of iodine.

Weight of compound = 0.15 g

Weight of silver iodide = 0.2682 g

Molecular weight of silver iodide =  $108 + 127 = 235$

235 g of silver iodide contains 127 g of iodine

$$0.2682 \text{ g of AgI contains} = \frac{127 \times 0.2682}{235}$$

$$= 0.144 \text{ g iodine}$$

0.15 g of compound contains 0.144 g of iodine

$$100 \text{ g of compound contains} = \frac{100 \times 0.1449}{0.15} = 96.6 \text{ g}$$

$$\therefore \text{Percentage of iodine} = 96.6$$

### Problems

#### Estimation of carbon and hydrogen

- 0.12 g of an organic compound gave on combustion 0.18 g of water and 0.11 g of  $\text{CO}_2$ . Calculate the percentage of C and H in the organic compound. [Ans : C = 25%, H = 16.66%]
- An organic compound contains C, H and O. 0.2475 g of the organic compound yielded on combustion 0.4950 g of  $\text{CO}_2$  and 0.2025 g of  $\text{H}_2\text{O}$ . Find the percentage composition of the organic compound. [Ans : C = 54.54%, H = 9.09%, O = 36.37%]

- 0.2004 g of glucose gave on combustion 0.2940 g of  $\text{CO}_2$  and 0.1202 g of  $\text{H}_2\text{O}$ . Find the percentage composition.  
[Ans : C = 40.01%, H = 6.66%, O = 53.33%]
- 0.2056 g of an organic compound gave on combustion 0.114 g of  $\text{H}_2\text{O}$  and 0.880 g of  $\text{CO}_2$ . Find the percentage of hydrogen and carbon in the organic compound. [Ans : C = 93.76%, H = 6.128]
- On complete combustion, 0.246 g of an organic compound gave 0.198 g of  $\text{CO}_2$  and 0.1014 of  $\text{H}_2\text{O}$ . Find the percentage composition of the organic compound. [Ans : C = 21.95%, H = 4.58%]

#### **Estimation of nitrogen**

- 1.15 g of an organic compound was analysed by Kjeldahl's method and the ammonia produced was collected in 30 mL of normal HCl solution. The excess of acid consumed 18.4 mL of normal sodium hydroxide solution for back titration. Calculate the percentage of nitrogen in the substance. [Ans : N = 14.12%]
- 0.80 g of a substance was digested with sulphuric acid and then distilled with an excess of caustic soda. The ammonia gas evolved was passed through 100 ml of 1N  $\text{H}_2\text{SO}_4$ . The excess of the acid required 80 ml of 1N caustic soda solution for its complete neutralisation. Calculate the percentage of nitrogen in the organic compound.  
[Ans : N = 35%]
- 0.36 g of a nitrogenous organic compound was Kjeldahlised and the ammonia liberated was exactly neutralised by 20 ml of 0.3 N  $\text{H}_2\text{SO}_4$ . Calculate the percentage of nitrogen in the compound.
- 0.257 g of an organic substance was Kjeldahlised and ammonia evolved was absorbed in 50 mL of N/10 HCl which required 23.2 ml of N/10 NaOH for neutralization. Determine the percentage of nitrogen in the compound. [Ans : N = 14.6%]
- During nitrogen estimation present in an organic compound by Kjeldahl's method, the ammonia evolved from 0.5 g of the compound in Kjeldahl's estimation of nitrogen neutralised 10 ml of 1 M  $\text{H}_2\text{SO}_4$ . Find the percentage of nitrogen in the compound. [Ans : N = 56%]

#### **Estimation of sulphur**

- 0.4037 g of an organic substance containing sulphur was heated with conc. nitric acid in a carius tube. On precipitation with  $\text{BaCl}_2$ , 0.1963 g of  $\text{BaSO}_4$  was produced. Determine the percentage of sulphur in the compound. [Ans : S = 7.66%]

- 0.316 g of an organic compound gives 0.466 g of barium sulphate by carius method. Calculate the percentage of sulphur?  
[Ans : S = 20.25%]
- 0.530 g of an organic compound gave 0.90 g of  $\text{BaSO}_4$  in carius determination of sulphur. Calculate the percentage of sulphur.  
[Ans : S = 23.32%]

#### Estimation of halogens

- 0.24 g of an organic compound gave 0.287 g of  $\text{AgCl}$  in the carius method. Calculate the percentage of chlorine in the compound.  
[Ans : Cl = 25%]
- In carious method of estimation of halogen 0.15 g of an organic compound gave 0.12 g of  $\text{AgBr}$ . Find the percentage of bromine in the compound. [Ans : Br = 34.04%]
- 0.301 g of an organic compound gave 0.282 g of silver bromide by carius method. Find the percentage of bromine. [Ans : Br = 39.83%]
- 0.196 g of an organic compound gave 0.22 g of  $\text{CO}_2$  and 0.0675 g of  $\text{H}_2\text{O}$ . In carius determination, 0.3925 g of the substance gave 0.717 g of dry  $\text{AgCl}$ . Find the percentage composition of the substance.  
[Ans : C = 30.6%, H = 3.8%, Cl = 45.2%, O = 20.4%]
- 0.25 g of an organic compound was found to produce 0.35 g of  $\text{AgCl}$  after heating with fuming  $\text{HNO}_3$  and  $\text{AgNO}_3$  in a sealed carius method. Determine the percentage of chlorine in the compound.  
[Ans : Cl = 34.75%]

#### SUMMARY

This chapter explains various methods of detection and estimation.

The principles behind various methods of detection and estimation are explained.

#### REFERENCES

- I.L. Finar organic chemistry Vol.1, ELBS edition.
- Vogel's Organic quantitative analysis ELBS.

## 18. HYDROCARBONS

### OBJECTIVES

*The main objectives of this chapter is to give*

- \* knowledge on sources, classification and nomenclature of hydrocarbons.*
- \* general methods of preparation of alkanes, alkenes and alkynes and their chemical properties.*

### 18.1 Classification of Hydrocarbons

Hydrocarbons are made of only carbon and hydrogen. They are obtained mainly from petroleum, natural gas and coal. They are divided into two main categories :

- \* aliphatic hydrocarbons
- \* aromatic hydrocarbons

The aliphatic hydrocarbons are further classified into saturated (alkanes), unsaturated (alkenes and alkynes) and alicyclic (cycloalkanes) hydrocarbons.

### Aliphatic Saturated Hydrocarbons

These are otherwise called alkanes. Alkanes are often referred to as paraffins. Alkanes show little chemical affinity towards other compounds and are chemically inert to most reagents.

### 18.2 IUPAC nomenclature

With the exception of the first four compounds (methane, ethane, propane and butane) whose names have historical roots, other alkanes are named from Greek number according to the number of carbon atoms present.

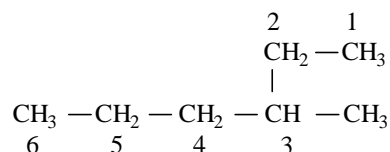
**Table 18.1**

Number of Carbon atoms	Name	Molecular formula $C_nH_{2n+2}$
1	Methane	$CH_4$
2	Ethane	$C_2H_6$
3	Propane	$C_3H_8$
4	Butane	$C_4H_{10}$
5	Pentane	$C_5H_{12}$
6	Hexane	$C_6H_{14}$

The suffix 'ane' is added to the end of the each name to indicate that the molecule identified is an alkane. Thus, pentane is a five-carbon alkane and hexane is a six carbon alkane and so on. According to IUPAC rules, branched chain alkanes can be named by the following four steps:

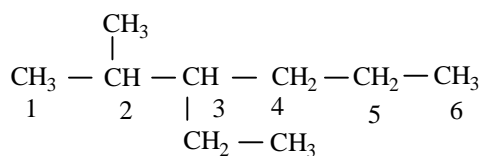
### Step 1 Finding out the parent hydrocarbon

- Find the longest continuous carbon chain present in the molecule and use the name of that chain as the parent name.



Named as a substituted hexane.

- If two different chains of equal length are present, select the chain with the larger number of branch points as the parent.



3-ethyl-2-methyl hexane

(correct name)

4- isopropylhexane

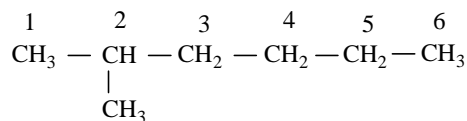
(wrong name)

The above compound is named as hexane with two substituents and not as hexane with one substituent.

### Step 2 Numbering the carbon atoms in the main chain

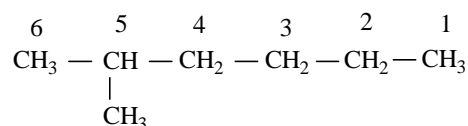
- Beginning either from the left or from the right nearer the first branch point, give the number to each carbon atom in the longest chain, you have identified.





2-methylhexane (correct)

(Not as)

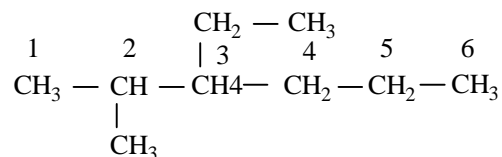


5-methylhexane (wrong)

- b. If there are branchings at equal distance from both ends of the parent chain, give numbering from the end which is nearer to the second branch point.

### Step 3 Identifying and numbering the substituents

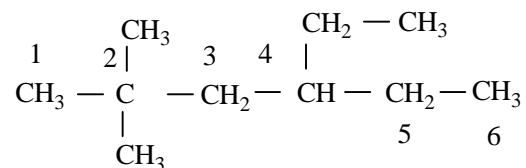
- a. Using the correct numbering system, assign a number to each substituent according to its point of attachment to the main chain e.g.



Substituents : On C<sub>2</sub>, there is a methyl group, and write it as 2-methyl.

On C<sub>3</sub>, there is an ethyl group, and write it as 3-ethyl.

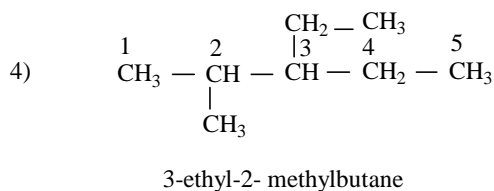
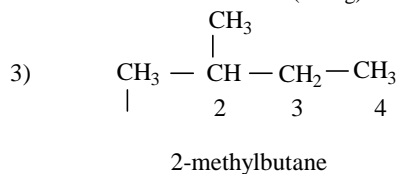
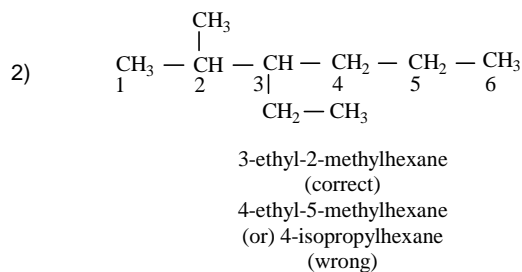
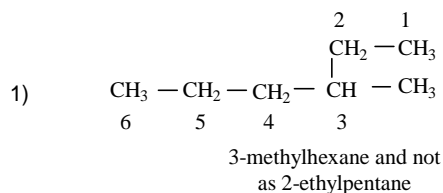
- b. If there are two substituents on the same carbon, give them the same number. There must always be as many numbers in the name as there are substituents :

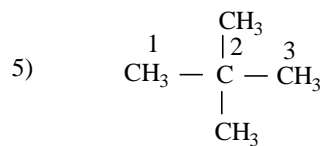


Substituents : On C<sub>2</sub> there are two methyl groups, they are written as 2,2 dimethyl, on C<sub>4</sub> there is an ethyl group, it is written as 4-ethyl.

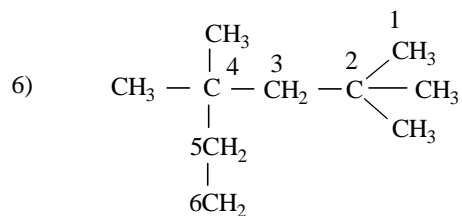
#### Step 4 Final naming

Write out the name as a single word, using hyphens to separate the different prefixes and using commas to separate numbers. If two or more different substituents are present, write them in alphabetical order. If two or more identical substituents are present use one of the prefixes di-, tri-, tetra- and so on. Don't use those prefixes for alphabetising purposes. The following are a few examples adopting the above IUPAC nomenclature.

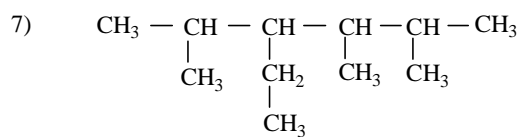




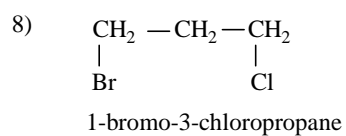
2,2-dimethylpropane



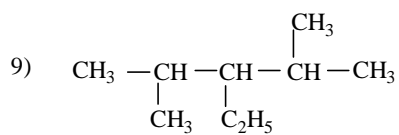
2,2,4,4,-tetramethylhexane



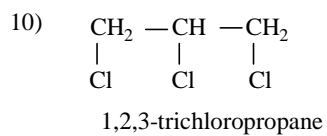
4-ethyl -2, 3-5-trimethylhexane



1-bromo-3-chloropropane



3-ethyl1-2,4-dimethylpentane



1,2,3-trichloropropane

### 18.3 Sources of alkanes (petroleum)

The major sources of alkanes are natural gas and petroleum deposits, which are derived from the decomposition of marine organic matter. Natural gas consists chiefly of methane but ethane, propane, butane and isobutane are also present. Petroleum is a highly complex mixture of hydrocarbons that must be refined into different fractions to get various lower member hydrocarbons.

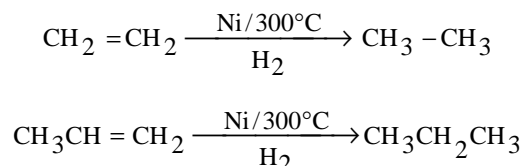
#### Cracking

When higher alkanes are passed through a chamber heated to 400-600°C in the presence of a catalyst (metallic oxides), the products are alkanes with less number of the carbon atoms and this is known as cracking.

### 18.4 General methods of preparation of alkanes

#### (i) By catalytic reduction of alkenes

Many alkenes (olefins) may be reduced by passing their vapours with hydrogen over finely divided nickel supported on Kieselguhr at 200-300°C. This reaction is referred to as the Sabatier-Senderens reduction.



Nickel adsorbs, activates and dissociates molecular hydrogen for addition to olefins.

Finely divided nickel may be replaced by Raney nickel introduced by Raney (1927). It is more active than finely divided nickel. It is active even at room temperature. It is prepared by removing aluminium from Al-Ni alloy using sodiumhydroxide. Olefins can also be hydrogenated at room temperature over platinum or palladium.

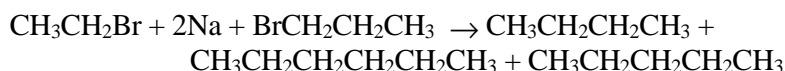
Unsaturated edible oils are hydrogenated to Vanaspathi ghee with nickel catalyst at 300°C.

### (ii) Wurtz reaction

An ethereal solution of an alkyl halide is treated with sodium to obtain an alkane.

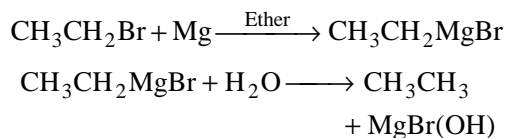


The reaction can be applied to mixed alkyl halides. The products are mixed alkanes.



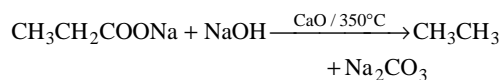
### (iii) From Grignard reagents

Alkyl magnesium halides ( $\text{RMgX}$ ,  $\text{X}$  = halogen) are known as Grignard reagents. Alkyl halides (chloride, bromide or iodide) react with magnesium in dry ether to give Grignard reagents. Grignard reagents react with water or dilute acids to give alkanes.



### (iv) By decarboxylation of carboxylic acids

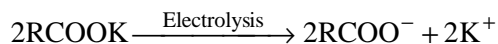
When sodium salts of carboxylic acids are heated with soda lime, alkanes are obtained.

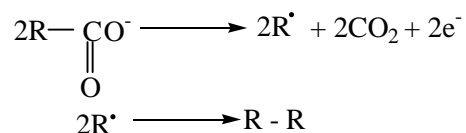
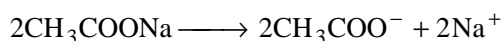
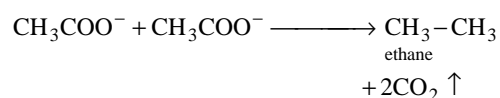


Sodalime is a 3:1 mixture of  $\text{NaOH}$  and  $\text{CaO}$ . The role of  $\text{CaO}$  is to fuse sodium hydroxide.

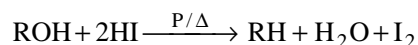
### (v) Kolbe's electrolytic method

When a concentrated solution of sodium or potassium salt of carboxylic acid is electrolysed, a higher homologue of the alkane series is obtained. During electrolysis, the anions ( $\text{RCOO}^-$ ) migrate towards the anode where they get decomposed to alkanes and carbon dioxide.



**At Anode****Example****At Anode****(vi) From alcohols**

Alcohols on heating with concentrated hydroiodic acid and red phosphorous at 150°C under pressure in a sealed tube get reduced to alkanes.

**18.5 Physical Properties**

The dipole moment of all alkanes, whether straight or branched-chain is zero. Hence the alkanes have very weak force of attraction (Vanderwaals forces) between them. The Vanderwaals force increases with increase in the area of contact. Hence in the n-alkanes, owing to their large surface area due to their linear structure, the Vanderwaals force is large. In the branched alkanes the molecules tend to become spherical hence they have less surface area and contact, and less Vanderwaals force. As a consequence these, C<sub>1</sub>-C<sub>4</sub> hydrocarbons are gases, C<sub>5</sub> - C<sub>17</sub> liquids, and from C<sub>18</sub> onwards are solids. The boiling points rise fairly regularly as the number of carbon atoms in the compound increases. Other physical properties such as melting point, density, viscosity etc., also changes, as the chain length of the compound increases.

**Account for the following**

- (i) The boiling point of butane (0°C) is more than 2-methyl propane(-120.0°C).

- (ii) The melting point of n-pentane (-129.7°C) is less than neopentane (-17°C).

### Solution

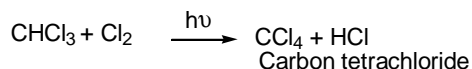
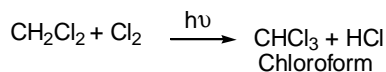
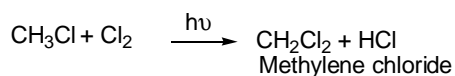
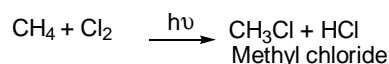
- (i) Due to more Vanderwaal's force of butane.
- (ii) The melting point of alkanes depends on the packing of the molecules in the crystal lattice. Packing in turn depends on molecular size. As neopentane is spherical in shape it will be better packed in the crystal lattice than n-butane. Hence the melting point of n-butane is less than neopentane.

All of them are colourless. Methane is soluble in water, but others are insoluble. Solubility of methane is due to its small molecular size. Due to its small size it can easily diffuse and dissolve in water. A useful rule in organic chemistry with respect to solubility is that 'like dissolves like', e.g., if a compound contains a hydroxyl group, then the best solvents usually contain the hydroxyl groups.

### 18.5.1 Chemical Properties

#### (i) Halogenation

Chlorination and bromination of alkanes may be brought about by light, heat or catalysts. In the presence of ultraviolet light ( $\lambda < 400 \text{ nm}$   $\lambda =$  wavelength of light) or at high temperature all the four hydrogen atoms of  $\text{CH}_4$  may be substituted. The reaction is of free radical type.



Iodides are prepared by treating the chloro- or bromoderivative with sodium iodide in methanol or acetone

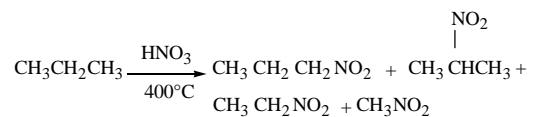


It is easy to separate the product from NaCl as the later is insoluble in methanol or acetone. This reaction is known as the **Finkelstein** or **Conant-Finkelstein** reaction.

Direct fluorination is usually explosive in nature. The great reactivity of fluorine is due to its low dissociation energy ( $150.6 \text{ kJ mol}^{-1}$ ). Also, one of the termination step is  $\text{R}^\bullet + \text{F}^\bullet \rightarrow \text{RF}$ . This reaction is very strongly exothermic (447.7 kJ). The energy liberated is larger than that required to break a C-C single bond (347.3 kJ), thereby resulting in the fragmentation of the organic molecule.

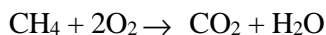
## (ii) Nitration

Nitration of alkanes is carried out between 150 and 475°C, and the reaction yields a complex mixture of products. The reaction may be of free radical type.



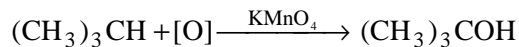
## (iii) Oxidation

Alkanes readily burn in excess air to form  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

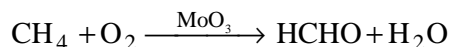


At controlled oxygen supply methane forms carbon black used in the manufacturing of ink and black pigments. It is also used as fillers.

Oxidising agents such as  $\text{KMnO}_4$  readily oxidise isobutane into tertiary butyl alcohol.

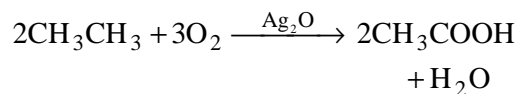


Molybdenum trioxide oxidises methane to formaldehyde



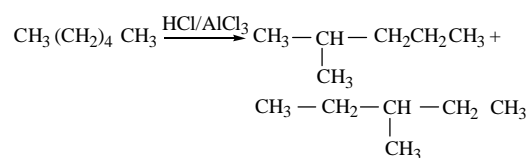
$\text{Ag}_2\text{O}$  oxidises ethane to acetic acid





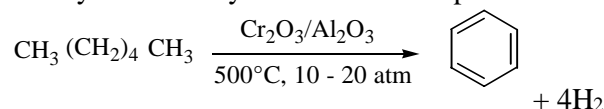
#### (iv) Isomerization

n-Alkanes can be isomerized into branched chain alkanes when heated with anhydrous aluminium chloride and hydrogen chloride at 300°C. The presence of an alkene impurity is shown to be important to initiate isomerization.



#### (v) Aromatization

When alkanes with six or more carbon atoms are passed over hot alumina supported chromium, vanadium or molybdenum oxide, dehydrogenative cyclization to yield aromatic compounds occurs.



$\text{Cr}_2\text{O}_3$  is the catalyst, and  $\text{Al}_2\text{O}_3$  merely disposes  $\text{Cr}_2\text{O}_3$  on it.

### 18.6 Alkenes

Alkenes are hydrocarbons that contain carbon-carbon double bond as functional group. They are otherwise known as olefins. Alkenes occur abundantly in nature. Following table contains details of a few simple alkenes.

Table 18.2

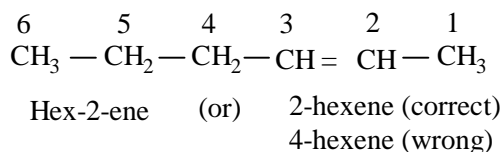
Molecular formula	Structural formula	Common name	IUPAC name
$\text{C}_2\text{H}_4$	$\text{CH}_2 = \text{CH}_2$	Ethylene	Ethene
$\text{C}_3\text{H}_6$	$\text{CH}_3 - \text{CH} = \text{CH}_2$	Propylene	Propene
$\text{C}_4\text{H}_8$	$\text{CH}_3 - \text{CH}_2 - \text{CH} = \text{CH}_2$	Butylene	1 - Butene

IUPAC Nomenclature : Alkenes are named systematically by following a series of rules similar to those followed for alkanes, with the suffix -ene instead of -ane. The following three basic steps are used.

**Step 1 Name the parent hydrocarbon**

Find the longest chain containing the double bond and name the compound accordingly using the suffix -ene.

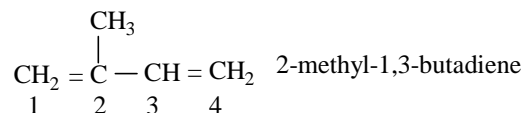
**Step 2** Number the carbon atoms in the chain beginning from the end which is nearer the double bond, e.g:



If the double bond is equidistant from the two ends, give the number from the end which gives the lowest number to the substituent.

**Step 3** If more than one double bond is present, indicate the position of each double bond and use the suffices as -diene, -triene, -tetrene etc.

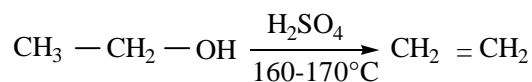
*Example*



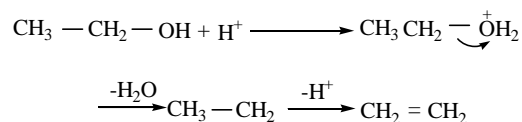
## 18.7 General methods of Preparation of alkenes

### i. By dehydration of alcohols

Alcohols can be dehydrated to olefins by heating with sulphuric acid.



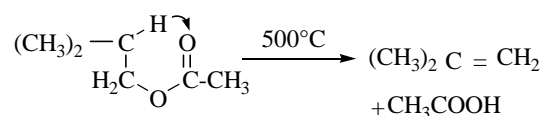
The mechanism is as follows



Sulphuric acid is a catalyst. For this reaction  $\text{H}_3\text{PO}_4$ , anhydrous zinc chloride and alumina can also be used as catalysts.

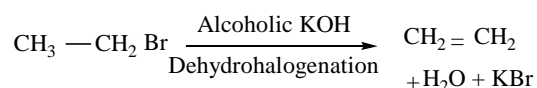
## ii. By pyrolysis of esters

Esters with more than one carbon in the alkyl portion of the esters can be pyrolysed to get olefins.



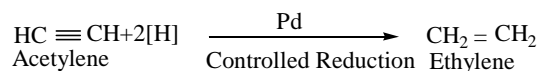
## iii. Dehydrohalogenation of alkyl halides

When an alkyl halide is treated with alcoholic potassium hydroxide, hydrogen halide is removed resulting in the formation of an alkene. For example



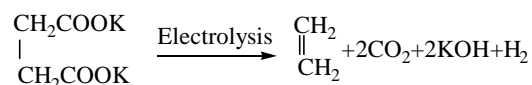
## iv. Hydrogenation of alkynes

Alkynes on controlled reduction with palladium and hydrogen give alkenes. For example



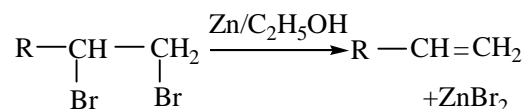
## v. By electrolysis of salts of dicarboxylic acids

Alkenes are formed by the electrolysis of the aqueous solutions of potassium salts of dibasic acids of the succinic acid series.



## vi. Dehalogenation of vicinal halides

Treatment of vicinal dihalides with zinc dust and ethyl alcohol gives the alkenes.

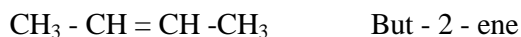


## 18.8 Physical Properties

The olefins with two to four carbon atoms are gases; five to seventeen liquids, eighteen onwards solids at room temperature and they burn in air with luminous smoky flame.

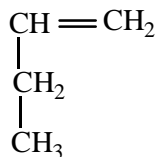
The exhibit isomerism

**i. Position isomerism :** It arises due to position of the double bond in a molecule. Ethene and propene do not show position isomerism, but butene shows.

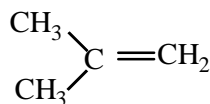


### ii. Chain isomerism

It is due to branching of the linear chain



But-1-ene

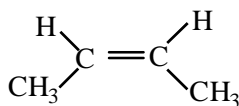


2-Methyl propene-1

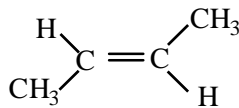
### iii. Geometrical Isomerism

When two isomers differ in their spatial arrangement of atoms or groups, they are said to be stereoisomers. This type of isomerism is called stereoisomerism. Types of stereoisomerism : 1. Optical isomerism, 2. Geometrical isomerism

Geometrical isomers are named as cis and trans compounds depending on whether the identical groups are on the same or opposite sides of the bonds.

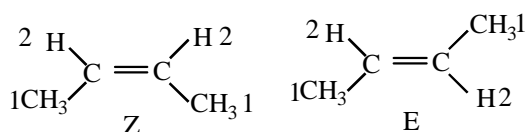


Cis-isomer



Trans-isomer

The necessary and sufficient condition for geometrical isomerism is that the two groups or atoms attached to the same carbon must be different. When the two groups or atoms of highest priority are on the same side of the double bond, the isomer is designated as Z (Zusammen in German means together), and when they are on the opposite sides, the isomer is designated as E (Entegen in German meaning opposite). The priority is decided by the atomic number of atoms to which the olefinic carbons are bonded. The sequence rules given by Cahn - Ingold and Prelog are applied.

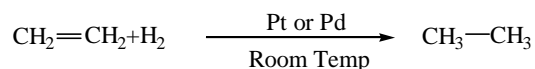


The atoms with the high atomic number is given the number 1 and other 2.

## 18.9 Chemical Properties

### i. Hydrogenation of alkenes

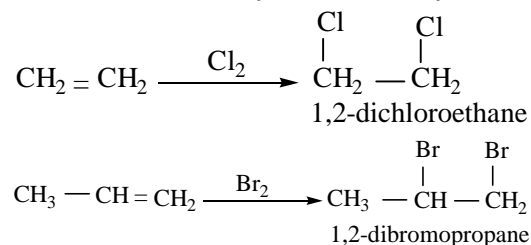
Alkenes can be readily hydrogenated under pressure in the presence of a catalyst.



Nickel supported on alumina is effective between 200 and 300°C (Sabatier -senderens reduction). Raney nickel is effective at room temperature and atmospheric pressure.

### ii. Addition of halogens

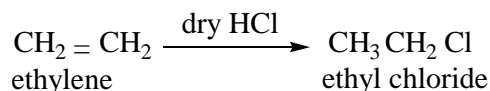
Bromine and chlorine add readily to alkenes to yield dihaloalkanes.



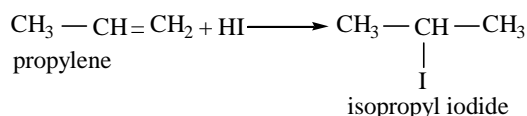
In this reaction bromine will be decolourised and this test is used to detect unsaturation.

### iii. Hydrohalogenation

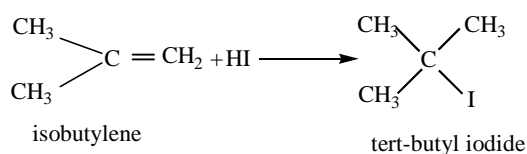
An alkene is converted into the corresponding alkyl halide by HX. The reaction is frequently carried out by passing dry gaseous HX directly into the alkene. For example,



Propylene can yield two possible products namely n-propyl iodide or isopropyl iodide with HI, depending upon the orientation of addition. Actually it is found that isopropyl iodide is the only product obtained.



In the same way, isobutylene can yield either of the two products, isobutyl iodide or tertiary butyl iodide. Here the orientation or addition is such that the tertiary butyl iodide is the only product.



In the above two reactions, though two products are possible, only one of the products is obtained. The Russian chemist Vladimir Markovnikov, explained the reason which is known as Markovnikov's rule, which states that, the negative part of addendum attaches itself to the carbon atom carrying less number of hydrogen atoms.

Carbocations are involved as intermediates in these reactions. Highly substituted carbocation is formed as an intermediate in preference to the less substituted one due to stability.

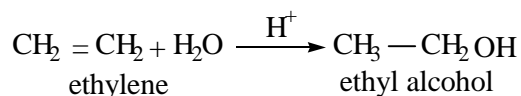


Hence in the above two reactions the formation of only one of the products can be accounted on the basis of the stability of the carbocation

intermediate. When HBr adds to alkene under normal conditions, we know that an intermediate carbocation is formed and Markovnikov's orientation will be observed (electrophilic addition). But in the presence of peroxides the electrophilic addition does not take place and the addition takes place through free radical mechanism.

#### iv. Hydration

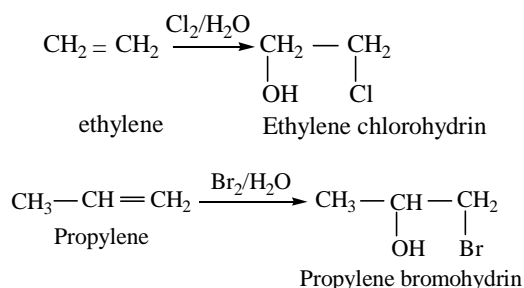
Water can be added to simple alkenes to yield alcohols. This hydration reaction takes place on treatment of the alkene with water in presence of a strong acid-catalyst.



#### v. Halohydrin formation

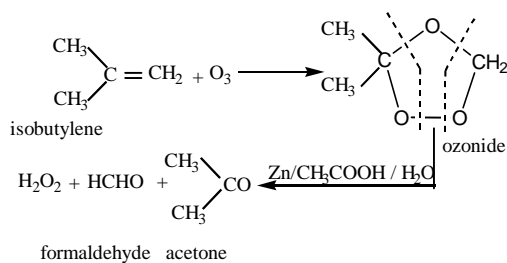
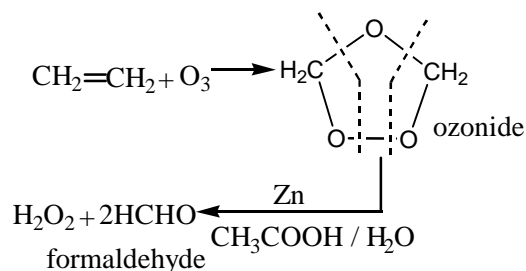
Alkenes can add HOCl or HOBr under suitable conditions to yield 1,2 haloalcohols or halohydrins. Halohydrin formation does not take place by direct reaction of an alkene with the reagents (HOCl or HOBr). But the addition is done indirectly by the reaction of the alkene with either Br<sub>2</sub> or Cl<sub>2</sub> in presence of water.

*Example*



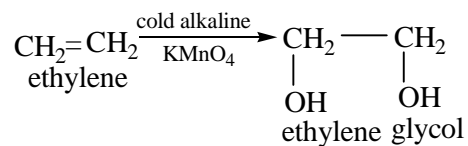
#### vi. Ozonolysis

Ozone is the most useful double bond cleavage reagent. When added to an alkene first an ozonide intermediate is formed. When the ozonide is further treated with a reducing agent such as zinc metal in acetic acid, it is converted into carbonyl compounds.



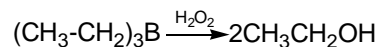
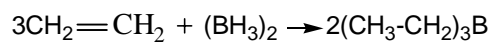
### vii. Hydroxylation

The addition of an -OH group to each of the two alkene carbons can be carried out with alkaline potassium permanganate. This reagent is known as Baeyer's reagent. Ethylene or any alkene decolourises potassium permanganate and this is a test for unsaturation.



### viii. Hydroboration

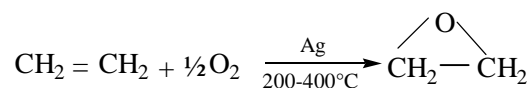
Alkenes readily react with diborane to form trialkyl boranes which on oxidation with alkaline hydrogen peroxide yield primary alcohols.



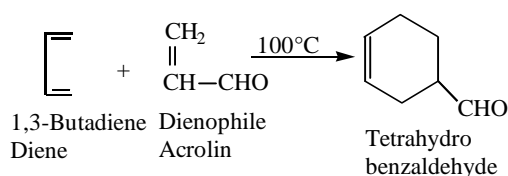


### ix. Epoxidation

When ethylene is mixed with oxygen, under pressure passed over at 200 - 400°C, epoxide is obtained.

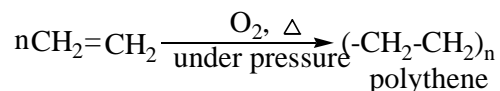


### x. Diels - Alder reaction



**Polymerisation** : A polymer is simply a large molecule built up by many smaller units called "monomers". Conversion of a large number of monomers into a single polymer is known as polymerisation.

When ethylene is heated under pressure in presence of oxygen, a compound of high molar mass known as polyethylene or polythene is formed.



### 18.10 Uses of Alkenes

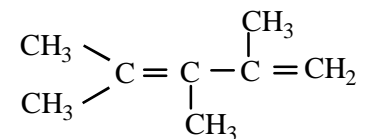
- (i) Ethylene is used for ripening of fruits.
- (ii) Ethylene is used to prepare industrial solvents like ethylene dichloride, glycol, dioxan etc.,
- (iii) Ethylene and propylene are important industrial organic chemicals. They are used in the synthesis of polymers like polythene, polypropylene, pvc, polystyrene, teflon, orlon, acrilan, polyvinyl acetate, polyvinyl alcohol etc.,
- (iv) Ethylene dichloride which is prepared from ethylene is used in the preparation of a synthetic rubber called thiokol.

### 18.10.1 Test for ethylene

- (i) Rapid decolourisation of bromine in carbontetrabromide without evolution of hydrogen bromide.
- (ii) Decolourisation of cold dilute aqueous potassium permanganate solution.

### 18.11 Unsaturated compounds with two or more double bonds

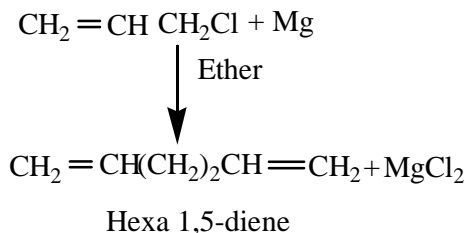
If a hydrocarbon contains two double bonds it is called diolefin or alkadiene. Alkadienes have general formula  $C_nH_{2n-4}$ . In the chain containing the maximum number of double bonds is chosen as the parent hydrocarbon, and the chain is so numbered as to give the lowest possible numbers to the double bonds.



2,3,4 - Trimethyl penta - 1,3-diene

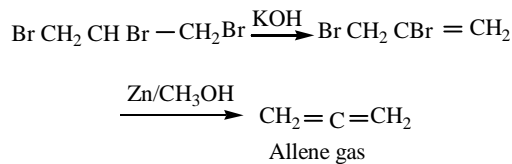
#### Preparation of alkadiene

- i. Alkadienes with isolated double bonds



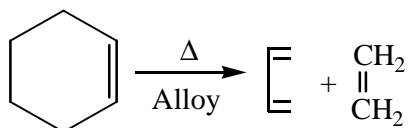
- ii. Alkadienes with cumulative double bonds

By heating 1,2,3-tribromopropane with solid KOH and then treating the resulting 2,3- dibromopropene with zinc dust in methanol.



- iii. Preparation of alkadienes with conjugated double bonds.

Buta - 1,3 - diene can be obtained by passing cyclohexene over a heated nichrome wire (an alloy of Ni, Cr and Fe).



Butadiene is used in the manufacture of Buna rubber.

### 18.12 Alkynes

**Alkynes** are also called acetylenes. They are hydrocarbons that contain a carbon-carbon triple bond. The first and the most important member of this series is acetylene and hence these are called acetylenes.

**IUPAC nomenclature of alkynes :** Alkynes follow the general rule of hydrocarbon nomenclature. The suffix -yne is substituted for '-ane' in the base hydrocarbon name to denote alkyne and the position of the triple bond is indicated by its number in the chain. Numbering begins from the chain end which is nearer the triple bond.

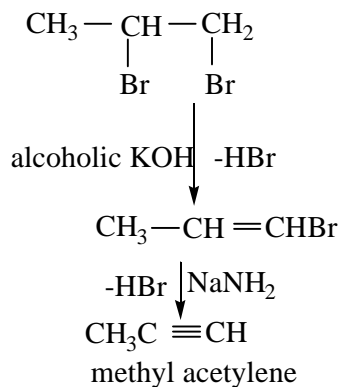
The following table contains details along a few of the simple alkynes.

**Table 18.3**

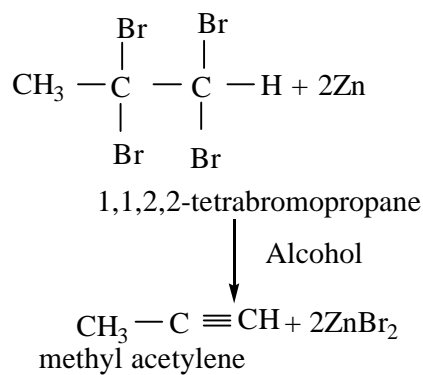
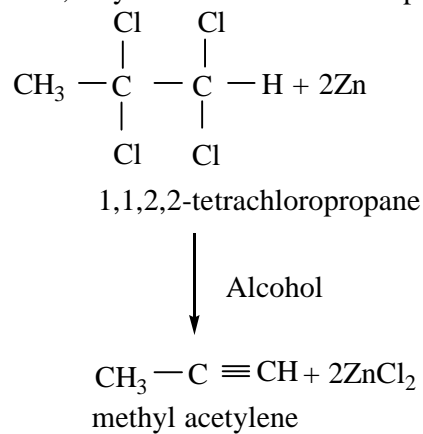
Structural formula	Common name	IUPAC name
$\text{CH} \equiv \text{CH}$	acetylene	ethyne
${}^3\text{CH}_3 {}^2\text{C} \equiv {}^1\text{CH}$	methyl acetylene	1-propyne
${}^4\text{CH}_3 {}^3\text{CH}_2 {}^2\text{C} \equiv {}^1\text{CH}$	ethyl acetylene	1-butyne
$\text{CH}_3 - \text{C} \equiv \text{C} - \text{CH}_3$	dimethyl acetylene	2-butyne

#### General methods of preparation

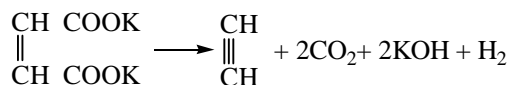
**(i) Dehydrohalogenation of vicinal dihalides :** Compounds that contain halogen atoms on adjacent carbon atoms are called vicinal dihalides. Alkynes are obtained by treatment of vicinal dihalides with alcoholic KOH followed by treatment with sodamide ( $\text{NaNH}_2$ ). For example



(ii) Dehalogenation of tetrahalides : When 1,1,2,2-tetrahalide is heated with zinc dust in alcohol, alkyne is formed. For example,



Electrolysis of salts of unsaturated dicarboxylic acids.



### 18.13 Physical properties of alkynes

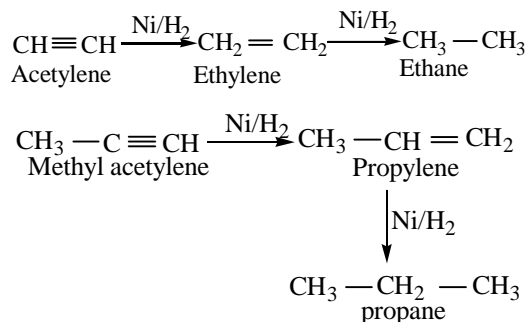
Alkynes have physical properties that are essentially the same as those of alkanes and alkenes. They are insoluble in water but quite soluble in organic solvents like benzene, carbon tetrachloride, ether etc. They are less dense than water. Their boiling points and melting points show a regular increase with increasing carbon number and the usual effects of chain branching are also observed.

### 18.14 Reactions of alkynes

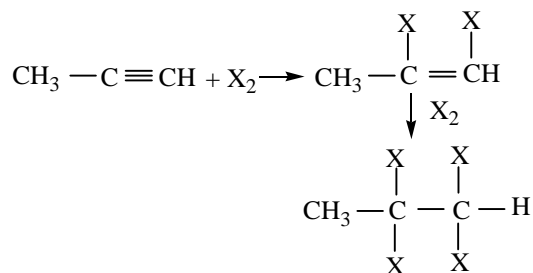
Alkynes contain carbon-carbon triple bond. One of them is strong carbon-carbon sigma ( $\sigma$ ) bond and the other two are weak carbon-carbon pi ( $\pi$ ) bonds. Alkynes undergo addition reactions with other compounds due to the cleavage of these weak pi ( $\pi$ ) bonds.

(i) **Addition of hydrogen** : Alkynes are easily converted to alkanes by addition of hydrogen in the presence of metal catalyst like nickel, platinum or palladium.

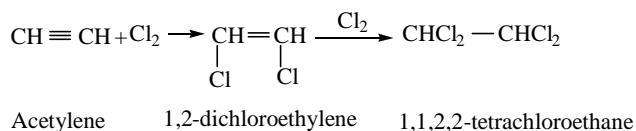
#### *Example*



(ii) **Addition of halogens** : Two molecules of halogens add to alkynes in two steps forming dihalides and then tetrahalides

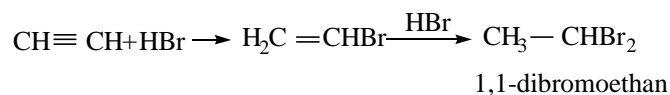


Direct combination of  $\text{C}_2\text{H}_2$  with chlorine may explode and this is prevented by using a metal chloride catalyst.

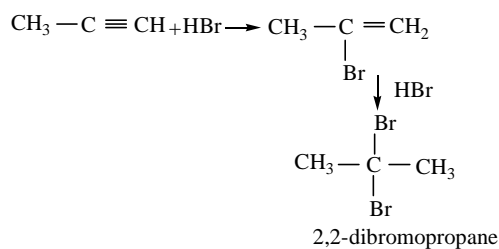


**(iii) Addition of halogen acids :** Halogen acids add to alkynes in the same way as in alkenes and give the expected addition product. Halogen acids add to symmetrical alkynes in two stages. After one molecule of the acid is added to a symmetrical alkyne, the product is an unsymmetrical derivative of alkene. The addition of a second molecule of the acid takes place in accordance with Markonikov's rule.

**Example**

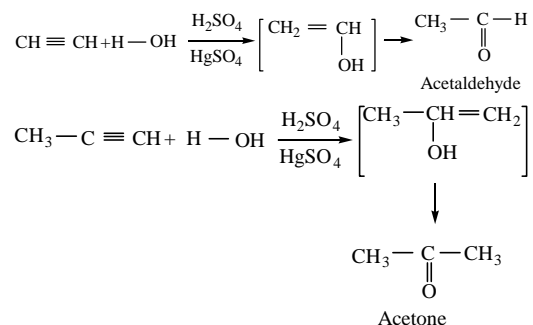


The addition of halogen acid to unsymmetrical alkynes follows Markonikov's rule both in the first and second steps.



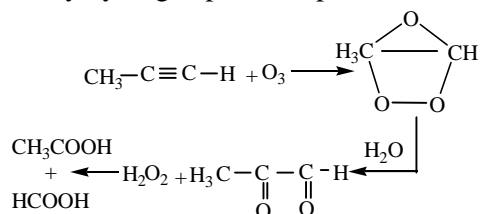
Peroxides have the same effect on the addition of hydrogen bromide to alkynes as in alkenes.

### Example

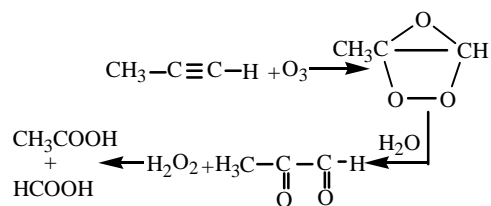

$$\text{CH}\equiv\text{CH}+\text{HOCl}\rightarrow\left[\begin{array}{cc}\text{CH}=\text{CH} \\ | \quad | \\ \text{Cl} \quad \text{OH}\end{array}\right]\xrightarrow{\text{HOCl}}\text{Cl}_2\text{CHCHO}$$

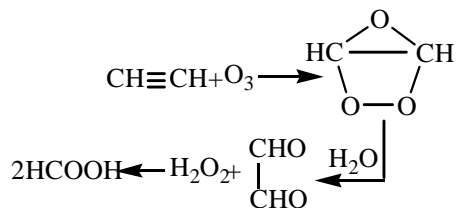
dichloroacetaldehyde

(vi) **Addition of ozone :** Alkynes react with ozone to give ozonides. These ozonides get decomposed with water to yield diketones. Diketones are oxidised to acids by hydrogen peroxide produced in the reaction.



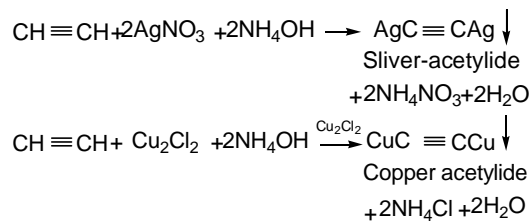
Acetylene is an exception as it gives both glyoxal and formic acid with ozone.



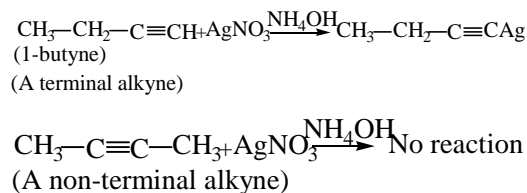


**(vii) Reactions of acidic hydrogen :** The most striking difference between alkenes and alkynes is that terminal alkynes are weakly acidic. In alkynes  $sp$  hybridization is taking place in carbon atoms and so they exhibit 50%  $s$  character. Hence an alkyne attracts the electrons towards itself and therefore the terminal H can be removed as  $\text{H}^+$ . When acetylene is passed into ammoniacal silver nitrate solution silver acetylide (white) is precipitated respectively.

**Example**



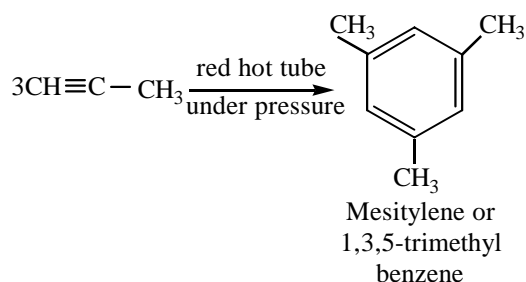
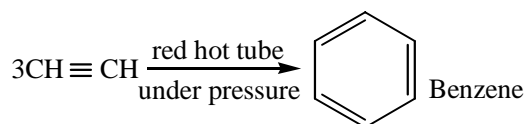
Dry copper and silver acetylides are very sensitive to shock and may explode violently. However, they can be decomposed by nitric acid to regenerate alkynes. This type of reaction is possible with only terminal alkynes. Non-terminal alkynes will not give this reaction.



Thus this reaction can be used to differentiate terminal alkynes and non-terminal alkynes.



**(viii) Polymerisation :** When alkynes are passed through red hot iron tube under pressure they polymerise to aromatic compounds. For example acetylene polymerises to benzene and propylene polymerises to mesitylene.



#### 18.14.1 Tests for acetylene

- (i) Acetylene decolourises bromine water.
- (ii) Acetylene decolourises alkaline potassium permanganate solution
- (iii) With ammoniacal solution of cuprous chloride it gives a red precipitate of cuprous acetylide.
- (iv) With ammoniacal solution of silver nitrate it gives a white precipitate of silver acetylide. The tests (iii) and (iv) will not be answered by ethylene and these two tests can be used to distinguish ethylene from acetylene.

#### 18.14.2 Uses of alkynes

- (1) Acetylene is used as a starting material for manufacture of industrially important compounds like acetaldehyde, acetone and benzene.
- (2) Acetylene is used in oxyacetylene torch used for welding and cutting metals.
- (3) Westron, a solvent which is tetrachloro derivative of acetylene is prepared from acetylene.
- (4) Acetylene is used as a starting material for the manufacture of PVC, polyvinyl acetate and synthetic rubber.

## Questions

### A. Choose the correct answer

- 1) Alkanes can be represented by the formula
  - a)  $C_nH_{2n+2}$
  - b)  $C_nH_{2n}$
  - c)  $C_nH_{2n-2}$
  - d)  $C_nH_{2n-3}$
- 2) Alkenes are represented by the formula
  - a)  $C_nH_{2n+2}$
  - b)  $C_nH_{2n}$
  - c)  $C_nH_{2n-2}$
  - d)  $C_nH_{2n-3}$
- 3) Alkynes are represented by the formula
  - a)  $C_nH_{2n+2}$
  - b)  $C_nH_{2n}$
  - c)  $C_nH_{2n-2}$
  - d)  $C_nH_{2n-3}$
- 4) The type of substitution reaction that takes place when methane is treated with  $Cl_2$  in presence of light
  - a) ionic
  - b) electrophilic
  - c) nucleophilic
  - d) radical
- 5) When n-hexane is passed over hot alumina supported chromium, vanadium or molybdenum oxide the compound formed is
  - a) cyclopentane
  - b) cyclohexane
  - c) toluene
  - d) benzene
- 6) When the identical groups are on the same or opposite sides of the bonds in alkenes the isomerism is called as
  - a) chain isomerism
  - b) geometrical isomerism
  - c) position isomerism
  - d) optical isomerism
- 7) Diels-Alder reaction is the reaction between
  - a) diene and dienophile
  - b) electrophile and nucleophile
  - c) oxidant and reductant
  - d) none.
- 8) Unsaturated compounds with two double bonds are called as
  - a) diene
  - b) alkadiene
  - c) olefins
  - d) paraffins.
- 9) The hybridization of carbons in ethylene is
  - a)  $sp^2$
  - b) sp
  - c)  $sp^3$
  - d)  $dsp^2$

- 10) Alcohols can be dehydrated to olefins using
  - a)  $\text{H}_2\text{SO}_4$       c) Pd
  - b)  $\text{SOCl}_2$       d) Zn/Hg
- 11) When alkyl halides are treated with alcoholic KOH, the products are
  - a) olefins      c) alcohols
  - b) alkanes      d) aldehydes
- 12) Witting reaction is used to prepare
  - a) an alkene      c) an alkane
  - b) an alkyne      d) none of the above.
- 13) Electrolysis of potassium succinate gives
  - a) ethylene      c) acetylene
  - b) ethane      d) none of the above.

**B. Fill up the blanks**

- 1) In alkanes, the carbon atoms are connected by \_\_\_\_\_ bonds.
- 2) Treatment of 1,2-dibromopropane with zinc and ethanol gives \_\_\_\_\_.
- 3) Cis But-2-ene is an \_\_\_\_\_ isomer.
- 4) Addition of HCl to an olefin follows \_\_\_\_\_ rule.
- 5) An alkene reacts with ozone to form \_\_\_\_\_.
- 6)  $\text{CaC}_2$  on hydrolysis gives \_\_\_\_\_.
- 7) Ethylenedibromide on treatment with KOH gives \_\_\_\_\_.
- 8) Electrolysis of sodium maleate gives \_\_\_\_\_.

**C. Explain briefly on the following**

- 1) Mention any five chemical properties of alkanes.
- 2) Discuss the general methods of preparing alkanes.
- 3) What is hydroboration?
- 4) What is ozonolysis?
- 5) What is witting reaction?
- 6) What is polymerisation?
- 7) How is ethylene hydrated?
- 8) What is the action of ozone on acetylene.
- 9) What happens when acetylene is passed through red-hot tube?

## 19. AROMATIC HYDROCARBONS

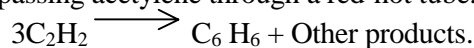
### OBJECTIVES

*The main objectives of this chapter are to provide*

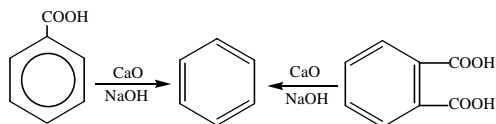
- *Details of nomenclature of aromatic hydrocarbons.*
- *Detail discussion on structure of benzene*
- *Explanatory note on aromaticity*
- *A discussion on orientation in aromatic electrophilic substitution*
- *General methods of preparation of benzene homologues*
- *Some examples for electrophilic substitution and some preliminary discussion of poly cyclic aromatic hydrocarbons.*

Natural sources like resins, balsams, aromatic oils etc., contain aliphatic compounds, and also a group of compounds with pleasant odour. These odorous compounds were arbitrarily classified as aromatic (Greek : aroma : pleasant smell). Most of the simple aromatic compounds were found to contain six carbon atoms. Further when aromatic compounds were subjected to various methods of treatment, they often produced benzene or a derivative of benzene. Hence these aromatic compounds are called benzenoid compounds.

Benzene, C<sub>6</sub>H<sub>6</sub>, was first isolated by Faraday (1825) from cylinders of compressed illuminating gas obtained from the pyrolysis of whale oil. In 1845, benzene was found in coal-tar by Hofmann, and this is still a source of benzene and its derivatives. Benzene was first synthesised by Berthelot (1870) by passing acetylene through a red-hot tube.



It may be prepared in the laboratory by decarboxylation of aromatic acids.

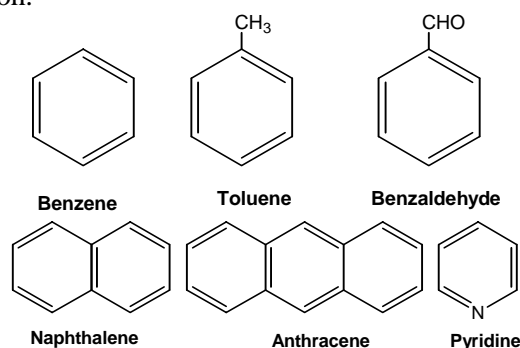


In the early days of organic chemistry the word aromatic was used to describe fragrant substances such as benzaldehyde, toluene etc. It was soon realised that substances grouped as aromatic behaved in a chemically different manner from other organic compounds. Today, we use the term aromatic to refer to benzene and its structural homologues. In this section,

aromatic compounds showing chemical properties quite different from that of aliphatic compounds are dealt with.

Many compounds isolated from natural sources are aromatic in part. In addition to benzene, toluene and benzaldehyde, complex compounds such as the female steroidal hormone estrone and the well known analgesic, morphine have aromatic rings. Many synthetic drugs used medicinally are also aromatic in part.

Benzene is the first member in the aromatic series of compounds. The whole series of compounds which contain one or more benzene rings in their molecules are called aromatic compounds. Certain heterocyclic compounds like pyridine which do not have benzene rings also come under this classification.



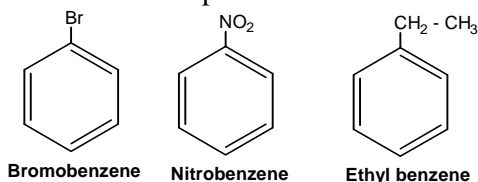
### Commercial preparation of benzene from coal tar

The two main sources of aromatic hydrocarbons are coal and petroleum. Coal is a complex substance made of primarily large arrays of highly unsaturated benzene like rings linked together. When coal is heated to 1000°C in the absence of air, thermal break down of coal molecules occur and a mixture of volatile products called "coaltar" distills off. The coaltar forms the source of many organic compounds. Further distillation of coaltar yields benzene, toluene, xylene, naphthalene and a host of other aromatic compounds.

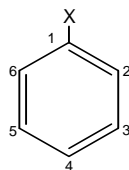
### 19.1 Nomenclature of aromatic compounds

Aromatic compounds acquired a large number of common, nonsystematic names. Although the use of such names is discouraged, IUPAC rules allow for some of the more widely used ones to be retained. eg. methyl benzene is familiarly known as toluene, hydroxy benzene as phenol, aminobenzene as aniline and so on. Mono substituted benzene

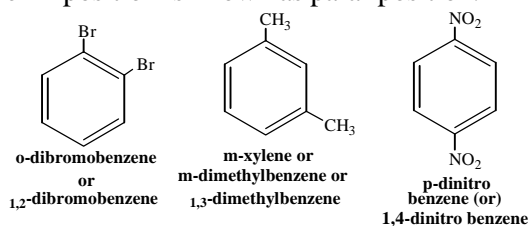
derivatives are systematically named in the same manner as other hydrocarbons with benzene as the parent name.



Disubstituted benzene derivatives are named using one of the prefixes ortho, meta or para. In a benzene ring there are six carbon atoms and they can be numbered as follows :

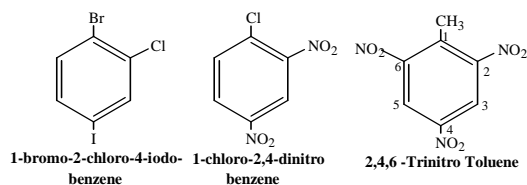


The 2 and 6 positions or the adjacent positions are known as ortho-positions. 3 and 5 or the alternate positions are known as meta-positions and the only one 4<sup>th</sup> position is known as para- position.



Benzene with more than two substituents must be named by numbering the position of each substituent on the ring. The numbering should be done in such a way that the lowest possible numbers are given to the substituents and the substituents are listed alphabetically.

#### Example



### 19.1.1 Aromaticity

Compounds which contain benzene rings or a condensed system of benzene rings have the following properties which are not shown by the analogous aliphatic and alicyclic compounds.

- They readily undergo substitution reactions.
- They are thermally stable.
- They resist addition and oxidation reactions.
- With respect to benzene the enthalpy of hydrogenation, the enthalpy change, when one mole of an unsaturated compound is hydrogenated is much smaller ( $-208.5\text{ kJ mol}^{-1}$ ) than the corresponding calculated value for hypothetical 1,3,5 - cyclohexatriene ( $-359.1\text{ kJ mol}^{-1}$ )

These distinguishing properties led to seek an explanation and define the term aromaticity.

#### Aromaticity in other related systems

The modern theory of aromaticity was introduced by Huckel in the year 1937. Delocalized electronic cloud and coplanar structure the compound are important for aromaticity. Any polynuclear compound, heterocyclic rings or cyclic ions may be aromatic if they are planar and have  $4n + 2$  ( $n = 0, 1, 2, 3$  etc) delocalized  $\pi$  electrons in a closed shell. Thus to be aromatic, a molecule must have  $2(n=0)$ ,  $6(n=1)$ ,  $10(n=2)$ .....  $\pi$  electrons.

### 19.1.2 Orientation in aromatic electrophilic substitution

Orientation in aromatic electrophilic substitution reactions of benzene aims at locating the position of the incoming substituent with respect to the one that is already present. The substituent which is already present in the ring directs the incoming group either to ortho and para or to meta position, and changes the reaction rate higher or lower than benzene.

If a substituent directs the incoming group to ortho and para positions, it is called ortho, para - directing, and if it directs to meta position it is called meta-directing. The substituents that increase the rate of substitution compared to benzene are called activating and those decreasing the rate are called deactivating. The activating groups increase the rate by increasing the electron density of ring, but the deactivating groups decrease the rate by decreasing the electron density of the ring.

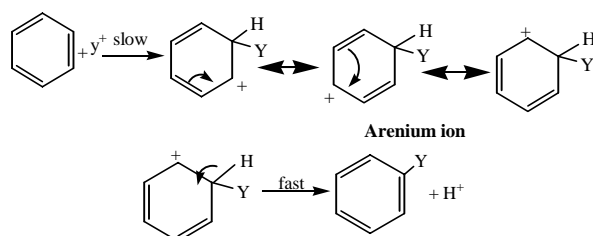
#### Ortho and Para Directing Groups

R, OH, OR,  $\text{NH}_2$ , NHR,  $\text{NHCOCH}_3$ , Cl, Br, I, F, SH etc.

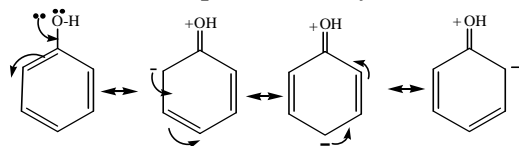
### Meta-Directing Groups

$\text{NO}_2$ ,  $\text{CHO}$ ,  $\text{COOH}$ ,  $\text{COOR}$ ,  $\text{SO}_3\text{H}$ ,  $\text{CN}$ ,  $\text{NH}_3^+$  etc. The directive influence of these groups are found to be predominant but not exclusive. Halogens behave in a different way, they are ortho, para-directing but deactivating as they withdraw electronic cloud from the ring.

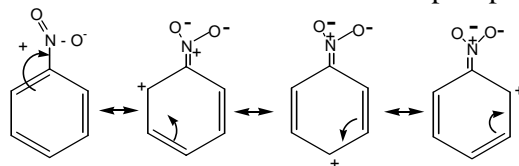
The orientation and activating or deactivating influence of the substituents can be explained based on the resonance and inductive effect of the substituents on the stability of the intermediate arenium ions formed in electrophilic substitution reactions as shown below.



With ortho and para directing groups, for example,  $\text{OH}$ , there is increased negative charge on the ortho and para positions as shown below. Hence electrophilic substitution predominantly occurs at these positions.



With meta directing groups positive charge is created on the ortho and para positions, but the meta positions are free of such charges, and hence these positions are more reactive than the ortho and para position.

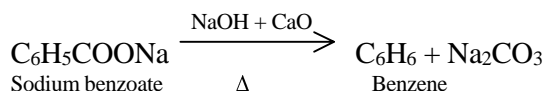


## 19.2 General methods of preparation of benzene and its homologous series

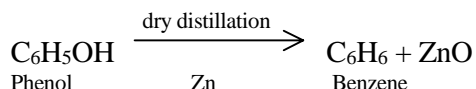
(i) **From aromatic acids** : When sodium salt of aromatic acids are heated with sodalime, the corresponding aromatic hydrocarbon is formed.



**Example**



(ii) When phenol is dry distilled with zinc dust benzene is formed.



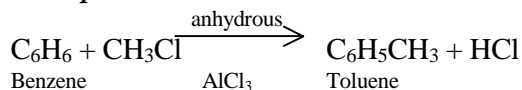
**(iii) Wurtz-Fittig reaction :** The derivatives of benzene can be prepared by a reaction known as Wurtz-Fittig reaction. When a mixture of aryl halide and an alkyl halide is treated with metallic sodium the derivatives of benzene are formed.

**Example**



**(iv) Friedel-Craft's reaction :** Benzene reacts with alkyl halides in presence of anhydrous aluminium chloride as catalyst to form alkyl benzenes.

**Example**



### 19.2.1 Commercial preparation of benzene

#### From Petroleum

Naphtha obtained by fractional distillation of petroleum is passed over platinum supported on alumina catalyst, benzene, toluene and other homologous of benzene are produced.

This process is now used for the large scale production of benzene and its homologous (toluene xylene). Benzene is separated from the resulting mixture by solvent extraction and by fractional distillation. 90% of commercial benzene is obtained from petroleum.

### 19.3 Physical Properties

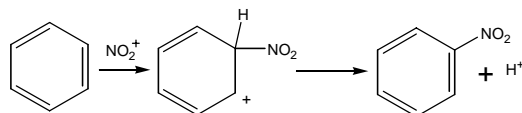
They are colourless liquids or solids with characteristic. They are insoluble in water but are miscible in all proportions with organic solvents such as ethanol, ether etc. They are inflammable, and burn with sooty flame. They are toxic and carcinogenic in nature. The boiling points increase with increase in molecular weight, but their melting points do not exhibit regular gradation. Melting point seems to depend on molecular symmetry than on molecular weight.

### 19.4 Chemical Properties : Reactions of aromatic compounds

Aromatic compounds readily undergo electrophilic substitution reactions. The reactions are normally irreversible and the products formed are kinetically controlled. Sulphonation of aromatics is reversible and at high temperature thermodynamically stable products predominate. There are three steps in electrophilic substitution on aromatics. In the first step an electrophile is produced, in the second step the electrophile attacks the aromatic ring to give an arenium ion, and in the third step the arenium ion gives out a proton to form the final product.

#### (1) Nitration

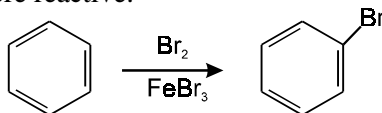
It is carried out in most of the cases with concentrated sulphuric acid and nitric acid. The temperature is between 30-40°C.  $\text{HNO}_3$  acid gives nitronium ion after protonation.



$\text{NO}_2^+$  is an electrophile. It attacks the benzene to give an arenium ion, and the later gives out a proton to yield nitrobenzene.

#### (ii) Halogenation

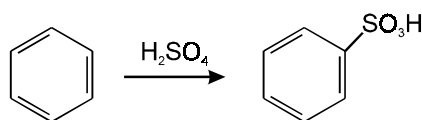
Benzene can be halogenated with chlorine and bromine in the presence of Lewis acid which, assists polarization of the attacking halogen molecule, thereby making it more reactive.



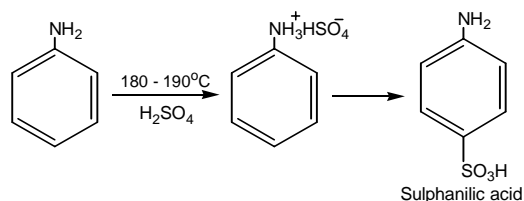
Fluorine reacts vigorously with aromatic hydrocarbons even in the absence of catalyst, however, iodine is very un reactive even in the presence of a catalyst.

### (iii) Sulphonation

Aromatic compounds react with concentrated sulphuric acid to give arene sulphonic acid. The electrophile is  $\text{SO}_3$ . Although it does not have positive charge, it is a strong electrophile. This is because the octet of electrons around the sulphur atom is not reached.

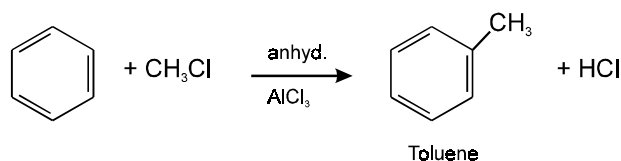


Aniline reacts with sulphuric acid to give a salt, which on strong heating rearranges to sulphanilic acid.



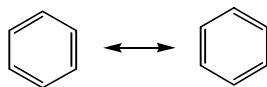
### (iv) Friedel Crafts Alkylation

It is an important reaction to prepare alkyl aromatics. Alkylation of aromatic hydrocarbon is achieved using alkylhalide and aluminium trihalide (Lewis Acid).



## 19.5 Resonance in benzene

- 1) The phenomenon in which two or more structures can be written for substance which involve identical position of atoms is called resonance. A double headed arrow ( $\leftrightarrow$ ) used to represent the resonance hybrid.



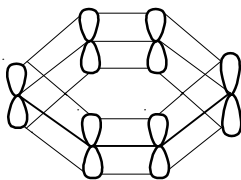
- 2) Structure of benzene is a single, unchanging hybrid structure that combines the characteristics of both resonance forms.
- 3) Resonance structures differ only in the position of their electrons. Different resonance structures of a substance need not be equivalent.
- 4) The resonance hybrid is more stable than any individual resonance structure.
- 5) More the resonance structures for a molecule more stable the molecule is.

### 19.6 Structure of benzene

The unusual stability of benzene was a great puzzle in the early days.

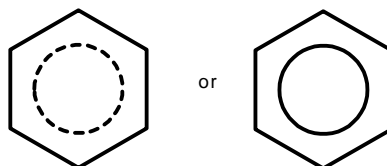
- 1) Although benzene with the molecular formula,  $C_6H_6$  indicates the presence of unsaturation and the Kekule's structure proposes three carbon-carbon double bonds, it does not show any of the characteristic behaviour of alkenes.
- 2) For example, alkenes react readily with potassium permanganate to give cleaved products, undergo addition reactions with acids followed by hydrolysis to give alcohols and react with HCl to give saturated alkyl chlorides. However benzene does not exhibit any of the above reactions.
- 3) In the presence of platinum benzene reacts with hydrogen to give cyclohexane, six membered ring. This proves that benzene is a hexagonal molecule with three double bonds.
- 4) However, benzene reacts with bromine in the presence of iron to give substituted  $C_6H_5Br$  rather than the possible addition product of  $C_6H_6Br_2$ . Further only one monobromo substitution product was formed. No isomers of  $C_6H_5Br$  was identified.
- 5) On further reaction with bromine three isomeric disubstituted products.  $C_6H_4Br_2$  are formed. On the basis of these results Kekule proposed that benzene consists of ring of carbon atoms with alternate single and double bonds.

- 6) The structure can readily account for the formation of a single mono substituted product and three disubstituted isomers (o-, m- and p-) since all six carbon atoms and all six hydrogen atoms are equivalent.
- 7) X-ray and electron diffraction studies indicated that all carbon-carbon bonds are of equal length 1.39 Å which is in between that of a single bond (1.54 Å) and that of a double bond (1.34 Å).
- 8) Localised chemical bonding may be defined in which the electrons are shared by two nuclei only. The delocalised chemical bonding is one in which electrons are shared by more than two nuclei. Certain compounds contain one or more bonding orbitals that are not restricted to two atoms, but spread over three or more atoms. Such bonding is said to be delocalised bonding.
- 9) Benzene is a flat hexagonal molecule with all carbons and hydrogen lying in the same plane with a bond angle of 120°. Each carbon atom has  $sp^2$  hybridisation.
- 10) The  $sp^2$  hybrid orbitals of carbon overlap with each other and with 's' orbitals of six hydrogen atoms forming six sigma ( $\sigma$ ) C-H bonds and six sigma ( $\sigma$ ) C-C bonds.
- 11) There are six p orbitals perpendicular to the plane containing six carbon atoms. Since all the six p orbitals are parallel to each other in benzene and are equivalent, it is not possible to define three localised alkene type pi ( $\pi$ ) bonds, in which a p orbital overlaps with only one neighbouring p orbital. In benzene each p orbital overlaps equally well with both neighbouring p orbitals leading to a picture of benzene in which the six pi ( $\pi$ ) electrons are completely delocalised around the ring. Thus benzene has two clouds of electrons one above and one below the ring. This is represented as follows.



### The delocalisation of $\pi$ orbitals in benzene

- 12) Thus the structure of benzene is now represented with either a full or a dotted circle to indicate the equivalence of all carbon-carbon bonds.

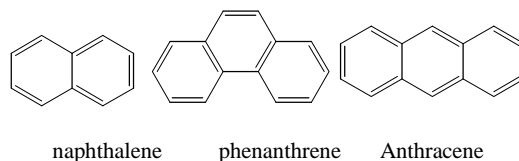


### 19.7 Uses

1. Benzene is used as a solvent for the extraction of fats and oils.
2. It is used as fuel along with petrol.
3. It is used for the production of maleic anhydride

### 19.8 Polynuclear aromatic hydro carbons

They have two or more fused aromatic rings. They have at least two adjacent carbons shared by aromatic rings. Some examples of these compounds which are carcinogenic.



### Questions

#### A. Choose the best answer :

1. Aromatic compounds are
  - a) benzenoid compounds
  - b) non-benzenoid compounds
  - c) aliphatic compounds
  - d) alicyclic compounds
2. Benzene was first isolated by
  - a) Huckel
  - b) Faraday
  - c) Hofmann
  - d) Barthelot
3. Benzene undergoes
  - a) addition reactions
  - b) oxidation reactions
  - c) polymerisation reactions
  - d) electrophilic substitution reactions

4. The modern theory of aromaticity was introduced by
  - a) Faraday                      c) Hofmann
  - b) Huckel                      d) Berthelot
5. Any compound can be aromatic if they have \_\_\_\_\_ delocalised  $\pi$  electrons.
  - a)  $4n + 2$                       b)  $4n + 1$                       c)  $4n$                       d)  $4n - 2$
6. The function of  $\text{FeCl}_3$  in chlorination of benzene is to produce
  - a)  $\text{Cl}$                       b)  $\text{Cl}^+$                       c)  $\text{Cl}^-$                       d)  $\text{C}$
7. The ortho and para directing groups are
  - a) activating group                      b) deactivating group                      c) both                      d) none
8. The purpose of adding conc.  $\text{H}_2\text{SO}_4$  in nitration of benzene is to produce
  - a)  $\text{NO}_2$                       b)  $\text{NO}_2^-$                       c)  $\text{NO}_2^+$                       d)  $\text{NO}_3^-$
9. An example of polycyclic aromatic hydrocarbon
  - a) pyridine                      b) pyrrole                      c) naphthalene                      d) cyclohexane
10. The compound which is used as a solvent for the extraction of fats and oils
  - a) naphthalene                      b) benzene                      c) cyclohexane                      d) butane

**B. Fill in the blanks**

1. Many synthetic drugs used are \_\_\_\_\_ in part.
2. The \_\_\_\_\_ forms the source of many organic compounds.
3. The modern theory of aromaticity was introduced by \_\_\_\_\_.
4. Ortho and para directing groups are called as \_\_\_\_\_ groups.
5. Meta directing groups are called as \_\_\_\_\_ groups.
6. Alkyl substituted benzenes are prepared by \_\_\_\_\_ reaction.
7. Naphtha obtained by fractional distillation of \_\_\_\_\_ is passed over platinum.
8. Aromatic compounds readily undergo \_\_\_\_\_ substitution reactions.
9. \_\_\_\_\_ reacts vigorously with aromatic hydrocarbons even in the absence of catalyst.
10. In the presence of \_\_\_\_\_ benzene reacts with hydrogen to give cyclohexane.

**C. Explain briefly on the following**

1. How is benzene is prepared commercially?
2. Explain the term aromaticity.
3. Write a note an activating groups in benzene.
4. How would you convert the following?
  - a) sodium benzoate to benzene
  - b) phenol to benzene
  - c) benzene to toluene
5. Write briefly on resonance in benzene.

**SUMMARY**

- Aromatic compounds are called as benzenoid compounds.
- Benzene is the first member in the aromatic series of compounds.
- Coal is a complex substance made of primarily large arrays of highly unsaturated benzene like rings linked together.
- Delocalized electronic cloud and coplanarity of the compound are important for aromaticity.
- Aromatic compounds readily undergo electrophilic substitution reactions.

**REFERENCES**

1. Organic Chemistry, I.L. Final volume 1, ELBS Edition.
2. Organic Chemistry, Morrison and Boyd.



## 20. ORGANIC HALOGEN COMPOUNDS

### OBJECTIVES

*The main objectives of this chapter are*

- \* *to highlight the medicinal importance of certain halogenated compounds.*
- \* *to understand the physical and chemical properties of the organic halogen compounds.*
- \* *to give brief account of classification and nomenclature of these compounds.*
- \* *to discuss mechanisms of substitution and elimination reactions which are important to halogen compounds.*
- \* *to provide students more exposure to named organic reactions.*
- \* *to raise the capability of students to design new synthetic routes for interested target materials.*
- \* *to provide proof that how much important these compounds are as intermediates in the synthesis of wide variety of organic compounds.*

In organic halogen compounds F, Cl, Br and I are bonded to the carbons of the aliphatic, aromatic and aralkyl hydrocarbons. Many organic halogen compounds occur in nature and some of them have medicinal value. Chloromycetin is a naturally occurring halogen compound used in the treatment of typhoid fever. Thyroxine is yet another one used in the treatment of goitre. There are many synthetic organic halogen compounds few of which are important in health care and medicine. Two such compounds to cite are chloroquine and halothane. The former is used in the treatment of malaria and the later is used as an anaesthetic during surgery. There are also compounds which are important in agriculture and industry, as intermediates in the synthesis of wide variety of other organic compounds.

### 20.1 Classification of halogen compounds

Depending on the type of halogen present, the halohydrocarbons are classified as follows.

Based on the number of alkyl groups bonded to the carbon that carries the halogen, the classification may be as follows.

Primary halides  $\text{CH}_3\text{CH}_2 - \text{X}$

Secondary halides  $\text{CH}_3 - \text{CH} - \text{X}$   
                                   $\begin{array}{c} | \\ \text{CH}_3 \end{array}$

Tertiary halides  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 - \text{C} - \text{X} \\ | \\ \text{CH}_3 \end{array}$

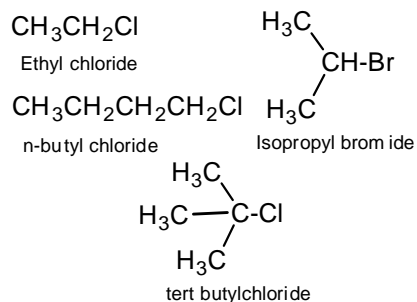
Where  $\text{X} = \text{Halogen}$

In the primary halides, the carbon bonded to the halogen is connected to one alkyl group, in the secondary halides two alkyl groups in the tertiary halides three alkyl groups.

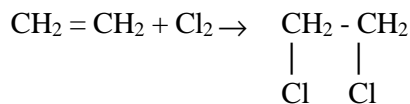
## 20.2 Nomenclature of alkyl halides : common and IUPAC

In this section the nomenclature of alkyl halides alone is presented, and the same for aryl halides and aralkyl halides are presented in their respective sections.

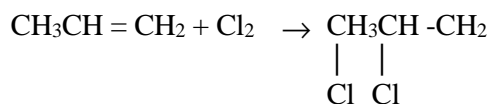
The common names of the monohalogen derivatives are derived by naming the alkyl group first and the halogen second.



If two halogen atoms are bonded to the same carbon, they are named as the alkylidene halides.  $\text{CH}_3\text{CHBr}_2$  Ethylidene bromide. If the two halogen atoms are bonded to adjacent carbons, they are named as the dihalides of the alkenes from which they are formed.



Ethylene dichloride

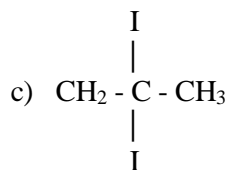


Propylene dichloride

Trihalomethane and tetrahalomethanes are named as haloforms and carbon tetra halides respectively.

### Example

Write the common names of the following halides



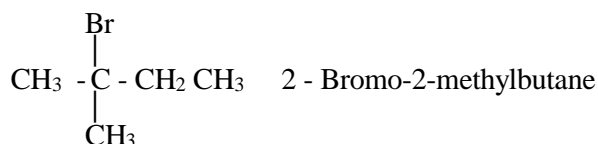
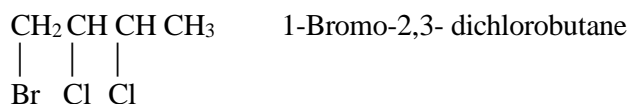
### Solution

- a. Isobutyl bromide
- b. Propylidene chloride
- c. Propylidene iodide
- d. Bromoform
- e. Carbon tetra chloride.

More complex halogen compounds are named according to IUPAC system.

- i. If any halogen is at the end of the chain, the carbon bearing the halogen is to be given the number 1.
- ii. If the halogen is present in the second or third carbon, numbering is to be started from that side of the chain which gives the least number for carbon bonded to halogen.

- iii. When two different halogens are present, the carbon bonded to higher atomic number halogen is to be given priority.
- iv. The names of the halogens and other substituents are to be arranged alphabetically.



### Example

Write the IUPAC names of the following halides.

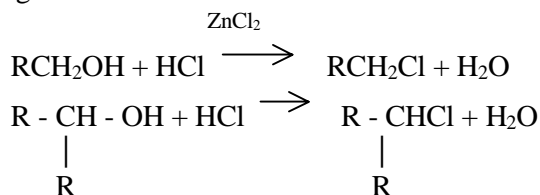
- a.  $\text{CH}_2\text{Br}.\text{CHCl}.\text{CH}_2\text{CH}_2\text{Cl}$
- b.  $\text{CH}_3\text{CCl}_2.\text{CHBr}.\text{CH}_3$
- c.  $\begin{array}{ccccccc} \text{CH}_3 & - & \text{CBr} & - & \text{CH} & - & \text{CH} & - & \text{CH}_3 \\ & & | & & | & & | & & \\ & & \text{CH}_3 & & \text{Cl} & & \text{CH}_3 & & \end{array}$

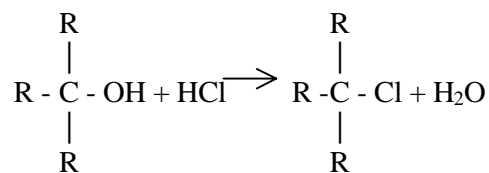
### Solution

- a. 1 - Bromo - 2,4 - dichlorobutane
- b. 2 - Bromo - 3,3 - dichlorobutane
- c. 2-Bromo-3-chloro-2,4-dimethylpentane

## 20.3 General methods of preparation

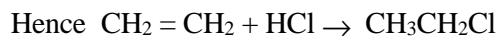
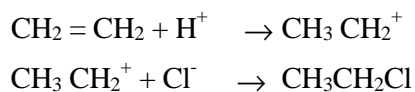
**i. From alcohols :** Preparation of alkyl halides from alcohols involves replacement of the hydroxyl group with halogen. It is done by using halogen acids.





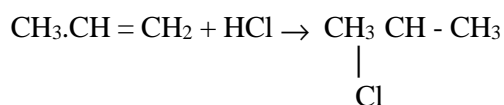
$\text{ZnCl}_2$  is the Lewis acid catalyst. It is required for both primary and secondary alcohols as they are not rapidly reacting. Tertiary alcohols do not require this reagent as they are more reactive.

**ii. From alkenes :** Alkenes react with halogen acids to give alkyl halides. The addition of HCl occurs with first proton and second with halogen.



**HBr and HI are added in a similar manner**

When a hydrogen halide is added to an unsymmetrical olefin, the position of the halogen in the product is predicted by Markovnikoff's rule : It states that when a hydrogen halide is added to an unsymmetrical olefin, the negative part of it is added to the carbon that carries least number of hydrogens.



It is based on the stability of the carbonium ion formed after the addition of the proton. The order of the stability of the carbonium ion is

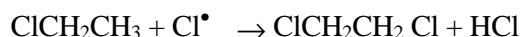
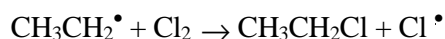
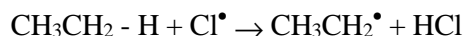
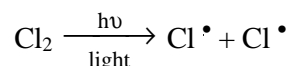
tertiary carbonium ion > secondary carbonium ion > primary carbonium ion

The stability of the carbonium ion depends on the extent to which the degree of the positive charge is decreased. In the tertiary carbonium ion the positive charge is more decreased by inductive effect and hyper conjugation and hence its degree of positive charge is more decreased than the secondary and primary carbonium ions.

### iii. From hydrocarbons

By treating alkanes with chlorine (or bromine) at room temperature in the presence of light, chloroalkanes are obtained. The reaction follows a free radical mechanism.

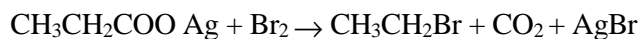
Chlorine molecule decomposes into chlorine atoms by absorption of light and the atoms then react with hydrocarbons.



It is a chain reaction with the formation of several products. The reaction may be stopped by absorption of the chlorine atoms on the wall, or by reaction if two chlorine atoms to form a chlorine molecule.

### iv. Hunsdiecker or Borodine - Hunsdiecker reaction

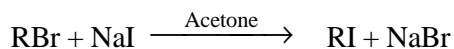
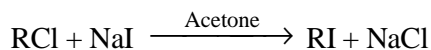
Silver carboxylates in carbon tetrachloride are decomposed by chlorine or bromine to form alkyl halide.



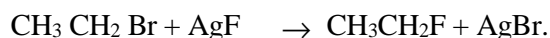
Bromine is better than chlorine as the later gives poor yield.

### v. By halogen exchange : Finkelstein reaction

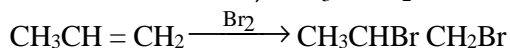
Alkyl iodides are prepared by treating the corresponding chloride or bromide with a solution of sodium iodide in acetone. The exchange of halogen between alkyl halide and sodium iodide occurs.



Alkyl fluorides are obtained by treating alkyl chloride or bromide with metallic fluoride, such as AgF or SbF<sub>3</sub>. It is the Swarts reaction.



## vi. Preparation of dihalogens



## 20.4 Properties

### 20.4.1 Physical properties

The lower members  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{CH}_2\text{Cl}$  are gases.  $\text{CH}_3\text{I}$  and the majority of higher members are sweet-smelling liquids. For a given alkyl group the boiling point of halides increases with increase in the atomic weight of the halogens.

Halide	$\text{CH}_3\text{F}$	$\text{CH}_3\text{Cl}$	$\text{CH}_3\text{Br}$	$\text{CH}_3\text{I}$
B.P ( $^{\circ}\text{C}$ )	-78	-24	4.0	92

It is due to increase in the Vanderwaals force with increase in the molecular size (molecular weight).

For a given halide, the boiling point increases with the length of the alkyl chains.

Halide	$\text{CH}_3\text{Cl}$	$\text{CH}_3\text{CH}_2\text{Cl}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$
B.P ( $^{\circ}\text{C}$ )	-22	12.5	47

It is due to increase in the Vanderwaals force with increase in the chain length. In a similar manner the boiling point of isomeric alkyl halides decreases in the order as shown below.

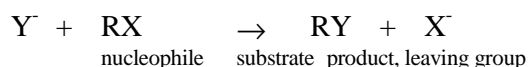
Halide	B.P ( $^{\circ}\text{C}$ )
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$	21.5
$\text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{CH}_3$	68
$(\text{CH}_3)_3\text{C-Cl}$	51

Organic halides are insoluble in water, as they are unable to form strong hydrogen bonds with water. They are less inflammable than the

hydrocarbons. It is due to dilution of oxygen during combustion by the released halogen. Carbon tetrachloride is used in fire extinguishers and as solvent. Tri- and tetrachloroethylenes are widely used as solvents, and they are good solvents for fats and oils. They do not catch fire easily.

## 20.5 Nucleophilic substitution reactions

The alkyl halides are important reagents in organic synthesis. The halogen can be displaced by other groups by which variety of other organic compounds can be prepared. The reaction can be written as

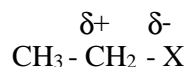


The nucleophile may be negatively charged or a neutral species with a lone pair of electrons.

Nucleophiles :  $\text{OH}^-$ ,  $\text{RO}^-$ ,  $\text{HS}^-$ ,  $\text{NO}_2^-$ ,  $\text{CN}^-$  etc.

Neutral :  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{CH}_3\text{NH}_2$  etc.

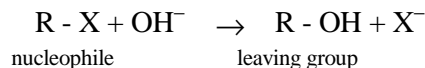
The R-X bond is polar with partial positive charge on carbon as shown below. It is due to more electronegativity of halogen than carbon.



The nucleophile attacks on the carbon ( $\text{CH}_2$ ) and displaces the leaving group. This reaction can occur by the following mechanisms.

## 20.6 Mechanism of nucleophilic substitution reactions

When a substitution reaction involves the attack of a nucleophile, the reaction is referred to as  $\text{S}_\text{N}$  (S-stands for substitution and N for nucleophile). The hydrolysis of alkyl halides by aqueous NaOH is an example of nucleophilic substitution.



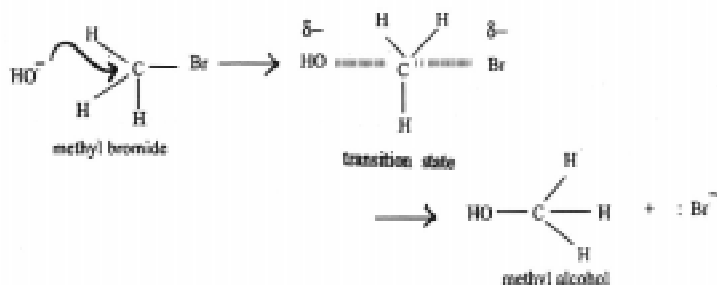
The nucleophilic substitution reactions are divided into two classes :  
(1)  $\text{S}_\text{N}^2$  reactions (2)  $\text{S}_\text{N}^1$  reactions.

**$\text{S}_\text{N}^2$  reactions** :  $\text{S}_\text{N}^2$  stands for bimolecular nucleophilic substitution. When the rate of nucleophilic substitution reaction depends on the



concentration of both the substrate and the nucleophile, the reaction is of second order and is represented as  $S_N2$ .

Consider the hydrolysis of methyl bromide by aqueous NaOH. The reaction is represented below.

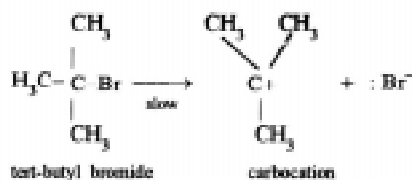


The hydroxide ion approaches the substrate carbon from the side opposite to the bromine atom. This is backside attack. This is because both hydroxide ion and the bromine atom are electron rich. They stay as far apart as possible. The transition state may be pictured as a structure in which both OH and Br are partially bonded to the substrate carbon. The C-Br bond is not completely cleaved and C-OH bond is not completely formed. Hydroxide ion has a diminished negative charge because it has started to share its electrons with the substrate carbon. The bromine atom also carries a negative charge because it has started removing its shared pair of electrons from the carbon atom. In the transition state the three C-H bond lie in one plane. The C-OH and C-Br bonds are perpendicular to the plane of the C-H bonds.

**$S_N1$  reactions:**  $S_N1$  stands for unimolecular nucleophilic substitution. When the rate of nucleophilic substitution reaction depends only on the concentration of the substrate (alkyl halide), the reaction is first order and is represented as  $S_N1$ .

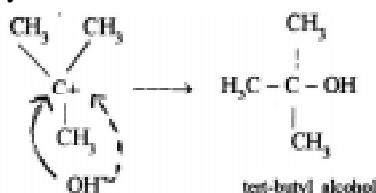
Consider the hydrolysis of tertiary butyl bromide. The reaction consists of two steps.

**Step 1:** The alkyl halide ionises to give the carbocation (carbonium ion). This step is the slow rate determining step.



The carbocation is planar. This is because the central positively charged carbon atom is  $\text{sp}^2$  hybridised.

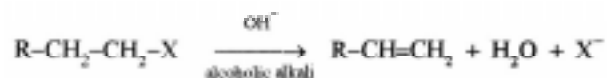
**Step 2 :** The nucleophile can attack the planar carbocation from either side to give tertiary butyl alcohol.



Primary alkyl halides undergo hydrolysis by  $\text{S}_\text{N}2$  mechanism. The tertiary alkyl halides undergo hydrolysis by  $\text{S}_\text{N}1$  mechanism. Secondary alkyl halides may undergo hydrolysis by both  $\text{S}_\text{N}1$  and  $\text{S}_\text{N}2$  mechanism.

## 20.7 Mechanism of elimination reaction

Elimination reactions are reverse of addition reactions. Here atoms or group attached to the adjacent carbon atoms in the substrate molecule are eliminated to form a double bond. Example, dehydrohalogenation of alkyl halides with alcoholic alkalis.



These reactions are divided into two classes

- 1) E2 reaction
- 2) E1 reactions

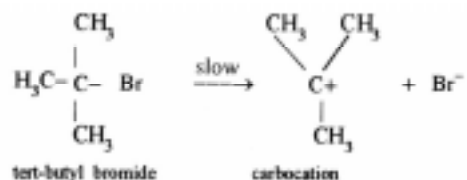
**E2 reactions:** E2 stands for bimolecular elimination. When the rate of an elimination reaction depends on the concentration of substrate and nucleophile, the reaction is second order and is represented as E2. E2 is a one step process in which the abstraction of the proton from the beta

carbon and expulsion of the halide ion from the alpha carbon occur simultaneously. The mechanism is shown below :

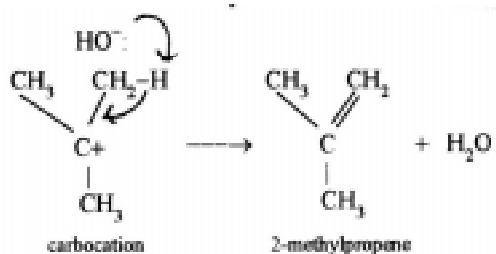


**E1 reactions:** E1 stands for unimolecular elimination. when the rate of an elimination reaction depends only on the concentration of the substrate, the reaction is of first order and is designated as E1. E1 reactions are two step processes.

**Step 1 :** The alkyl halide ionise to give the carbocation.



**Step 2 :** The nucleophile ( $\text{OH}^-$ ) abstracts a proton and forms an alkene.

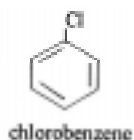


### Uses of alkyl halides

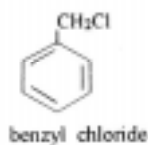
- 1) Alkyl chlorides such as trichloromethane (chloroform) and tetrachloromethane (carbon tetrachloride) are widely used as industrial solvents.
- 2) Chloroform is used as anaesthetic
- 3) Iodoform is used as an antiseptic
- 4) Carbon tetrachloride is used as a fire extinguisher
- 5) dichlorodifluoromethane (a freon) is used as a refrigerant
- 6) Alkyl halides are used for the preparation of Grignard reagents.

## 20.8 Aryl halides

When the halogen atom is substituted in the place of a hydrogen atom in an aromatic ring, the compound is called aryl halide. Example,



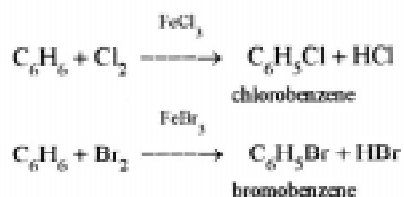
The halogen atom may be linked to carbon atom in the side chain of an aromatic hydrocarbon. Such a compound is called aralkyl halide. Example,



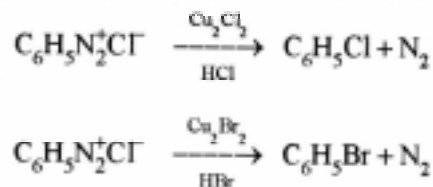
### 20.8.1 General methods of preparation, properties and uses of aryl halides

The methods of preparation of chlorobenzene can be taken as general methods of preparation of aryl halides.

**1. Direct halogenation :** Aryl chlorides and aryl bromides are generally prepared from arenes by action with chlorine or bromine in presence of a catalyst such as  $\text{FeCl}_3$  or  $\text{FeBr}_3$ .



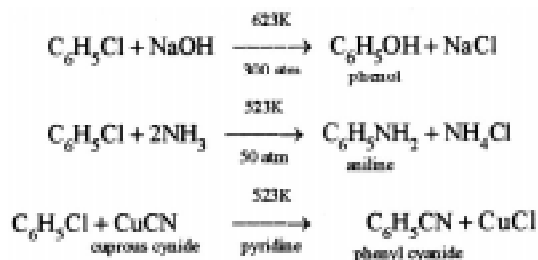
**2. Decomposition of diazonium salts :** Aryl halides can be prepared by the decomposition of aryl diazonium salts in the presence of appropriate metal halides.



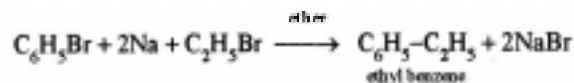
## 20.9 General properties :

The molecule of an aryl halide is made of (i) an aromatic ring and (ii) halogen atom directly bonded to the ring. The reactions of aryl halides are, therefore, due to the aromatic ring and the halogen atom.

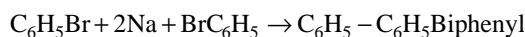
**Reactions involving the halogen atom : Nucleophilic aromatic substitution :** 1) Aryl halides do not readily undergo nucleophilic substitution reactions, as those of alkyl halides. The reason for such low reactivity is given below. One reason is that the C-X bond in aryl halides is short and strong compared to that of alkyl halides. Another reason is that the aromatic ring is a centre of high electron density because of the delocalised  $\pi$  electrons. However nucleophilic substitution of halogen of aryl halides can take place under vigorous conditions. Example,



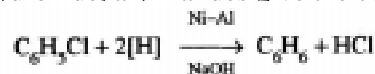
**2) Wurtz-Fittig reaction :** Aryl halides react with alkyl halides when heated with sodium in ether solution to form alkylbenzene.



**3) Fittig reaction :** In the absence of alkyl halides, aryl halides in ether solution react with sodium to give biaryl compounds in which two benzene rings are bonded together.



**4) Reduction :** When reduced with nickel-aluminium alloy in the presence of sodium hydroxide, aryl halides give the corresponding arenes.



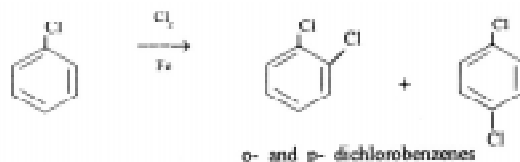
**5) Formation of Grignard reagents :** Aryl bromides and iodides form Grignard reagents when refluxed with magnesium powder in dry ether. Aryl chlorides do so in presence of tetrahydrofuran ( THF) instead of ether.



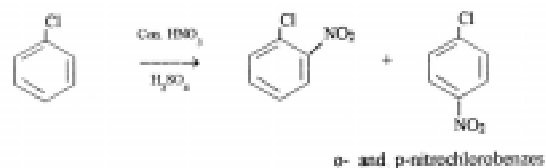
#### 6) Reactions involving the aromatic ring: Electrophilic aromatic substitution reactions

Aryl halides undergo the typical electrophilic aromatic substitution reactions like halogenation, nitration, sulphonation and alkylation. Here the halogen of the aryl halide directs the electrophilic reagents to ortho and para positions. The electrophilic substitution reactions of aryl halides are illustrated by taking the example of chlorobenzene.

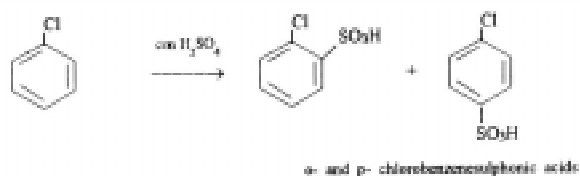
##### i. Chlorination



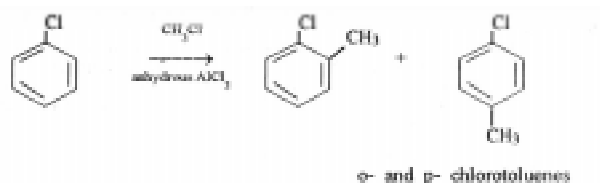
##### ii. Nitration



##### iii. Sulphonation



#### iv. Alkylation



**v. Formation of DDT :** Chlorobenzene reacts with trichloroacetaldehyde (chloral) in the presence of concentrated sulphuric acid to give p-p'-dichloro diphenyltrichloroethane (DDT). It is an effective insecticide.



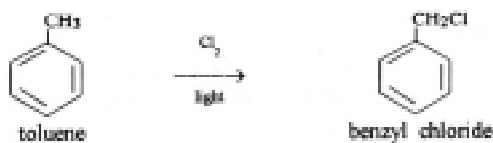
#### 20.10 Uses of aryl halides :

Chlorobenzene is used for the preparation of phenol and nitrochlorobenzenes which are required for the manufacture of azo and sulphur dyes; DDT and BHC (benzenehexachloride) which are insecticides.

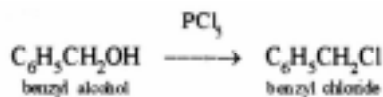
#### Side-chain halogenated compounds or aralkyl halides

A typical example of this class of compounds is benzyl chloride which can be prepared as follows:

1. Side chain halogenation is favoured by high temperature and light. It occurs in the absence of halogen carriers. For example, benzyl chloride is prepared by chlorination of boiling toluene in light.



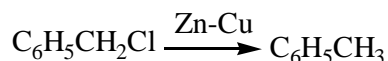
2. It can also be prepared by the action of phosphorus pentachloride on benzyl alcohol.



## Properties

### i) Reduction of aralkyl halides

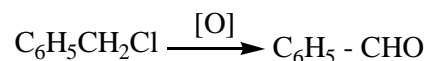
Reduction of benzyl chloride with Zn-Cu couple gives toluene.



### ii) Oxidation

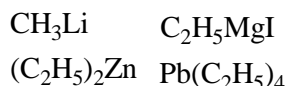
Benzyl chloride on oxidation with alkaline potassium permanganate gives benzoic acid.

On mild oxidation with  $\text{Cu}(\text{NO}_3)_2$  gives benzaldehyde.



## 20.11 Grignard reagents

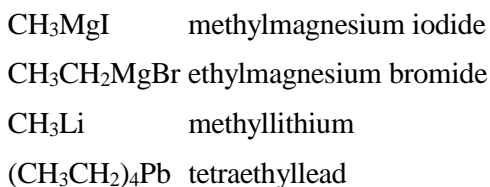
Organic Compounds in which alkyl or aryl groups are directly attached to a metal are called organometallic compounds. Many metals form organometallic compounds. For example,



Organomagnesium halides are called Grignard reagents. They are named after the French Chemist, Victor Grignard, who discovered them and developed them as synthetic reagents.

**General formula and nomenclature :** Their general formula can be written as  $\text{RMgX}$  where R=alkyl or aryl group and X=Cl, Br or I. Examples,  $\text{CH}_3\text{MgBr}$  and  $\text{CH}_3\text{CH}_2\text{MgBr}$ .

**Nomenclature :** Grignard reagents are named by simply adding the name of the metal to that of the organic group bonded to the metal. For example,

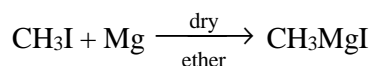




### 20.11.1 Preparation of methylmagnesium iodide

Methylmagnesium iodide is prepared by the action of methyl iodide on magnesium suspended in dry ether. All the reagents used should be pure and dry. Dry magnesium ribbon is washed with ether to remove grease and then with dilute acid to remove any oxide and then dried. The ether is kept absolutely dry by distilling over metallic sodium to make it free from ethanol. Methyl iodide is dried over anhydrous calcium chloride and then distilled over phosphorus pentoxide.

Clean dry magnesium is placed in dry ether in a flask fitted with reflux condenser. Pure dry methyl iodide is added gradually. When the reaction starts, the ether becomes cloudy and also begins to boil. It is necessary to cool the mixture. If the reaction does not start, one or two crystals of iodine are dropped into the flask. When the reaction is complete, a clear solution of methyl magnesium iodide is obtained. This is used as such in all the reactions.

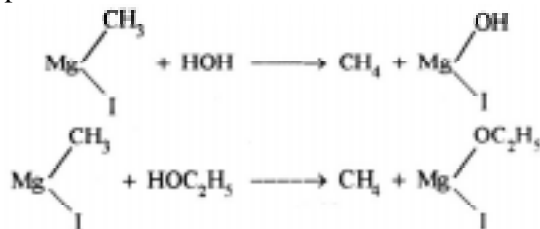


### 20.12 Synthetic uses of methylmagnesium iodide

Grignard reagents are generally one of the most reactive compounds. These are used for the synthesis of a variety of organic compounds. The following reactions illustrate the synthetic uses of methylmagnesium iodide.

#### 1. Preparation of alkanes

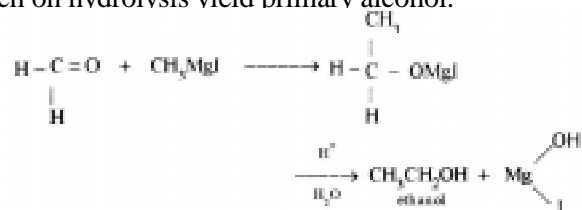
Methylmagnesium iodide undergoes double decomposition with water and alcohol to produce alkanes.



#### 2. Preparation of primary alcohols

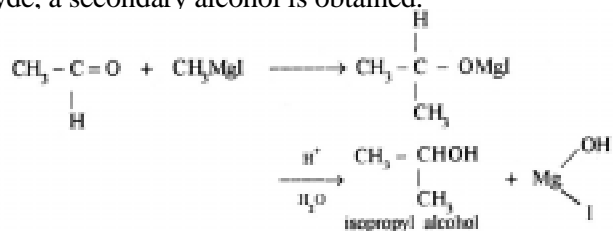
Formaldehyde reacts with methylmagnesium iodide to give addition

product which on hydrolysis yield primary alcohol.



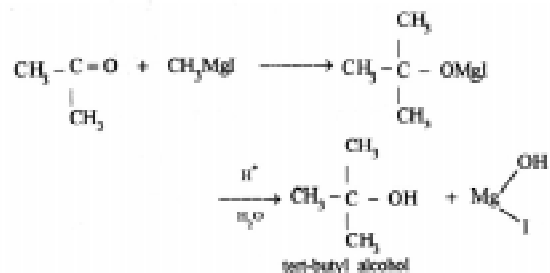
### 3. Preparation of secondary alcohols

When methylmagnesium iodide is treated with any aldehyde other than formaldehyde, a secondary alcohol is obtained.



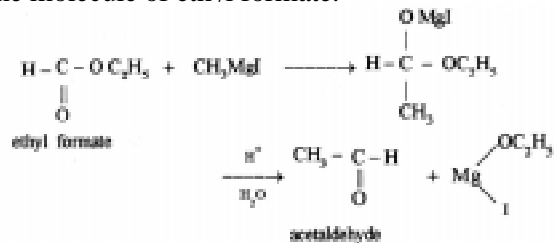
### 4. Preparation of tertiary alcohols

Methylmagnesium iodide reacts with ketones to give an addition compound which on hydrolysis yield tertiary alcohols.

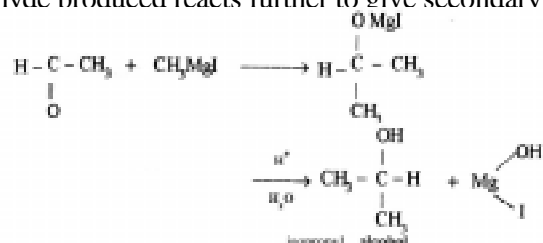


### 5. Preparation of aldehydes

An aldehyde is prepared by treating one molecule of methylmagnesium iodide with one molecule of ethyl formate.

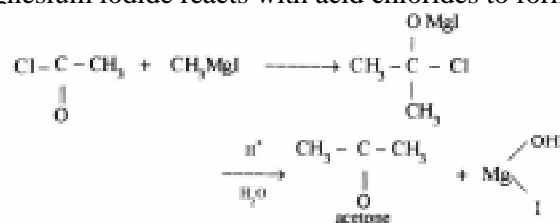


A secondary alcohol is obtained if methylmagnesium iodide is in excess. Aldehyde produced reacts further to give secondary alcohol.



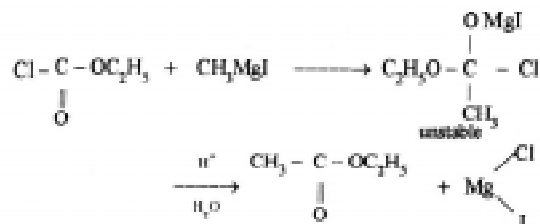
## 6. Preparation of ketones

Methylmagnesium iodide reacts with acid chlorides to form ketones.



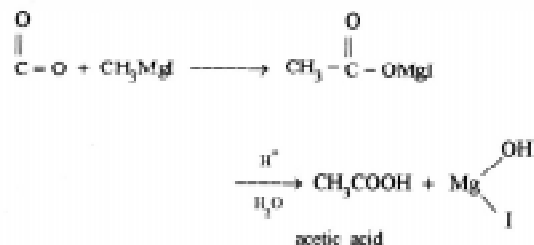
## 7. Preparation of esters

7. Methylmagnesium iodide reacts with ethyl chloroformate to form higher esters



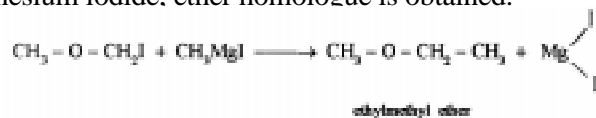
## 8. Preparation of acids

Methylmagnesium iodide reacts with solid carbon dioxide to give addition product which on hydrolysis in the presence of acid yields carboxylic acid.



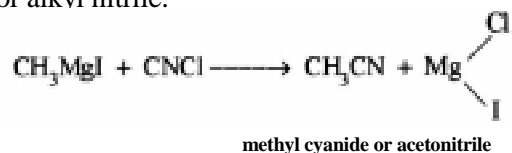
## 9. Preparation of ethers

When a monohalogen derivative of an ether is treated with methylmagnesium iodide, ether homologue is obtained.



## 10. Preparation of alkyl cyanide

Methylmagnesium iodide reacts with cyanogen chloride to form an alkyl cyanide or alkyl nitrile.



## Questions

### A. Choose the correct answer

- The IUPAC name of  

$$\begin{array}{ccccccc} & & & & \text{CH}_3 & & \\ & & & & | & & \\ \text{CH}_3 & .\text{CH} & - & \text{CH}_2 & - & \text{CH} & - & \text{CH}_3 \\ & | & & | & & & & \\ & \text{Br} & & \text{Cl} & & & & \end{array}$$
  - 2-Bromo-3-chloro-4-methylpentane
  - 2-Methyl-3-chloro-4-bromopentane
  - 2-Bromo-3-chloro-3-isopropyl propane
  - 2,4-Dimethyl-4-Bromo-3-chloro butane.
- For reacting with HCl, the alcohol which does not require  $\text{ZnCl}_2$  is  
  - $\text{CH}_3\text{CH}_2\text{OH}$
  - $\text{CH}_3 - \text{CH}_2\text{CH}_2\text{OH}$
  - $\text{CH}_3 - \underset{\begin{array}{c} | \\ \text{CH}_3 \end{array}}{\text{CH}}\text{OH}$
  - $\text{C}(\text{CH}_3)_3\text{C-OH}$ .
- For converting alcohols into alkyl halides, the best reagent is  
  - $\text{PCl}_3$
  - $\text{PCl}_5$
  - $\text{SOCl}_2$
  - None of the above
- The olefin, which is not important for Markovni Koff's addition of HCl, is  
  - Propene
  - But-1-ene
  - 2-Methyl-propene
  - Ethylene
- The  $\text{S}_{\text{N}}1$  reaction of alkyl halides is not affected by the nature of the  
  - alkyl group
  - the halogen
  - medium
  - nucleophile

## 20. ORGANIC HALOGEN COMPOUNDS

### OBJECTIVES

*The main objectives of this chapter are*

- \* to highlight the medicinal importance of certain halogenated compounds.*
- \* to understand the physical and chemical properties of the organic halogen compounds.*
- \* to give brief account of classification and nomenclature of these compounds.*
- \* to discuss mechanisms of substitution and elimination reactions which are important to halogen compounds.*
- \* to provide students more exposure to named organic reactions.*
- \* to raise the capability of students to design new synthetic routes for interested target materials.*
- \* to provide proof that how much important these compounds are as intermediates in the synthesis of wide variety of organic compounds.*

In organic halogen compounds F, Cl, Br and I are bonded to the carbons of the aliphatic, aromatic and aralkyl hydrocarbons. Many organic halogen compounds occur in nature and some of them have medicinal value. Chloromycetin is a naturally occurring halogen compound used in the treatment of typhoid fever. Thyroxine is yet another one used in the treatment of goitre. There are many synthetic organic halogen compounds few of which are important in health care and medicine. Two such compounds to cite are chloroquine and halothane. The former is used in the treatment of malaria and the later is used as an anaesthetic during surgery. There are also compounds which are important in agriculture and industry, as intermediates in the synthesis of wide variety of other organic compounds.

### 20.1 Classification of halogen compounds

Depending on the type of halogen present, the halohydrocarbons are classified as follows.

Based on the number of alkyl groups bonded to the carbon that carries the halogen, the classification may be as follows.

Primary halides  $\text{CH}_3\text{CH}_2 - \text{X}$

Secondary halides  $\begin{array}{c} \text{CH}_3 - \text{CH} - \text{X} \\ | \\ \text{CH}_3 \end{array}$

Tertiary halides  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 - \text{C} - \text{X} \\ | \\ \text{CH}_3 \end{array}$

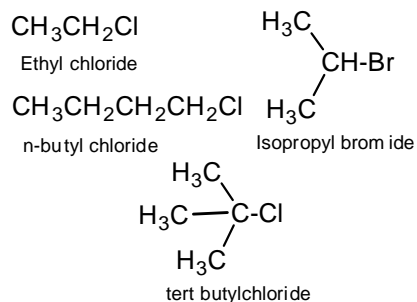
Where  $\text{X} = \text{Halogen}$

In the primary halides, the carbon bonded to the halogen is connected to one alkyl group, in the secondary halides two alkyl groups in the tertiary halides three alkyl groups.

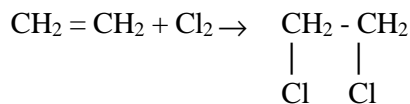
## 20.2 Nomenclature of alkyl halides : common and IUPAC

In this section the nomenclature of alkyl halides alone is presented, and the same for aryl halides and aralkyl halides are presented in their respective sections.

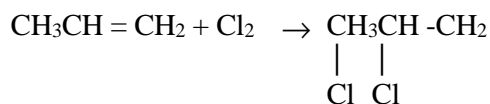
The common names of the monohalogen derivatives are derived by naming the alkyl group first and the halogen second.



If two halogen atoms are bonded to the same carbon, they are named as the alkylidene halides.  $\text{CH}_3\text{CHBr}_2$  Ethylidene bromide. If the two halogen atoms are bonded to adjacent carbons, they are named as the dihalides of the alkenes from which they are formed.



Ethylene dichloride

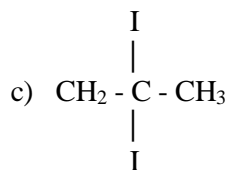


Propylene dichloride

Trihalomethane and tetrahalomethanes are named as haloforms and carbon tetra halides respectively.

### Example

Write the common names of the following halides



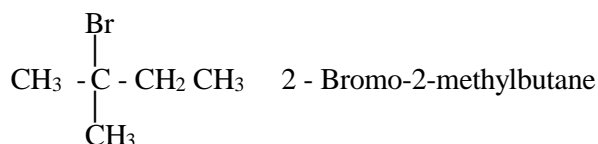
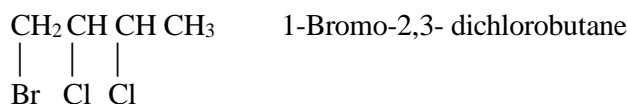
### Solution

- Isobutyl bromide
- Propylidene chloride
- Propylidene iodide
- Bromoform
- Carbon tetra chloride.

More complex halogen compounds are named according to IUPAC system.

- If any halogen is at the end of the chain, the carbon bearing the halogen is to be given the number 1.
- If the halogen is present in the second or third carbon, numbering is to be started from that side of the chain which gives the least number for carbon bonded to halogen.

- iii. When two different halogens are present, the carbon bonded to higher atomic number halogen is to be given priority.
- iv. The names of the halogens and other substituents are to be arranged alphabetically.



### Example

Write the IUPAC names of the following halides.

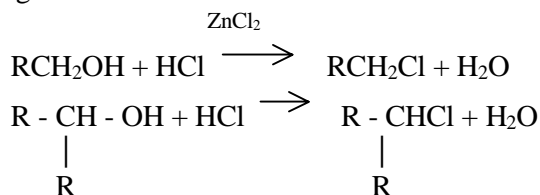
- a.  $\text{CH}_2\text{Br}.\text{CHCl}.\text{CH}_2\text{CH}_2\text{Cl}$
- b.  $\text{CH}_3\text{CCl}_2.\text{CHBr}.\text{CH}_3$
- c.  $\begin{array}{ccccccc} \text{CH}_3 & - & \text{CBr} & - & \text{CH} & - & \text{CH} & - & \text{CH}_3 \\ & & | & & | & & | & & \\ & & \text{CH}_3 & & \text{Cl} & & \text{CH}_3 & & \end{array}$

### Solution

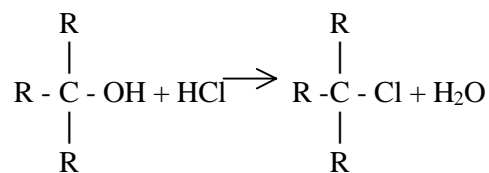
- a. 1 - Bromo - 2,4 - dichlorobutane
- b. 2 - Bromo - 3,3 - dichlorobutane
- c. 2-Bromo-3-chloro-2,4-dimethylpentane

## 20.3 General methods of preparation

**i. From alcohols :** Preparation of alkyl halides from alcohols involves replacement of the hydroxyl group with halogen. It is done by using halogen acids.

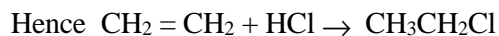
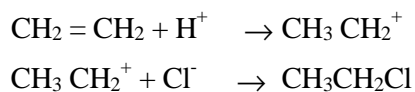






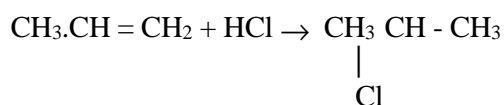
$\text{ZnCl}_2$  is the Lewis acid catalyst. It is required for both primary and secondary alcohols as they are not rapidly reacting. Tertiary alcohols do not require this reagent as they are more reactive.

**ii. From alkenes :** Alkenes react with halogen acids to give alkyl halides. The addition of HCl occurs with first proton and second with halogen.



**HBr and HI are added in a similar manner**

When a hydrogen halide is added to an unsymmetrical olefin, the position of the halogen in the product is predicted by Markovnikoff's rule : It states that when a hydrogen halide is added to an unsymmetrical olefin, the negative part of it is added to the carbon that carries least number of hydrogens.



It is based on the stability of the carbonium ion formed after the addition of the proton. The order of the stability of the carbonium ion is

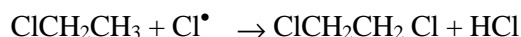
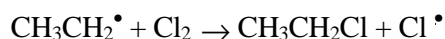
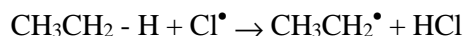
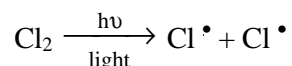
tertiary carbonium ion > secondary carbonium ion > primary carbonium ion

The stability of the carbonium ion depends on the extent to which the degree of the positive charge is decreased. In the tertiary carbonium ion the positive charge is more decreased by inductive effect and hyper conjugation and hence its degree of positive charge is more decreased than the secondary and primary carbonium ions.

### iii. From hydrocarbons

By treating alkanes with chlorine (or bromine) at room temperature in the presence of light, chloroalkanes are obtained. The reaction follows a free radical mechanism.

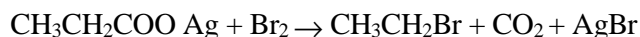
Chlorine molecule decomposes into chlorine atoms by absorption of light and the atoms then react with hydrocarbons.



It is a chain reaction with the formation of several products. The reaction may be stopped by absorption of the chlorine atoms on the wall, or by reaction if two chlorine atoms to form a chlorine molecule.

### iv. Hunsdiecker or Borodine - Hunsdiecker reaction

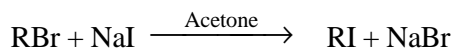
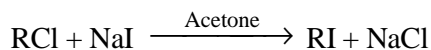
Silver carboxylates in carbon tetrachloride are decomposed by chlorine or bromine to form alkyl halide.



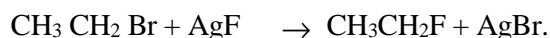
Bromine is better than chlorine as the later gives poor yield.

### v. By halogen exchange : Finkelstein reaction

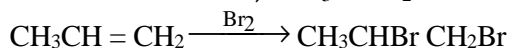
Alkyl iodides are prepared by treating the corresponding chloride or bromide with a solution of sodium iodide in acetone. The exchange of halogen between alkyl halide and sodium iodide occurs.



Alkyl fluorides are obtained by treating alkyl chloride or bromide with metallic fluoride, such as AgF or SbF<sub>3</sub>. It is the Swarts reaction.



## vi. Preparation of dihalogens



## 20.4 Properties

### 20.4.1 Physical properties

The lower members  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{CH}_2\text{Cl}$  are gases.  $\text{CH}_3\text{I}$  and the majority of higher members are sweet-smelling liquids. For a given alkyl group the boiling point of halides increases with increase in the atomic weight of the halogens.

Halide	$\text{CH}_3\text{F}$	$\text{CH}_3\text{Cl}$	$\text{CH}_3\text{Br}$	$\text{CH}_3\text{I}$
B.P ( $^{\circ}\text{C}$ )	-78	-24	4.0	92

It is due to increase in the Vanderwaals force with increase in the molecular size (molecular weight).

For a given halide, the boiling point increases with the length of the alkyl chains.

Halide	$\text{CH}_3\text{Cl}$	$\text{CH}_3\text{CH}_2\text{Cl}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$
B.P ( $^{\circ}\text{C}$ )	-22	12.5	47

It is due to increase in the Vanderwaals force with increase in the chain length. In a similar manner the boiling point of isomeric alkyl halides decreases in the order as shown below.

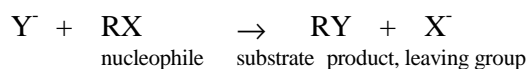
Halide	B.P ( $^{\circ}\text{C}$ )
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$	21.5
$\text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{CH}_3$	68
$(\text{CH}_3)_3\text{C-Cl}$	51

Organic halides are insoluble in water, as they are unable to form strong hydrogen bonds with water. They are less inflammable than the

hydrocarbons. It is due to dilution of oxygen during combustion by the released halogen. Carbon tetrachloride is used in fire extinguishers and as solvent. Tri- and tetrachloroethylenes are widely used as solvents, and they are good solvents for fats and oils. They do not catch fire easily.

## 20.5 Nucleophilic substitution reactions

The alkyl halides are important reagents in organic synthesis. The halogen can be displaced by other groups by which variety of other organic compounds can be prepared. The reaction can be written as

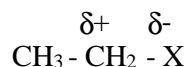


The nucleophile may be negatively charged or a neutral species with a lone pair of electrons.

Nucleophiles :  $\text{OH}^-$ ,  $\text{RO}^-$ ,  $\text{HS}^-$ ,  $\text{NO}_2^-$ ,  $\text{CN}^-$  etc.

Neutral :  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{CH}_3\text{NH}_2$  etc.

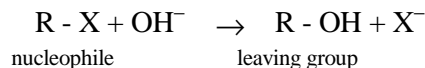
The R-X bond is polar with partial positive charge on carbon as shown below. It is due to more electronegativity of halogen than carbon.



The nucleophile attacks on the carbon ( $\text{CH}_2$ ) and displaces the leaving group. This reaction can occur by the following mechanisms.

## 20.6 Mechanism of nucleophilic substitution reactions

When a substitution reaction involves the attack of a nucleophile, the reaction is referred to as  $\text{S}_\text{N}$  (S-stands for substitution and N for nucleophile). The hydrolysis of alkyl halides by aqueous NaOH is an example of nucleophilic substitution.

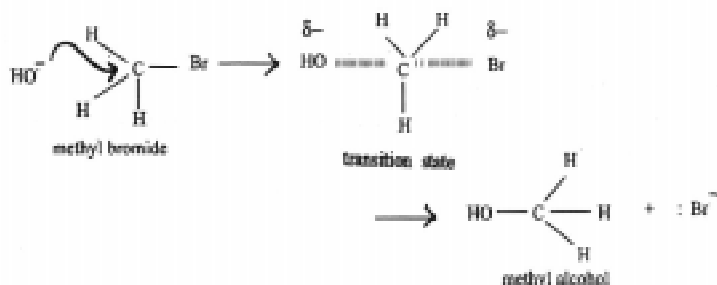


The nucleophilic substitution reactions are divided into two classes :  
(1)  $\text{S}_\text{N}^2$  reactions (2)  $\text{S}_\text{N}^1$  reactions.

**$\text{S}_\text{N}^2$  reactions** :  $\text{S}_\text{N}^2$  stands for bimolecular nucleophilic substitution. When the rate of nucleophilic substitution reaction depends on the

concentration of both the substrate and the nucleophile, the reaction is of second order and is represented as  $S_N2$ .

Consider the hydrolysis of methyl bromide by aqueous NaOH. The reaction is represented below.

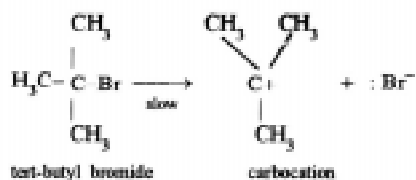


The hydroxide ion approaches the substrate carbon from the side opposite to the bromine atom. This is backside attack. This is because both hydroxide ion and the bromine atom are electron rich. They stay as far apart as possible. The transition state may be pictured as a structure in which both OH and Br are partially bonded to the substrate carbon. The C-Br bond is not completely cleaved and C-OH bond is not completely formed. Hydroxide ion has a diminished negative charge because it has started to share its electrons with the substrate carbon. The bromine atom also carries a negative charge because it has started removing its shared pair of electrons from the carbon atom. In the transition state the three C-H bond lie in one plane. The C-OH and C-Br bonds are perpendicular to the plane of the C-H bonds.

**$S_N1$  reactions:**  $S_N1$  stands for unimolecular nucleophilic substitution. When the rate of nucleophilic substitution reaction depends only on the concentration of the substrate (alkyl halide), the reaction is first order and is represented as  $S_N1$ .

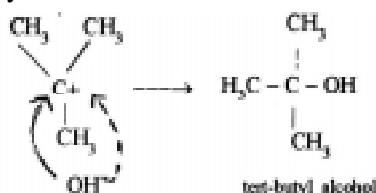
Consider the hydrolysis of tertiary butyl bromide. The reaction consists of two steps.

**Step 1:** The alkyl halide ionises to give the carbocation (carbonium ion). This step is the slow rate determining step.



The carbocation is planar. This is because the central positively charged carbon atom is  $\text{sp}^2$  hybridised.

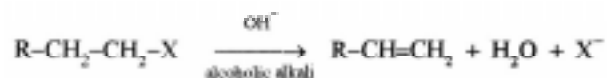
**Step 2 :** The nucleophile can attack the planar carbocation from either side to give tertiary butyl alcohol.



Primary alkyl halides undergo hydrolysis by  $\text{S}_\text{N}2$  mechanism. The tertiary alkyl halides undergo hydrolysis by  $\text{S}_\text{N}1$  mechanism. Secondary alkyl halides may undergo hydrolysis by both  $\text{S}_\text{N}1$  and  $\text{S}_\text{N}2$  mechanism.

## 20.7 Mechanism of elimination reaction

Elimination reactions are reverse of addition reactions. Here atoms or group attached to the adjacent carbon atoms in the substrate molecule are eliminated to form a double bond. Example, dehydrohalogenation of alkyl halides with alcoholic alkalis.



These reactions are divided into two classes

- 1) E2 reaction
- 2) E1 reactions

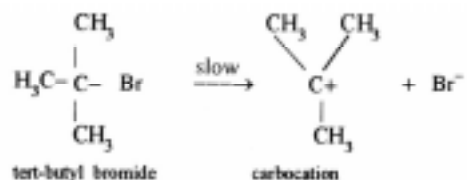
**E2 reactions:** E2 stands for bimolecular elimination. When the rate of an elimination reaction depends on the concentration of substrate and nucleophile, the reaction is second order and is represented as E2. E2 is a one step process in which the abstraction of the proton from the beta

carbon and expulsion of the halide ion from the alpha carbon occur simultaneously. The mechanism is shown below :

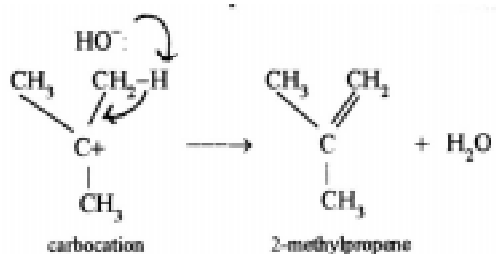


**E1 reactions:** E1 stands for unimolecular elimination. when the rate of an elimination reaction depends only on the concentration of the substrate, the reaction is of first order and is designated as E1. E1 reactions are two step processes.

**Step 1 :** The alkyl halide ionise to give the carbocation.



**Step 2 :** The nucleophile ( $\text{OH}^-$ ) abstracts a proton and forms an alkene.

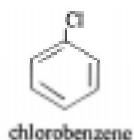


### Uses of alkyl halides

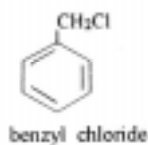
- 1) Alkyl chlorides such as trichloromethane (chloroform) and tetrachloromethane (carbon tetrachloride) are widely used as industrial solvents.
- 2) Chloroform is used as anaesthetic
- 3) Iodoform is used as an antiseptic
- 4) Carbon tetrachloride is used as a fire extinguisher
- 5) dichlorodifluoromethane (a freon) is used as a refrigerant
- 6) Alkyl halides are used for the preparation of Grignard reagents.

## 20.8 Aryl halides

When the halogen atom is substituted in the place of a hydrogen atom in an aromatic ring, the compound is called aryl halide. Example,



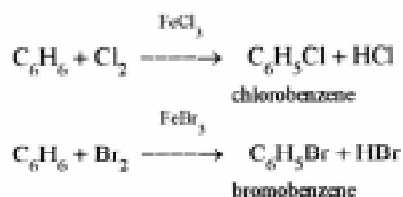
The halogen atom may be linked to carbon atom in the side chain of an aromatic hydrocarbon. Such a compound is called aralkyl halide. Example,



### 20.8.1 General methods of preparation, properties and uses of aryl halides

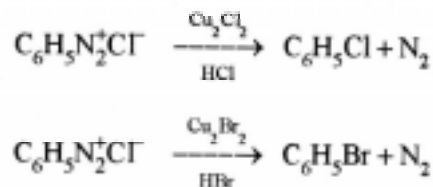
The methods of preparation of chlorobenzene can be taken as general methods of preparation of aryl halides.

**1. Direct halogenation :** Aryl chlorides and aryl bromides are generally prepared from arenes by action with chlorine or bromine in presence of a catalyst such as  $\text{FeCl}_3$  or  $\text{FeBr}_3$ .



**2. Decomposition of diazonium salts :** Aryl halides can be prepared by the decomposition of aryldiazonium salts in the presence of appropriate metal halides.

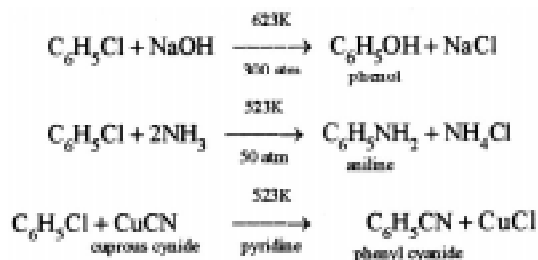




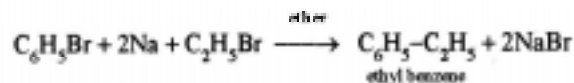
## 20.9 General properties :

The molecule of an aryl halide is made of (i) an aromatic ring and (ii) halogen atom directly bonded to the ring. The reactions of aryl halides are, therefore, due to the aromatic ring and the halogen atom.

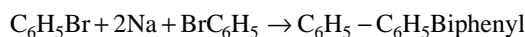
**Reactions involving the halogen atom : Nucleophilic aromatic substitution :** 1) Aryl halides do not readily undergo nucleophilic substitution reactions, as those of alkyl halides. The reason for such low reactivity is given below. One reason is that the C-X bond in aryl halides is short and strong compared to that of alkyl halides. Another reason is that the aromatic ring is a centre of high electron density because of the delocalised  $\pi$  electrons. However nucleophilic substitution of halogen of aryl halides can take place under vigorous conditions. Example,



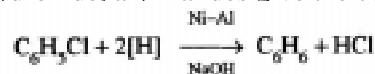
**2) Wurtz-Fittig reaction :** Aryl halides react with alkyl halides when heated with sodium in ether solution to form alkylbenzene.



**3) Fittig reaction :** In the absence of alkyl halides, aryl halides in ether solution react with sodium to give biaryl compounds in which two benzene rings are bonded together.



**4) Reduction :** When reduced with nickel-aluminium alloy in the presence of sodium hydroxide, aryl halides give the corresponding arenes.



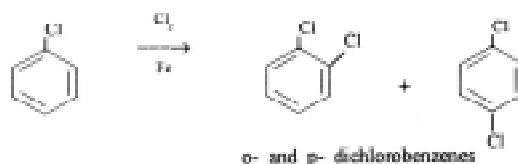
**5) Formation of Grignard reagents :** Aryl bromides and iodides form Grignard reagents when refluxed with magnesium powder in dry ether. Aryl chlorides do so in presence of tetrahydrofuran ( THF) instead of ether.



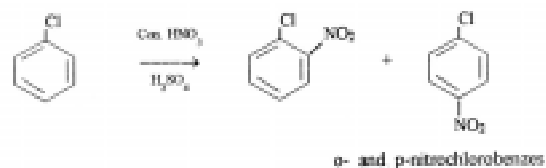
#### 6) Reactions involving the aromatic ring: Electrophilic aromatic substitution reactions

Aryl halides undergo the typical electrophilic aromatic substitution reactions like halogenation, nitration, sulphonation and alkylation. Here the halogen of the aryl halide directs the electrophilic reagents to ortho and para positions. The electrophilic substitution reactions of aryl halides are illustrated by taking the example of chlorobenzene.

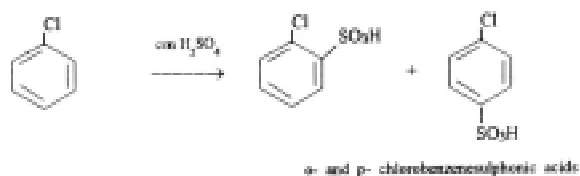
##### i. Chlorination



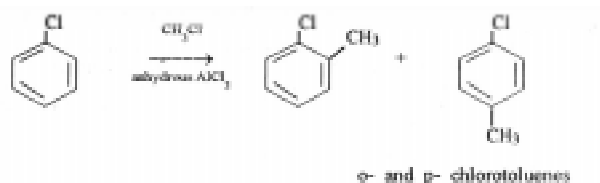
##### ii. Nitration



##### iii. Sulphonation



#### iv. Alkylation



**v. Formation of DDT :** Chlorobenzene reacts with trichloroacetaldehyde (chloral) in the presence of concentrated sulphuric acid to give p-p'-dichloro diphenyltrichloroethane (DDT). It is an effective insecticide.



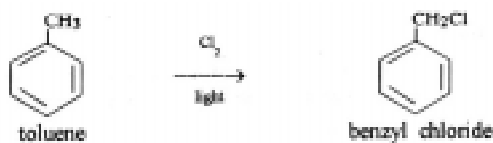
#### 20.10 Uses of aryl halides :

Chlorobenzene is used for the preparation of phenol and nitrochlorobenzenes which are required for the manufacture of azo and sulphur dyes; DDT and BHC (benzenehexachloride) which are insecticides.

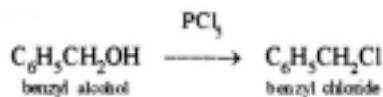
##### Side-chain halogenated compounds or aralkyl halides

A typical example of this class of compounds is benzyl chloride which can be prepared as follows:

1. Side chain halogenation is favoured by high temperature and light. It occurs in the absence of halogen carriers. For example, benzyl chloride is prepared by chlorination of boiling toluene in light.



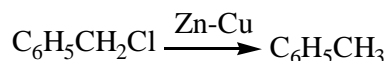
2. It can also be prepared by the action of phosphorus pentachloride on benzyl alcohol.



## Properties

### i) Reduction of aralkyl halides

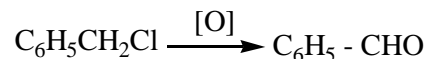
Reduction of benzyl chloride with Zn-Cu couple gives toluene.



### ii) Oxidation

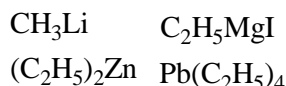
Benzyl chloride on oxidation with alkaline potassium permanganate gives benzoic acid.

On mild oxidation with  $\text{Cu}(\text{NO}_3)_2$  gives benzaldehyde.



## 20.11 Grignard reagents

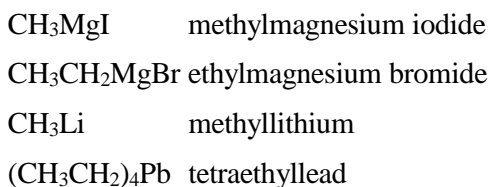
Organic Compounds in which alkyl or aryl groups are directly attached to a metal are called organometallic compounds. Many metals form organometallic compounds. For example,



Organomagnesium halides are called Grignard reagents. They are named after the French Chemist, Victor Grignard, who discovered them and developed them as synthetic reagents.

**General formula and nomenclature :** Their general formula can be written as  $\text{RMgX}$  where R=alkyl or aryl group and X=Cl, Br or I. Examples,  $\text{CH}_3\text{MgBr}$  and  $\text{CH}_3\text{CH}_2\text{MgBr}$ .

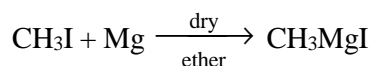
**Nomenclature :** Grignard reagents are named by simply adding the name of the metal to that of the organic group bonded to the metal. For example,



### 20.11.1 Preparation of methylmagnesium iodide

Methylmagnesium iodide is prepared by the action of methyl iodide on magnesium suspended in dry ether. All the reagents used should be pure and dry. Dry magnesium ribbon is washed with ether to remove grease and then with dilute acid to remove any oxide and then dried. The ether is kept absolutely dry by distilling over metallic sodium to make it free from ethanol. Methyl iodide is dried over anhydrous calcium chloride and then distilled over phosphorus pentoxide.

Clean dry magnesium is placed in dry ether in a flask fitted with reflux condenser. Pure dry methyl iodide is added gradually. When the reaction starts, the ether becomes cloudy and also begins to boil. It is necessary to cool the mixture. If the reaction does not start, one or two crystals of iodine are dropped into the flask. When the reaction is complete, a clear solution of methyl magnesium iodide is obtained. This is used as such in all the reactions.

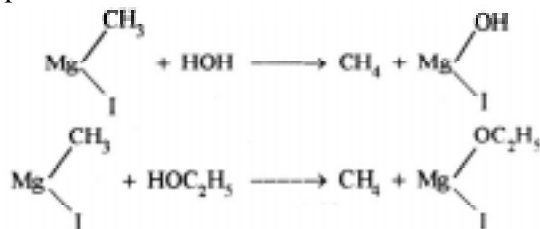


### 20.12 Synthetic uses of methylmagnesium iodide

Grignard reagents are generally one of the most reactive compounds. These are used for the synthesis of a variety of organic compounds. The following reactions illustrate the synthetic uses of methylmagnesium iodide.

#### 1. Preparation of alkanes

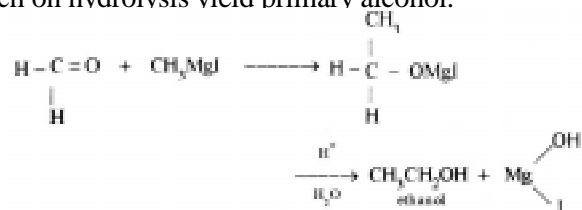
Methylmagnesium iodide undergoes double decomposition with water and alcohol to produce alkanes.



#### 2. Preparation of primary alcohols

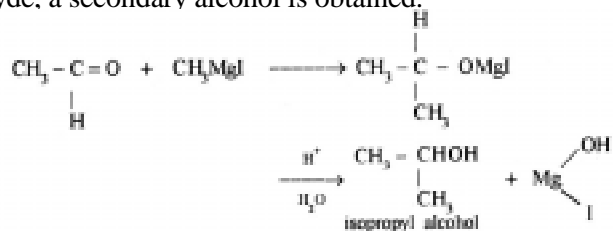
Formaldehyde reacts with methylmagnesium iodide to give addition

product which on hydrolysis yield primary alcohol.



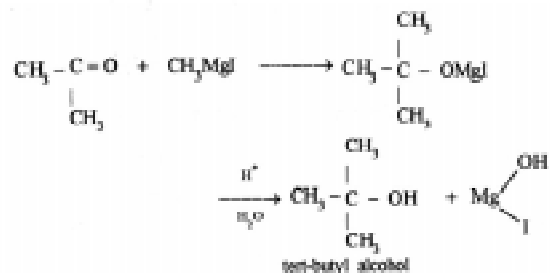
### 3. Preparation of secondary alcohols

When methylmagnesium iodide is treated with any aldehyde other than formaldehyde, a secondary alcohol is obtained.



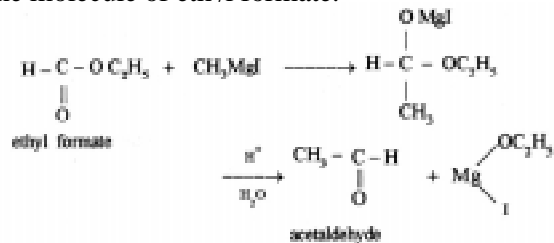
### 4. Preparation of tertiary alcohols

Methylmagnesium iodide reacts with ketones to give an addition compound which on hydrolysis yield tertiary alcohols.

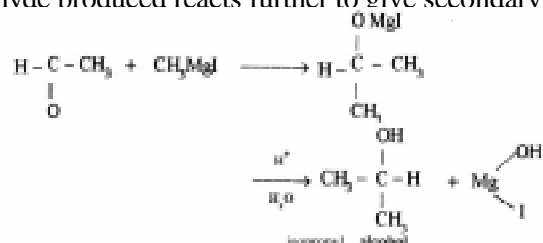


### 5. Preparation of aldehydes

An aldehyde is prepared by treating one molecule of methylmagnesium iodide with one molecule of ethyl formate.

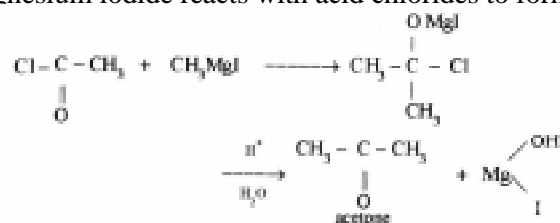


A secondary alcohol is obtained if methylmagnesium iodide is in excess. Aldehyde produced reacts further to give secondary alcohol.



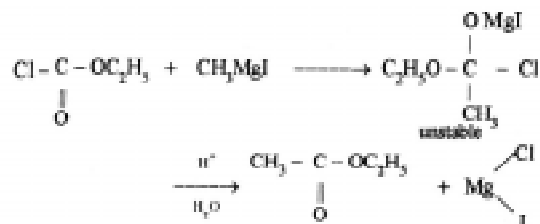
## 6. Preparation of ketones

Methylmagnesium iodide reacts with acid chlorides to form ketones.



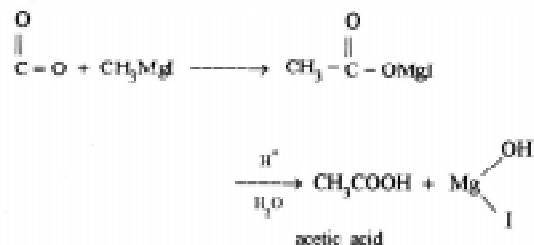
## 7. Preparation of esters

7. Methylmagnesium iodide reacts with ethyl chloroformate to form higher esters



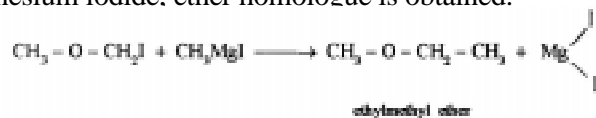
## 8. Preparation of acids

Methylmagnesium iodide reacts with solid carbon dioxide to give addition product which on hydrolysis in the presence of acid yields carboxylic acid.



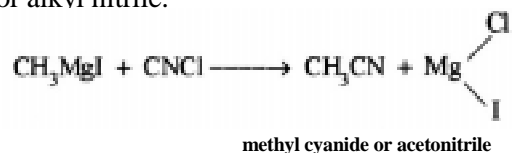
## 9. Preparation of ethers

When a monohalogen derivative of an ether is treated with methylmagnesium iodide, ether homologue is obtained.



## 10. Preparation of alkyl cyanide

Methylmagnesium iodide reacts with cyanogen chloride to form an alkyl cyanide or alkyl nitrile.



## Questions

### A. Choose the correct answer

- The IUPAC name of  

$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH} - \text{CH}_3 \\ | \quad | \\ \text{Br} \quad \text{Cl} \end{array}$$
 is
  - 2-Bromo-3-chloro-4-methylpentane
  - 2-Methyl-3-chloro-4-bromopentane
  - 2-Bromo-3-chloro-3-isopropyl propane
  - 2,4-Dimethyl-4-Bromo-3-chloro butane.
- For reacting with HCl, the alcohol which does not require  $\text{ZnCl}_2$  is
  - $\text{CH}_3\text{CH}_2\text{OH}$
  - $\text{CH}_3 - \text{CH}_2\text{CH}_2\text{OH}$
  - $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 - \text{CH} - \text{OH} \end{array}$
  - $\text{C}(\text{CH}_3)_3\text{C-OH}$ .
- For converting alcohols into alkyl halides, the best reagent is
  - $\text{PCl}_3$
  - $\text{PCl}_5$
  - $\text{SOCl}_2$
  - None of the above
- The olefin, which is not important for Markovni Koff's addition of HCl, is
  - Propene
  - But-1-ene
  - 2-Methyl-propene
  - Ethylene
- The  $\text{S}_{\text{N}}1$  reaction of alkyl halides is not affected by the nature of the
  - alkyl group
  - the halogen
  - medium
  - nucleophile



**B. Fill in the blanks**

1. Markonikoff's rule is followed for the addition of HCl to.....
2. In Swarts reaction metallic fluorides are added to.....
3. Hoffman's rule is applicable to elimination .....
4. Chloropicrin is prepared by adding nitric acid to.....

**C. Write in one or two sentence**

1. What are Lewis acids?
2. What is an electrophilic addition?
3. What is Hunsdiecker reaction?
4. What is Finkelstein reaction?
5. What is Swarts reaction?

**D. Explain briefly on the following**

1. Discuss  $S_N1$  mechanism
2. Discuss  $S_N2$  mechanism
3. Discuss E1 elimination
4. Discuss E2 elimination
5. What are the uses of alkyl halides?
6. What are the general reactions of aryl halides.
7. What are aralkyl halides ? How are they prepared?
8. What are Grignard reagents? Discuss its synthetic uses.
9. Discuss the general methods of preparation of alkyl halides.

**SUMMARY**

- Organic halogen compounds are classified into alkyl, aryl and aralkylhalides.
- Alkyl halides are very good synthetic compounds from which various compounds are synthesised.
- In Aryl halides chloro group is ortho and meta directing.
- If a halogenoalkane is reacted with magnesium metal in dry ethoxyethane, a Grignard reagent is the product - these act as nucleophiles and are commonly used to form new carbon-carbon bonds.

**REFERENCES**

1. Organic Chemistry IL Finar ELBS
  2. Organic Chemistry by Morrison and Boyd.
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