

CY8151 - Engineering Chemistry  
PREPARED FOR R2017 STUDENTS  
(AVAILABLE ONLY IN STUCOR)

Unit I

# WATER AND ITS TREATMENT

Hardness of water – types – expression of hardness – units – estimation of hardness of water by EDTA – numerical problems – boiler troubles (scale and sludge) – treatment of boiler feed water – Internal treatment (phosphate, colloidal, sodium aluminate and calgon conditioning) external treatment – Ion exchange process, zeolite process – Desalination of brackish water - Reverse Osmosis.

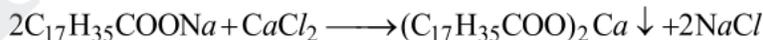
## CHAPTER 1 : Water and its Treatment

### INTRODUCTION

The nature's most abundant supply i.e., water is essential for the survival of all the living beings on earth i.e., man, animals and plants. Water is not only essential for the survival of life, but it is also used for the operation in a large number of industries as coolant, solvent, for steam generation, for air conditioning, fire-fighting etc. Water is also used for all domestic purposes like bathing, drinking, washing, sanitary, irrigation etc.

### HARDNESS OF WATER

“Hardness of water is the characteristic of preventing lather formation of water with soap”. Generally salts like chlorides, bicarbonates and sulphates of  $Ca^{2+}$ ,  $Mg^{2+}$  and  $Fe^{2+}$  make water hard. This hard water on treatment with soap which is stearic or palmitic acid salts of sodium or potassium causes white precipitate formation of calcium or magnesium stearate or palmitate.



Sodium Stearate  
(soap)

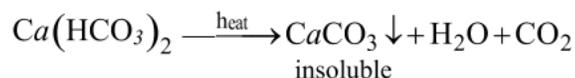
Hardness  
causing  
substance

Calcium Stearate  
(insoluble)

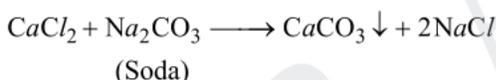
Thus the cause of hardness is the precipitation of the soap and hence prevents lathering at first. When the hardness causing ions are removed as insoluble soaps, water becomes soft and forms lather.

**TYPES OF HARDNESS**

- (i) *Temporary Hardness* is due to the bicarbonates of  $Ca^{2+}$  and  $Mg^{2+}$  and carbonate of  $Fe^{2+}$ . Since bicarbonates readily get precipitated on boiling the water, the temporary hardness can be easily removed, viz.



- (ii) *Permanent Hardness* is due to the presence of chlorides and sulphates of  $Ca$ ,  $Mg$ ,  $Fe$ , etc. Permanent Hardness cannot be removed on boiling.

**EXPRESSION OF HARDNESS AND UNITS OF HARDNESS**

Both temporary and permanent hardness are expressed in ppm (parts per million) as  $CaCO_3$ . The choice of  $CaCO_3$  is due to the fact that its molecular weight is 100 and equivalent weight is 50 and it is the most insoluble salt in water.

Equivalent of  $CaCO_3$

$$\begin{aligned} & \text{(Mass of hardness producing substance)} \\ & \times \text{(Chemical equivalent of } CaCO_3) \\ = & \frac{\hspace{10em}}{\text{Chemical equivalent of hardness producing substance}} \\ = & \frac{\text{Mass of hardness producing substance} \times 50}{\text{Chemical equivalent of hardness producing substance}} \end{aligned}$$

Hardness is principally expressed in ppm unit. Other limits include French degree of hardness, English degree of hardness or Clark, USA degree of hardness and German degree of hardness.

- 1. Parts per million (ppm):** It is the number of parts of calcium carbonate equivalent hardness present in one million parts of water.

1 ppm = 1 part of  $CaCO_3$  equivalent hardness in  $10^6$  parts of water.

- 2. Milligram per litre (mg/L):** It is the number of milligrams of Calcium carbonate equivalent hardness present in one litre of water.

1 mg/lit. = 1 mg of  $CaCO_3$  equivalent hardness in 1 litre of water.

3. **Degree Clarke ( $^{\circ}Cl$ ):** It is the number of parts of  $CaCO_3$  equivalent hardness present in 70,000 parts of water.
4. **Degree French ( $^{\circ}Fr$ ):** It is the number of parts of  $CaCO_3$  equivalent hardness present in  $10^5$  (1 Lakh) parts of water.

$1^{\circ}Fr = 1$  part of  $CaCO_3$  equivalent hardness in  $10^5$  parts of water.

The above four units are correlated as given below:

$$1 \text{ ppm} = 1 \text{ mg/L} = 0.07^{\circ}Cl = 0.1^{\circ}Fr$$

$$1 \text{ ppm} = \frac{1 \text{ part of hardness}}{10^6 \text{ parts of water}}$$

#### Relation between various units of hardness

1 ppm	= 1 mg/l	= 0.1 $^{\circ}Fr$	= 0.07 $^{\circ}Cl$
1 mg/l	= 1 ppm	= 0.1 $^{\circ}Fr$	= 0.07 $^{\circ}Cl$
1 $^{\circ}Cl$	= 1.43 $^{\circ}Fr$	= 14.3 ppm	= 14.3 mg/l
1 $^{\circ}Fr$	= 10 ppm	= 10 mg/l	= 0.7 $^{\circ}Cl$

#### 1.4.1 Disadvantages of Hard Water

- (a) **In domestic uses.** For washing and bathing, hard water creates difficulties, since it does not form lather freely with soap. It also creates sticky precipitates that deposit on bath tub, body, clothes etc. until all the  $Ca/Mg$  salts get precipitated. Thus a lot of soap gets wasted also.

For cooking hard water creates similar difficulties by producing scum on the bottom of the vessels. Due to the presence of hardness producing salts in hard water, boiling point gets elevated and during cooking a lot of fuel is wasted. Pulses etc. do not cook in hard water. Taste of tea, coffee becomes unpleasant.

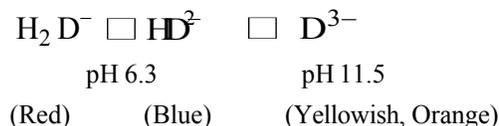
Drinking of hard water is also problematic since it affects the digestive system and at the same time the possibility of deposition of calcium oxalate crystals in the urinary tract is alarming.

- (b) **In industrial uses.** For textile industry and dyeing industry, hard water causes the usual problem of deposition of insoluble salts that interfere with the proper dyeing and printing of the fabrics. The stains of iron salts also are undesirable on fabrics. Hard water also hampers the economy by wastage of soap as it does not form good lather.

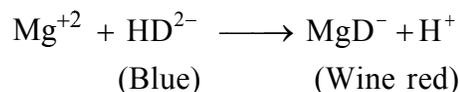
- For sugar industry, the salts responsible for hardness create difficulties in sugar refining and crystallization of sugar and the sugar becomes deliquescent.
- Calcium and magnesium salts also interfere with the smooth and glossy finish of the papers in the paper industry. Iron salts interfere with the colour of the paper.
- In laundry, hard water causes wastage of costly soap and also interferes with the coloration due to the staining of iron salts.
- The hydration of cement and final hardening of cement are affected by use of hard water in concrete making.
- Hard water is not suitable for preparing drug solutions in pharmaceutical industry
- For steam generation in boilers, hard water creates many problems like:
  - (i) scale and sludge formation,
  - (ii) corrosion,
  - (iii) priming and foaming and
  - (iv) caustic embrittlement.

### 1.5 ESTIMATION OF HARDNESS OF WATER BY EDTA

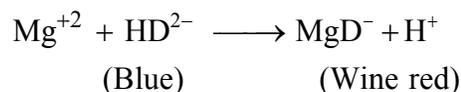
Eriochrome Black-T (EBT) is the metal ion indicator used in the determination of hardness by complexometric titration with EDTA. This dye-stuff tends to polymerize in strongly acidic solutions to a red brown product, and hence the indicator is generally used in EDTA titration with solutions having pH greater than 6.5. The sulphuric acid group loses its proton much before the pH range of 7-12, which is of interest for metal ion indicator use. The dissociation of the two hydrogen atoms of the phenolic groups only should therefore be considered and hence the dye stuff may be represented by the formula  $H_2D^-$ . This functions as acid-base indicator with two colour changes as follows:



In the pH range 8-10, the blue form of the indicator  $HD^{2-}$  gives a wine red complex with  $Mg^{2+}$ :

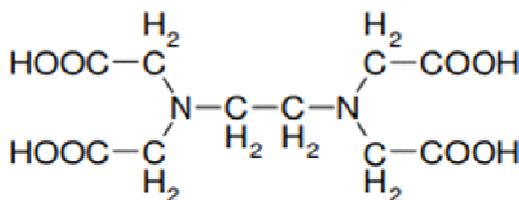


Now if EDTA( $\text{H}_2\text{Y}^{2-}$ ) is added to such a solution  $\text{Mg}^{2+}$  preferentially complexes with EDTA (since the metal EDTA complex is more stable than the metal-indicator complex) and liberates the free indicator  $\text{HD}^{2-}$  at the end point, thereby producing a sharp colour change from wine red to blue. These reactions during the EDTA titration may be summarized as follows:



**Theory:** EDTA (Ethylenediamine tetra acetic acid) forms colorless stable complexes with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions present in water at  $\text{pH} = 9-10$ . To maintain the  $\text{pH}$  of the solution at 9-10, buffer solution ( $\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$ ) is used. Eriochrome Black-T (E.B.T) is used as an indicator.

The sample of hard water must be treated with buffer solution and EBT indicator which forms unstable, wine-red colored complexes with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  present in water.



Structure of EDTA

**Procedure***(a) Total hardness*

- (i) Take 25 or 50 ml or well mixed sample in a conical flask
- (ii) Then add 1 to 2 ml buffer solution followed by 1 ml inhibitor
- (iii) Add a pinch of Eriochrome black-T and titrate with standard EDTA (0.01M) till wine red colour changes to blue, then note down the volume of EDTA required (A).
- (iv) Run a reagent blank. Note the volume of EDTA (B).
- (v) Calculate volume of EDTA required by sample,  $C = A - B$  (from volume of EDTA required in steps (iii & iv).

*(b) Calcium hardness*

- (i) Take 25 or 50 ml sample in a conical flask
- (ii) Add 1 ml NaOH to raise pH to 12.0 and add a pinch of murexide indicator.
- (iii) Titrate immediately with EDTA till pink colour changes to purple. Note the volume of EDTA used (A1).
- (iv) Run a reagent blank. Note the ml of EDTA required (B1) and keep it aside to compare end points of sample titrations.
- (v) Calculate the volume of EDTA required by sample,  $C1 = A1 - B1$ .

<b>PROBLEMS BASED ON CALORIFIC VALUE</b>
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**Problem 1:** If a sample of water contains 50 mgs of  $Ca^{2+}$  ions per litre, calculate its hardness in terms of  $CaCO_3$  equivalent?

**Solution: Given:** The amount of  $Ca^{2+}$  ions = 50 mgs/lit.

We know that, the molecular weight of calcium = 40

$$\therefore \text{Amount equivalent to } CaCO_3 = \frac{50 \times 100}{40} = 125 \text{ mgs/lit.}$$

**Problem 2:** A water sample contains 204 mgs of  $CaSO_4$  and 73 mgs of  $Mg(HCO_3)_2$  per litre. What is the total hardness in terms of  $CaCO_3$  equivalent?

**Solution: Given:** Hardness producing salt

(i)  $CaSO_4$  (molecular weight = 136)

$$\begin{aligned} \text{Amounts equivalent to } CaCO_3 &= \frac{204 \times 100}{136} \\ &= 150 \text{ mgs/lit.} \end{aligned}$$

(ii)  $Mg(HCO_3)_2$  (Molecular weight = 146)

$$\begin{aligned} \text{Amounts equivalent to } CaCO_3 &= \frac{73 \times 100}{146} \\ &= 50 \text{ mgs/lit.} \end{aligned}$$

Temporary hardness =  $Mg(HCO_3)_2$  = 50 mgs/lit

Permanent hardness =  $CaSO_4$  = 150 mgs/lit

Total hardness =  $Mg(HCO_3)_2 + CaSO_4$

$$\Rightarrow 50 + 150 = 200 \text{ mgs/lit.}$$

**Problem 3: Calculate the carbonate and non-carbonate hardness of a sample of water containing the dissolved salts as given below in mgs/lit.  $Mg(HCO_3)_2 = 7.3$ ;  $Ca(HCO_3)_2 = 40.5$ ;  $CaSO_4 = 13.6$ ;  $MgCl_2 = 21.75$  and  $NaCl = 50$ .**

**Solution: Given:**

(i) Hardness producing salt  $Mg(HCO_3)_2$  (Mol. Wt = 146), Amount in mgs/lit = 7.3

$$= \frac{7.3 \times 100}{146} = 5 \text{ mgs/lit.}$$

(ii)  $Ca(HCO_3)_2$  (Mol. Wt = 162), Amount in mgs/lit = 40.5

$$= \frac{40.5 \times 100}{162} = 25 \text{ mgs/lit.}$$

(iii)  $CaSO_4$  (Mol. Wt. = 136), Amount in mgs/lit = 13.6

$$= \frac{13.6 \times 100}{136} = 10 \text{ mgs/lit.}$$

(iv)  $MgCl_2$  (Mol. Wt. = 95), Amount in mgs/lit = 21.75

$$= \frac{21.75 \times 100}{95} = 22.9 \text{ mgs/lit.}$$

(v)  $NaCl$ , Amount in mgs/lit = 50.

But  $NaCl$  does not contribute any hardness to water, hence it is ignored.

Carbonate hardness =  $Mg(HCO_3)_2 + Ca(HCO_3)_2$

$$= 5 + 25 = 30 \text{ mgs/lit}$$

Non-Carbonate hardness =  $CaSO_4 + MgCl_2$

$$= 10 + 22.9 = 32.9 \text{ mgs/lit.}$$

Total hardness = Carbonate Hardness + Non-Carbonate Hardness

$$= 30 + 32.9 = 62.9 \text{ mgs/lit.}$$

**Problem 4:** A sample of water is found to contain the following analytical data in mgs/lit.  $\text{Mg}(\text{HCO}_3)_2 = 14.6$ ;  $\text{MgCl}_2 = 9.5$ ;  $\text{MgSO}_4 = 6.0$ ;  $\text{Ca}(\text{HCO}_3)_2 = 16.2$ . Calculate the temporary and Permanent hardness of the sample of water.

**Solution: Given: Hardness producing salt.**

(i)  $\text{Mg}(\text{HCO}_3)_2$  (Mol. Wt. = 146), Amount in mgs/lit. = 14.6

$$= \frac{14.6 \times 100}{146} = 10 \text{ mgs/lit.}$$

(ii)  $\text{MgCl}_2$  (Mol. Wt. = 95), Amount in mgs/lit. = 9.5

$$= \frac{9.5 \times 100}{95} = 10 \text{ mgs/lit.}$$

(iii)  $\text{MgSO}_4$  (Mol. Wt. = 120), Amount in mgs/lit = 6.0

$$= \frac{6.0 \times 100}{120} = 5 \text{ mgs/lit.}$$

(iv)  $\text{Ca}(\text{HCO}_3)_2$  (Mol. Wt. = 162), Amount in mgs/lit = 16.2

$$= \frac{16.2 \times 100}{162} = 10 \text{ mgs/lit.}$$

Temporary hardness =  $\text{Mg}(\text{HCO}_3)_2 + \text{Ca}(\text{HCO}_3)_2$

$$= 10 + 10 = 20 \text{ mgs/lit.}$$

Permanent hardness =  $\text{MgCl}_2 + \text{MgSO}_4$

$$= 10 + 5 = 15 \text{ mgs/lit.}$$

## BOILER TROUBLES

### Scale and Sludge

When hard water is used for boilers, on continuous evaporation, the salts present in the hard water gets saturated and are finally deposited in the areas where the flow is slow. When the precipitates formed are loose and slimy in nature, it is called *sludge*, whereas when the precipitates formed are hard and adhere strongly on the inner walls of the boiler, they are called *scale*.

Sludge can be easily removed by scrapping with a brush. Sludge is formed by the presence of  $MgCO_3$ ,  $MgSO_4$ ,  $MgCl_2$ ,  $CaCl_2$  etc. These salts are more soluble in hot water.

Disadvantages of sludge formation are:

- (i) poor heat conduction due to the presence of sludge on the surface;
- (ii) difficulty in the operation of the boiler;
- (iii) if sludge is formed along with the scale and is trapped within the scale formed and so it is difficult to remove and
- (iv) it clogs the pipe lines and other connections to the vessel near the places where water circulation rate is slow.

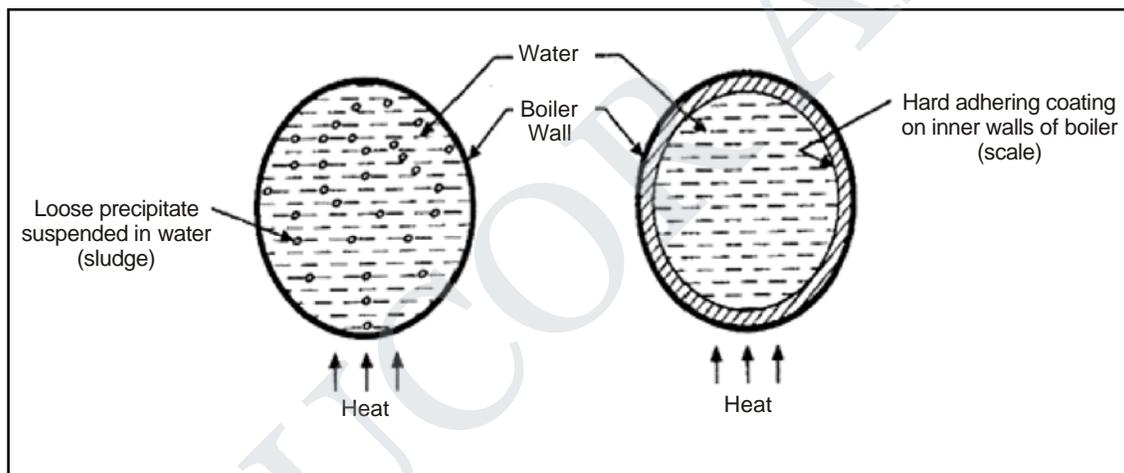


Figure 1.1: Scale and sludge formation in boilers

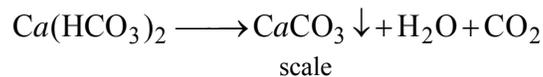
### **Removal of Sludge**

Sludge formation can be prevented by:

- (i) using soft water for boiler operation and
- (ii) removing the concentrated salty water from time to time so that deposition of sludge is prevented. Scales are the hard deposits on the inner surface of the boilers which are difficult to remove.

This scale formation takes place due to the following reasons:

- (a) In low pressure boilers scale formation occurs due to the formation of  $\text{CaCO}_3$  from  $\text{Ca}(\text{HCO}_3)_2$ .



- (b) In high pressure boilers this  $\text{CaCO}_3$  gets converted to soluble  $\text{Ca}(\text{OH})_2$ . But here  $\text{CaSO}_4$  forms the hard scale. Since the solubility of  $\text{CaSO}_4$  decreases with increase in temperature, and at high temperature the precipitated  $\text{CaSO}_4$  forms hard scale. Similar hard scales are formed when  $\text{SiO}_2$  is present in the hard water. It deposits as  $\text{CaSiO}_3$  or  $\text{MgSiO}_3$ . These calcium or magnesium silicate scales are very difficult to remove. Dissolved magnesium salts also precipitate as  $\text{Mg}(\text{OH})_2$  forming soft type of scale.

**Disadvantages of scale formation** are similar to sludge formation but the severity is more, since its removal is more difficult.

*Disadvantages include*

- (i) Poor heat transfer from boiler to water leading to increase in fuel consumption. The increase in thickness of the scale from 1.25 mm to 12 mm leads to increase in fuel consumption from over 50% to 150%.
- (ii) Due to the overheating of the boiler, different parts of the boiler become weak and distorted and so the operation of the boiler becomes unsafe, particularly the high pressure boilers. The thick scales may sometimes lead to explosion due to sudden development of high pressure.
- (iii) Valves and condensers of the boilers are choked due to scale formation and Boiler efficiency decreases.

*Removal of scales can be done by:*

- (i) Wooden scraper or wire brush, suitable for removing loose scales.
- (ii) Blow down operations for loose scales. The operation actually involves the removal of very hard water from a tap at the bottom of the boiler and replenishing the water with softened water called 'make up' water.

- (iii) Giving thermal shocks, which involve alternate heating and cooling to make the scales brittle.
- (iv) Chemical treatment with 5-10% HCl for carbonates and EDTA treatment for Ca/Mg salts forming complexes.

### ***Differences between Sludge and Scale***

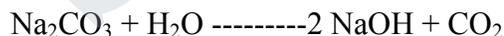
S.No.	Sludge	Scale
1.	Loose, slim, non-adherent precipitate	Hard, thick, strong adherent precipitate
2.	Due to salts like MgSO <sub>4</sub> , MgCl <sub>2</sub>	Due to salts like CaSO <sub>4</sub> , Ca(HCO <sub>3</sub> ) <sub>2</sub>
3.	Due to poor conductance, they decrease the boiler efficiency to lesser extent and causing chocking in the pipelines.	Due to poor conductance, they decrease the boiler efficiency to maximum extent, cause reduced fuel economy, improper boiling, boiler explosion etc.,
4.	It can be prevented by periodical replacement of concentrated hard water by fresh water. This process is known as "blow down" method.	It can be prevented by special methods like i) External treatment of ion exchange, ii) Internal carbonate, phosphate, Calgon conditioning and iii) Mechanical hard scrubbing methods.

## **2. Caustic embrittlement**

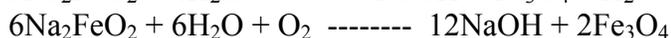
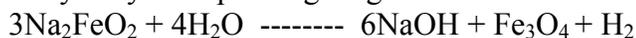
**Definition:** Intercrystalline cracking of boiler material

It is a form of stress corrosion that takes place in boilers operating at high temperature (200-250° C) and pressure. Caustic embrittlement occurs at stressed parts of boilers such as cracks, rivets, bends, joints etc.

The boiler feed water usually contains some residual sodium carbonate (used for softening process). At high temperature and pressure it undergoes hydrolysis to form sodium hydroxide.



The alkali water sweeps through the minute cracks, crevices between the rivets and joints by capillary action. Inside the cracks water gets evaporated leaving behind NaOH. The concentrations of the NaOH gradually increase on these sites due to poor circulation of water. When concentrations of the NaOH reaches a value of 10% it attacks the metal at the stressed region dissolving it in the form of sodium ferroate (Na<sub>2</sub>FeO<sub>2</sub>). Sodium ferroate undergoes hydrolysis-depositing magnetite as follows



So NaOH is regenerated in the process and its concentration is kept on increasing maintaining a required environment. Thus corrosion process develops cracks and making the metal brittle by the deposition of the product.

## **3. Priming and foaming**

Bubbles produced in the water due to heat and pass out with the steam. This is called foaming and it is caused by high concentration of impurities in the boiler water.

**Priming**

It is the carry over of varying amounts of droplets of water in the steam, which lowers the energy efficiency of the steam and leads to the deposit of water droplets of impurities and cause the damage of boiler.

**Prevention:**

To prevent it, use of chemicals like anti-foaming and anti-priming agents which prevents the formation of priming and foaming in the boiler water.

**4) Boiler Corrosion**

It may be due to three major reasons:

- i) Dissolved Oxygen
- ii) Dissolved CO<sub>2</sub>
- iii) Dissolved salts like MgCl<sub>2</sub>

**i) Corrosion Due to dissolved oxygen :**

Dissolved oxygen in presence of water, causes corrosion.



**Prevention from oxygen:**

**a) Chemical method –**

i) Adding Sodium Sulphite:



This method results in other precipitates which can have some side effects. So this method is less preferred.

ii) Adding Hydrazine:



This method results in inert gas and pure water, and has no side effects

**b) Mechanical deaeration method:**

1. This is based on the principle that at high temperature , low pressure and high exposed area, the solubility of gases in water is decreased. So, the gases can be expelled easily.
2. Here, the water is fed into the mechanical deaerator which is provided with vacuum pump, heaters and perforated plates.
3. The out coming water will be free from dissolved gases.

**2. Corrosion due to CO<sub>2</sub>**

Salts like Calcium bicarbonate on heating produces CO<sub>2</sub> . CO<sub>2</sub> dissolves in water to form carbonic acid which corrodes the boiler metal. Δ



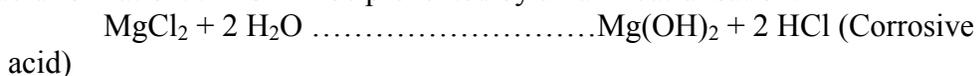
**Prevention from CO<sub>2</sub>**

1. Chemical method: By adding calculated amount of ammonium hydroxide

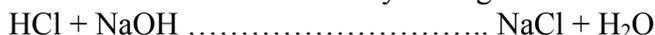


2. Mechanical deaeration method ( similar to oxygen method)

cause acid formation. This will be prevented by alkali neutralisation.

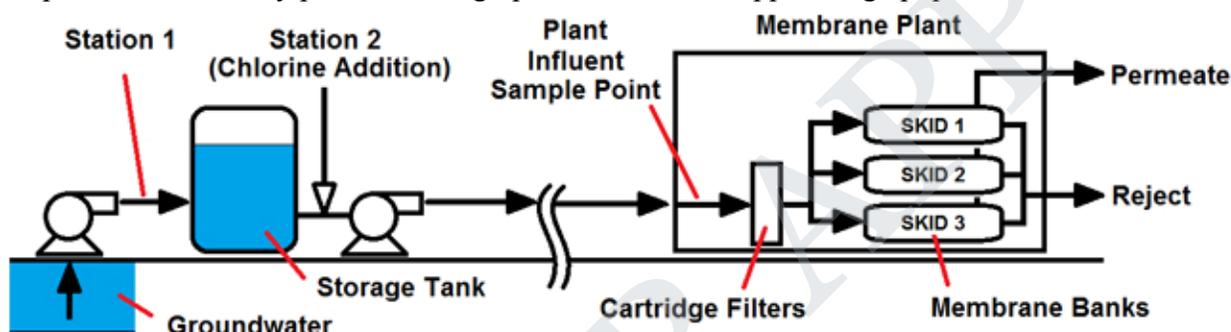


Neutralisation: Excess acidic nature is neutralized by adding alkalis and vice versa.



### DESALINATION PROCESS

Definition: Process of removing common salt from sea water.. Seawater desalination has the potential to reliably produce enough potable water to support large populations .



Types of process:

Reverse osmosis (RO) and Nanofiltration (NF) are the leading pressure driven membrane processes. Contemporary membranes are primarily polymeric materials with cellulose acetate still used to a much lesser degree. Operating pressures for RO and NF are in the range of 50 to 1,000 psig (3.4 to 68 bar, 345 to 6896 kPa).

Electrodialysis (ED) and Electrodialysis Reversal (EDR) processes are driven by direct current (DC) in which ions (as opposed to water in pressure driven processes) flow through ion selective membranes to electrodes of opposite charge.

#### Reverse osmosis

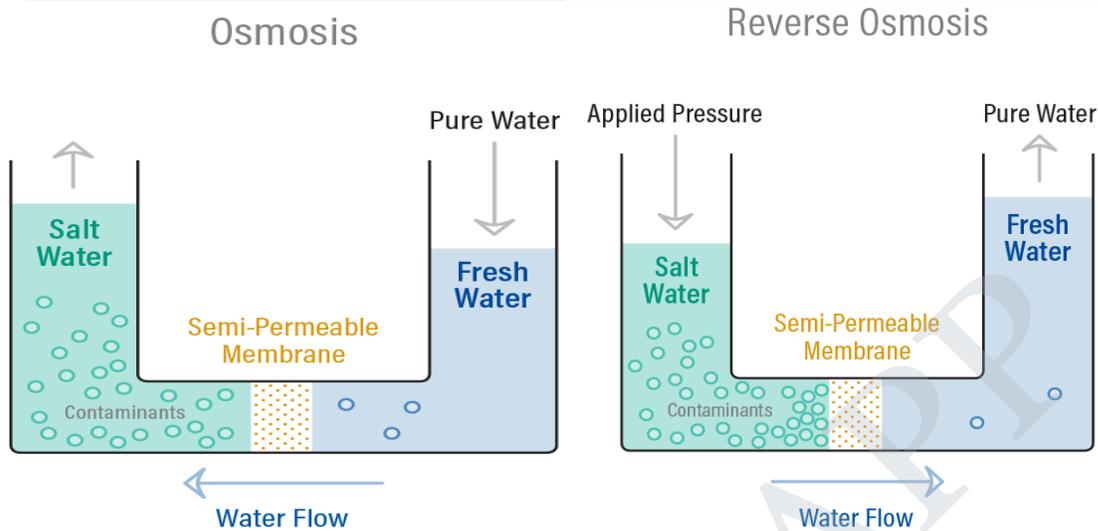
##### Osmosis:

If two solutions of different concentration are separated by a semi-permeable membrane which is permeable to the smaller solvent molecules but not to the larger solute molecules, then the solvent will tend to diffuse across the membrane from the less concentrated to the more concentrated solution. This process is called osmosis.

Osmosis is of great importance in biological processes where the solvent is water. The transport of water and other molecules across biological membranes is essential to many processes in living organisms. The energy which drives the process is usually discussed in terms of osmotic pressure..

##### Reverse osmosis

If hydrostatic pressure greater than the osmotic pressure is applied then the flow of solvent from high concentration to low concentration occurs. This is called reverse osmosis .this can also be called as Superfiltration



### TREATMENT OF BOILER FEED WATER

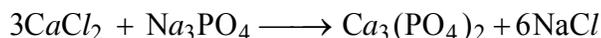
These are methods for the removal of the scales, when they are formed. There are also some methods for the prevention of scale formation by internal or external treatment.

#### Internal Treatment

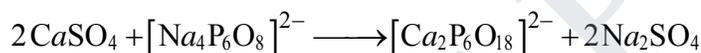
Internal Treatment involves addition of chemical to the boiler water either to (i) precipitate the scale forming impurities in the form of sludges, which can be easily removed or (ii) convert the impurities to soluble compounds, so that scale formation can be avoided. Important internal treatments involve.

- (a) **Colloidal Conditioning:** Organic substances like kerosene, tannin, agar-agar are added to form gels and form loose non-sticky deposits with scale-forming precipitates, which can be easily removed by blow-down operations in low pressure boilers.

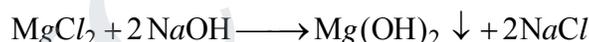
- (b) **Different Sodium Phosphates** like  $\text{NaH}_2\text{PO}_4$ ,  $\text{Na}_2\text{HPO}_4$  and  $\text{Na}_3\text{PO}_4$  are added to high pressure boilers to react with the hardness forming impurities to form soft sludge of calcium and magnesium phosphates and finally this can be removed by blow down operation.



- (c) **Calgon Conditioning:** Calgon i.e., sodium hexa meta phosphate when added to boiler water, reacts with scale forming  $\text{CaSO}_4$  and forms soluble complex compound.



- (d) **Sodium Aluminate Conditioning:** Sodium aluminate is hydrolysed yielding  $\text{NaOH}$  and gelatinous  $\text{Al}(\text{OH})_3$ . The  $\text{NaOH}$  formed reacts with magnesium salts to precipitate  $\text{Mg}(\text{OH})_2$ . This  $\text{Mg}(\text{OH})_2$  and  $\text{Al}(\text{OH})_3$  are flocculent and entraps the colloidal as well as the finely divided impurities like silica in the boiler water and the loose precipitate is finally removed by blow down operation.

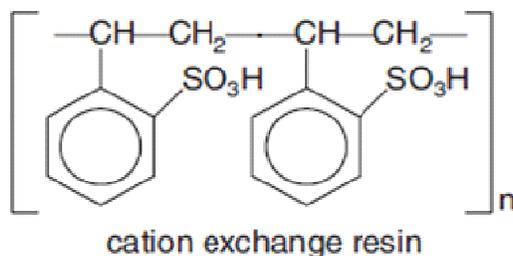


## External Treatment

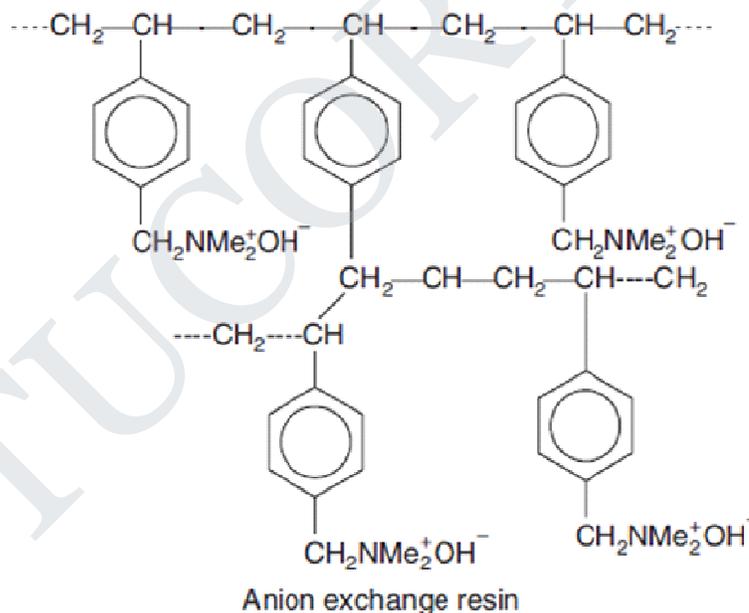
### Ion Exchange or Demineralization

Ion Exchange Resins are organic polymers which are crosslinked having microporous structure and the functional groups are attached to the chains which are responsible for the ion exchange properties.

- (i) **Cation Exchange Resins ( $\text{RH}^+$ )** are phenol-sulphonic acid-formaldehyde resin, styrene- divinyl benzene copolymers which exchange their  $\text{H}^+$  ions with the cations present in the water i.e.,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ .

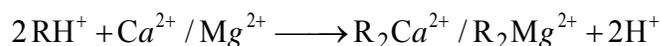


- (ii) **Anion Exchange Resins (ROH<sup>-</sup>):** The styrene divinyl benzene or amine formaldehyde copolymers contain quaternary ammonium tertiarysulphonium or amino group in the resin. The resin on treatment with hard water is capable of exchanging the OH<sup>-</sup> with different anions of water i.e., Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> etc.

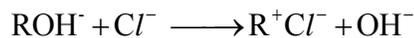


**Method**

The hard water is passed first through cation exchange resin, the cations like Ca<sup>2+</sup>, Mg<sup>2+</sup> are removed from the hard water and exchanged with H<sup>+</sup> as follows:



After this the hard water is again passed through anion exchange column, which exchanges all the anions like  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  etc. present in the water with  $\text{OH}^-$ .



These  $\text{H}^+$  from cation exchanger and  $\text{OH}^-$  from anion exchanger combine to form water molecule. Thus the water coming out finally from the two exchangers is ion free and called deionized or demineralized water.

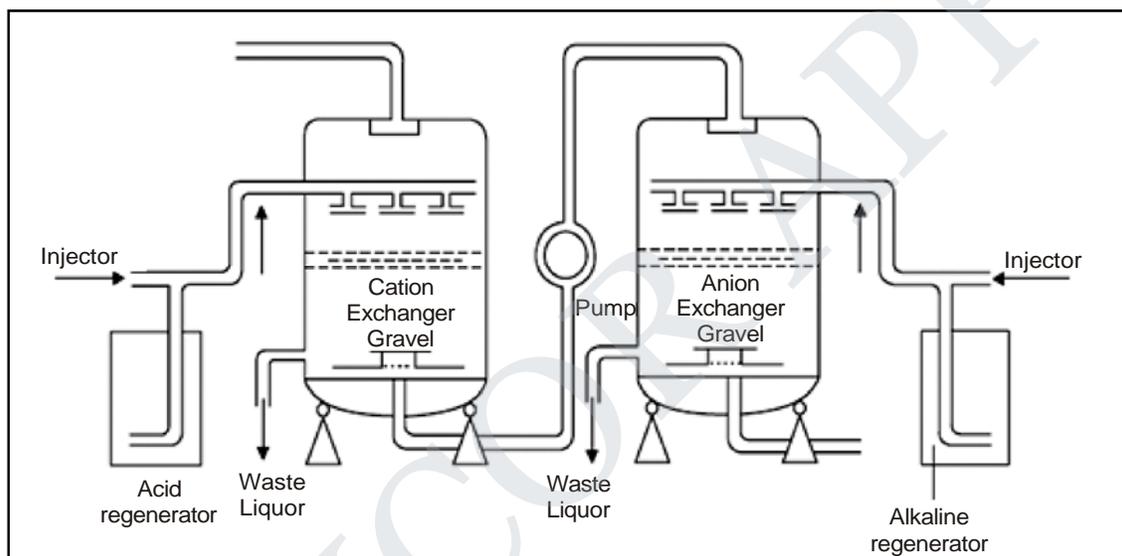
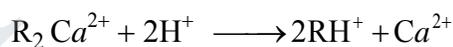


Figure 1.2: Demineralization of Water

**Regeneration:** The inactivated or exhausted cation exchange resin is regenerated by passing a dil.  $\text{H}_2\text{SO}_4/\text{HCl}$  solution.



Similarly, the exhausted anion exchange resin is regenerated by passing a dil.  $\text{NaOH}$  solution.



The columns are finally washed with deionized water and the washings are discarded.

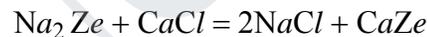
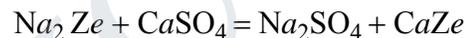
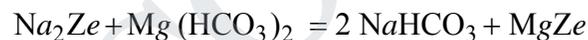
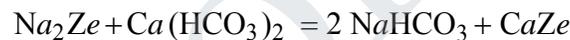
### Permutit or Zeolite Process

Zeolite is hydrated sodium aluminosilicate capable of exchanging reversibly its sodium ions for  $Ca^{2+}$  and  $Mg^{2+}$ , having the general formula  $Na_2O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$ . Common zeolite is  $Na_2O \cdot Al_2O_3 \cdot 3SiO_2 \cdot 2H_2O$  and is known as natrolite. Others gluconites, green sand etc. are used for water softening.

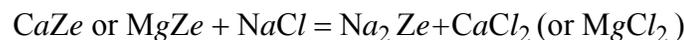
Artificial Zeolite used for softening purpose is permutit. These are porous and glassy and have greater softening capacity than green sand. They are prepared by heating together with china clay, feldspar and soda ash.

**Method of Softening:** Hard water is passed through a bed of zeolite at a specific rate at ordinary temperature; the hardness causing cations i.e.,  $Ca^{2+}$  and  $Mg^{2+}$  are exchanged for  $Na^+$  and it is converted to  $CaZe$  and  $MgZe$ .

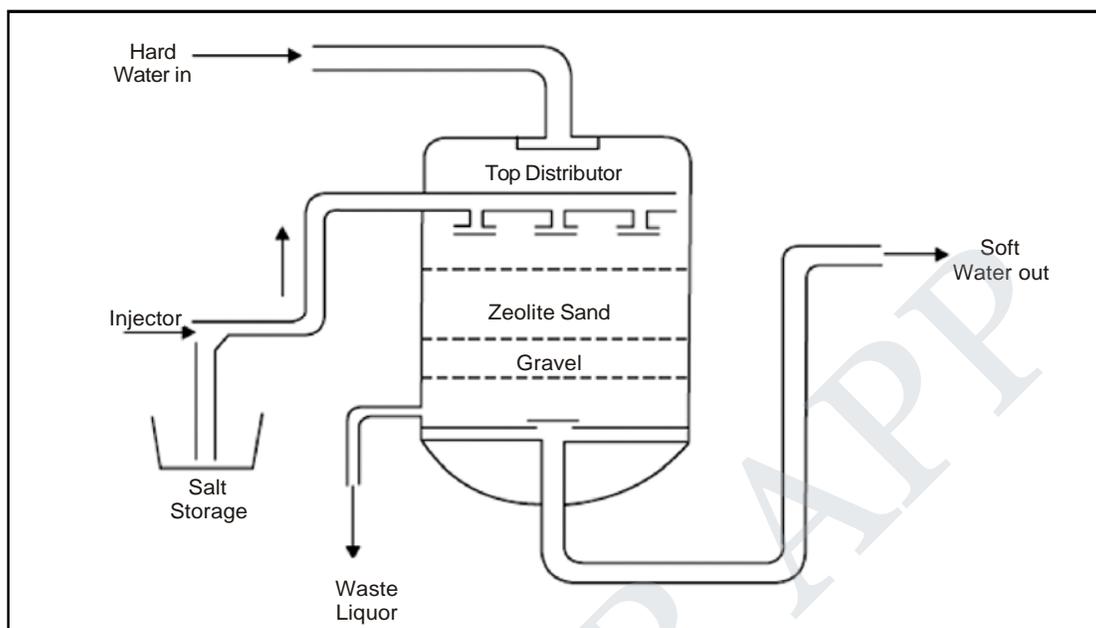
*Reactions taking place are:*



*Regeneration of Zeolite:* The process is also commercially successful since the  $Ca/Mg$  zeolites formed by passing hard water through the bed can be easily regenerated into  $Na_2Ze$  by passing brine through the bed of inactivated zeolite.



The washings containing  $CaCl_2$  or  $MgCl_2$  are wasted. The water softened by this process can be used for laundry purposes.



**Figure 1.3: Softening of hard water by permutit process**

**Advantages:**

- (i) Hardness of water can be removed completely upto about 10 ppm.
- (ii) The equipment used is small and easy to handle.
- (iii) It requires less time for softening.
- (iv) There is no sludge formation, hence the process is clean.
- (v) Easy to regenerate.
- (vi) Any hardness can be removed without any adjustment of the process.

**Disadvantages:**

- (i) Coloured water or water containing suspended impurities cannot be used before filtration.
- (ii) Water containing acid cannot be used for softening since acid may destroy the zeolite.
- (iii) Since on removal of  $Ca^{2+}$  and  $Mg^{2+}$  the soft water contains large amount of  $NaHCO_3$ , this on heating liberates  $CO_2$ , which causes corrosion in the boilers and hence this soft water is not suitable for boilers.



## Unit II

# SURFACE CHEMISTRY AND CATALYSIS

Introduction - Terminologies in surface chemistry - Difference between adsorption and absorption - Types of adsorption - Adsorption isotherm- Freundlich Adsorption Isotherms- Langmuir Adsorption Isotherm - Contact Theory (or) Mechanism of Heterogeneous Catalysis - Kinetics of Surface Reaction - Kinetics of Bimolecular Reaction (Langmuir-Hinshelwood) - Types of Adsorption Isotherm - Application of Adsorption- Terms - Mechanism of Catalytic Reaction- Criteria (or) Characteristics for Catalyst Types of Catalysis - Homogeneous Catalysis - Heterogeneous Catalysis- Catalytic Poisoning and Promoters Application of Catalysis- Biological Catalyst – – Enzymes - Kinetics of Enzyme Catalysed Reaction Or Michaelis and Menten equation - Factors Affecting Enzyme Activity

## CHAPTER 2: Surface Chemistry

### INTRODUCTION

Surface Chemistry is closely related to interface and colloidal science. Surface chemistry is important in many critical chemical processes, such as enzymatic reactions at biological interfaces found in cell walls and membranes, in electronics at the surfaces and interfaces of microchips used in computers, and the heterogeneous catalysts found in the catalytic converter used for cleaning emissions in automobile exhausts.

### DEFINITION

*Surface science is the study of chemical phenomena that occur at the interface of two phases (solid–liquid interfaces, solid–gas interfaces, solid–vacuum interfaces, and liquid–gas interfaces).* (or)

It is defined as the *study of chemical reactions at interfaces.*

### TERMINOLOGIES IN SURFACE CHEMISTRY

- **Adsorbate:** The substance which gets adsorbed on any surface is called *adsorbate*.
- **Adsorbent:** The substance on the surface of which adsorption takes place is called **adsorbent**.
- **Adsorption:** The process whereby molecules of gases or liquids adhere chemically to the surface of a solid.

(Eg.) Occlusion of Hydrogen gas on Palladium where palladium is adsorbent and hydrogen gas is adsorbate.

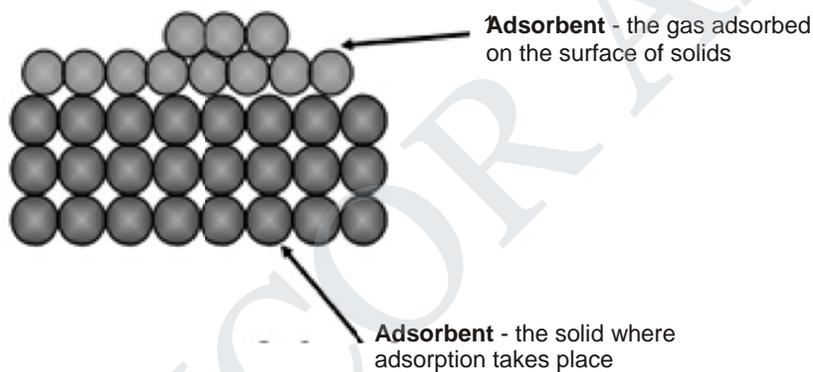


Figure 2.1 : Adsorption Process

- **Desorption:** The removal of the adsorbed substance from a surface is called *desorption*.
- **Interface:** The plane which separates any two phase is generally called an *interface*.
- **Absorption:** When the molecules of a substance are uniformly distributed throughout the body of a solid or liquid. This phenomenon is called *absorption*.
- **Sorption:** The phenomenon in which adsorption and absorption occur simultaneously is called *sorption*.
- **Occlusion:** When adsorption of gases occurs on the surface of metals it is called *occlusion*.

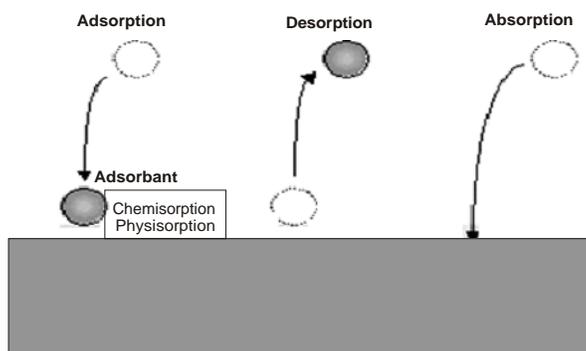


Figure 2.2 : Occlusion Process

- Positive adsorption:** When the concentration of solute adsorbed on the solid adsorbent surface is greater than in the bulk it is called *positive adsorption*.  
 (Eg.) Concentrated solution of  $KCl$  is shaken with blood charcoal, it shows positive adsorption
- Negative adsorption:** When the solvent from the solution may be absorbed by the adsorbent so that the concentration of the solute decreases and the concentration of solution increases than the initial concentration and it is called *negative adsorption*.  
 (Eg.) Dilute solution of  $KCl$  is shaken with blood charcoal it shows negative adsorption.

### *Enthalpy or heat of adsorption*

Amount of heat evolved when 1 mole of an adsorbate gets adsorbed on the surface of an adsorbent is called **Molar Heat or Molar Enthalpy of Adsorption**.

### DIFFERENCE BETWEEN ADSORPTION AND ABSORPTION

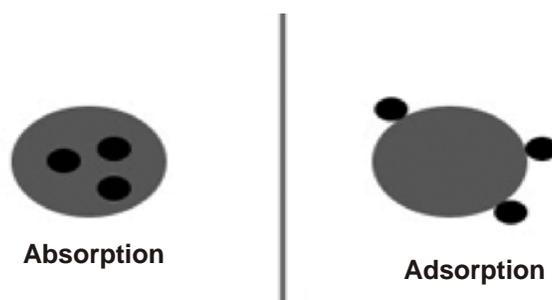


Figure 2.3 : Illustration of Absorption and Adsorption

S.No.	ABSORPTION	ADSORPTION
1.	It is a bulk phenomenon	It is a surface phenomenon
2.	It is a slow process	It is a fast process
3.	Substance uniformly distributed throughout the surface	Higher concentration of molecular species in the surface than in the bulk
4.	Attainment of equilibrium takes time	Equilibrium attained easily
5.	Eg.: Ammonia adsorbed in charcoal	Eg.: Ammonia adsorbed in water

### TYPES OF ADSORPTION

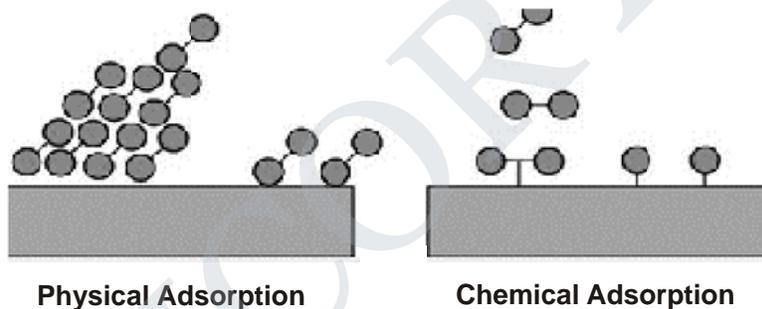


Figure 2.4 : Illustration of Physical and Chemical Adsorption

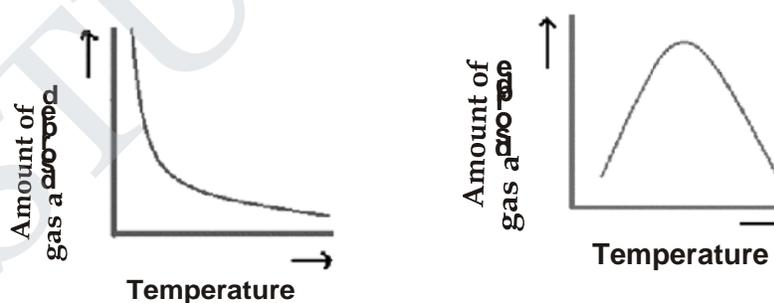


Figure 2.5 : Amount of gas adsorbed vs temperature

S.No	Physical adsorption or Physisorption	Chemical adsorption or Chemisorption
1.	Caused by intermolecular vanderwaal's forces	Caused by chemical bond formation
2.	Not specific in nature	Highly specific in nature
3.	Reversible in nature	Irreversible in nature
4.	Multimolecular layers are formed on the adsorbed surface	Unimolecular layers are formed on the surface
5.	Heat of adsorption is less (20 to 40 KJ/mole)	Heat of adsorption is large (80 to 240 KJ/mole)
6.	No activation energy is required	High activation energy is required
7.	Depends on nature of gas. Easily Liquefiable gases are adsorbed easily	Depends on nature of adsorbent and adsorbate
8.	Occurs at low temperature	Increases with increase in temperature
9.	Increase in pressure increase adsorption	High pressure is favourable. Decrease in pressure does not cause desorption

### Adsorption of Gases on Solids

In adsorption of gases on solid surface, the solid surface is called the adsorbent and the gas adsorbed is called **adsorbate**. The extent of adsorption depends on many factors.

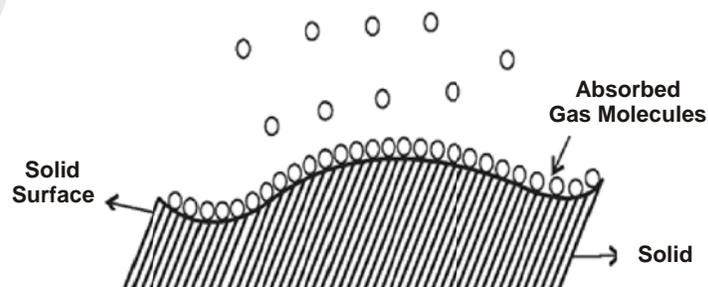


Figure 2.6 : Adsorption of gases on solids

## 2.2 FACTORS AFFECTING THE EXTENT OF ADSORPTION

### (i) Nature of Adsorbent

The adsorption depends on the type of adsorbents used. When the adsorbent is highly porous the rate of adsorption increases. Activated carbon, metal oxides like aluminum oxide, silica gel and clay are commonly used adsorbents. The rate of adsorption can be increased by activation process. It helps in enhancing the pores in the adsorbent **Eg. charcoal adsorbs 0.011 gms of  $\text{CCl}_4$  at  $24^\circ\text{C}$  and activated charcoal adsorbs 1.48 gm of at  $24^\circ\text{C}$ .**

#### *Activation of adsorbent*

During activation, the adsorbent is heated in steam to about  $1500^\circ\text{C}$ . Heating drives out all impurities and leads to a larger free surface for adsorption. It can be done in 3 given ways

- By making the surface of adsorbent rough.
- By heating the adsorbent in vacuum so that the water vapour present in pores leave those pores.
- By increasing the surface area of adsorbent

### (ii) Surface area of adsorbent

Increase in surface area of the adsorbent increases the adsorption of gases and the extent of adsorption depends on two factors

- Greater the surface area greater the adsorption-Increase in surface area increases the number of adsorbing sites.
- Larger the porosity greater the adsorption-Finely divided and highly porous materials acts as good adsorbents.

Eg. Charcoal and silica gel (excellent adsorbents).

### (iii) Nature of Gases

The amount of gas adsorbed by a solid depends on the nature of the gas. Easily liquefiable gases like  $\text{HI}$ ,  $\text{NH}_3$ ,  $\text{Cl}_2$ ,  $\text{SO}_2$  etc., are adsorbed more easily than the permanent gases like  $\text{H}_2$ ,  $\text{N}_2$ , and  $\text{O}_2$  etc. Physical adsorption is non-specific in nature, so any gas will be adsorbed on the surface under any given conditions of temperature and pressure. Chemisorption is specific in nature so only those gases which forms chemical bonds will be adsorbed.

*The nature of gas depends on two factors:*

- **Critical Temperature** (maximum temperature above which the gas cannot be liquefied). Liquefactions of gases depend on critical temperature. When the critical temperature is more the gases will be liquefied and more adsorption occurs.
- **Van der Waal's forces:** Easily liquefiable gases possess greater Vander Waal's forces than permanent gases, so they are adsorbed more readily.

#### (iv) Exothermic Nature

Heat of adsorption is defined as the energy liberated when 1 g mol of a gas is adsorbed on a solid surface. Increase in temperature increases the kinetic energy of the gas molecules and it results in more number of collisions of gas molecules over the adsorbent surface.

#### (v) Pressure

When pressure is increased then the rate of adsorption increases initially. The extent of adsorption is expressed as  $x/m$  where 'x' is amount of adsorbate; 'm' is mass of adsorbent when the dynamic equilibrium is established between free gas and the adsorbed gas. But after some time it reaches appoint where no more adsorption occurs and at this point adsorption is independent of pressure.

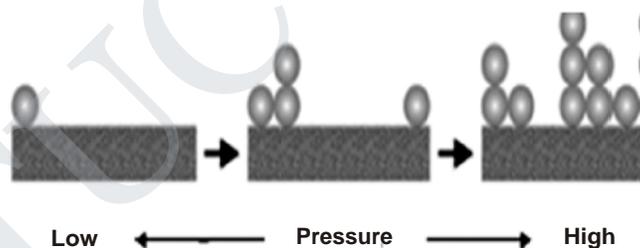


Figure 2.7 : Rate of adsorption

### 3. ADSORPTION OF SOLUTE FROM SOLUTIONS

The process of adsorption of solutes on solid surface can take place from solutions. For example the activated animal charcoal adsorbs colouring matter present in sugar solution and clarifies the sugar solution. It also has the capacity to adsorb acetic acid and oxalic acid from water thereby reducing the concentration of acids in water.

There are two (or more) components present in a solution namely **solute** and **solvent**. The solute may be present in the molecular or ionic form. The extent of adsorption from solution

depends upon the concentration of the solute in the solution, and can be expressed by the **Freundlich Isotherm**.

$$\frac{x}{m} = k \cdot c^{(1/n)}$$

(or)

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log C$$

where,  $x$ - is the mass of the solute adsorbed,

$m$  -is the mass of the solid adsorbent,

$c$  -is the concentration of the solute in the solution &

$n$  -is a constant having value greater than one,

$k$  -is the proportionality constant.

The value of  $k$  depends upon the nature of solid, its particle size, temperature, and the nature of solute and solvent etc. If the graph is plot between  $x/m$  against  $c$  which gives a straight line which is similar to Freundlich adsorption isotherm.

### FACTORS AFFECTING ADSORPTION OF SOLUTES FROM SOLUTION

#### Nature of adsorbent

Adsorption of solute from solution is highly specific. Adsorption depends mainly on nature of adsorbent.

#### Temperature

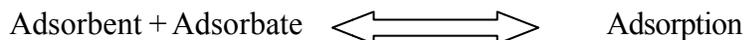
Adsorption from solution decreases with rise in temperature.

#### Concentration of solute

Adsorption from solution decrease with decrease in concentration of solution. eg charcoal adsorbs water from dilute KCl solution whereas charcoal adsorbs KCl from concentrated KCl solution.

### 4. ADSORPTION ISOTHERM

The process of adsorption is usually studied through graphs know as adsorption isotherm. It is the graph between the amounts of adsorbate ( $x$ ) adsorbed on the surface of adsorbent ( $m$ ) and pressure (P) at constant temperature.



Adsorption isotherm shows the amount of molecules adsorbed on the solid surface as a function of the equilibrium partial pressure at constant temperature.

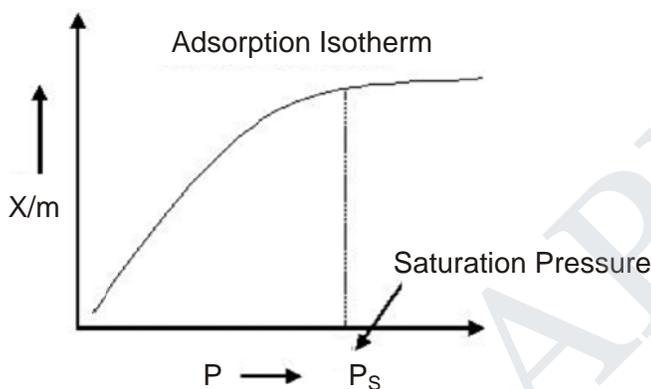


Figure 2.8 : Adsorption Isotherm

A plot of  $x/m$  vs  $P$  is plotted to obtain adsorption at constant temperature,  $P_s$  is called the *saturation pressure*.

### FREUNDLICH ADSORPTION ISOTHERMS

In 1909, Herbert Freundlich gave an expression representing the isothermal variation of adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure. Freundlich adsorption isotherm is an empirical relation between the concentration of a solute on the surface of an adsorbent to the concentration of the solute in the liquid with which it is in contact. The isotherm is given as:

$$\frac{x}{m} = k \cdot p^{\left(\frac{1}{n}\right)} \quad [n > 1]$$

$$\text{(or)} \quad \log \frac{x}{m} = \log k + \frac{1}{n} \log P$$

where  $x$  – is mass of adsorbate,

$m$  – is mass of adsorbent,

$P$  – is the equilibrium pressure of adsorbate,

$K$  &  $n$  – are constants.

At low pressure, extent of adsorption is directly proportional to pressure:

$$\frac{x}{m} \propto p^1$$

At high pressure, extent of adsorption is independent of pressure:

$$\frac{x}{m} \propto p^0$$

At intermediate value of pressure, adsorption is directly proportional to pressure raised to power  $\frac{1}{n}$ .  $n$  value is greater than 1.

$$\frac{x}{m} \propto p^{(1/n)}$$

To remove proportionality a proportionality constant ' $k$ ' is used which is known as adsorption constant and we get

$$\frac{x}{m} = k \cdot p^{(1/n)}$$

The above equation is known as **Freundlich Adsorption equation**.

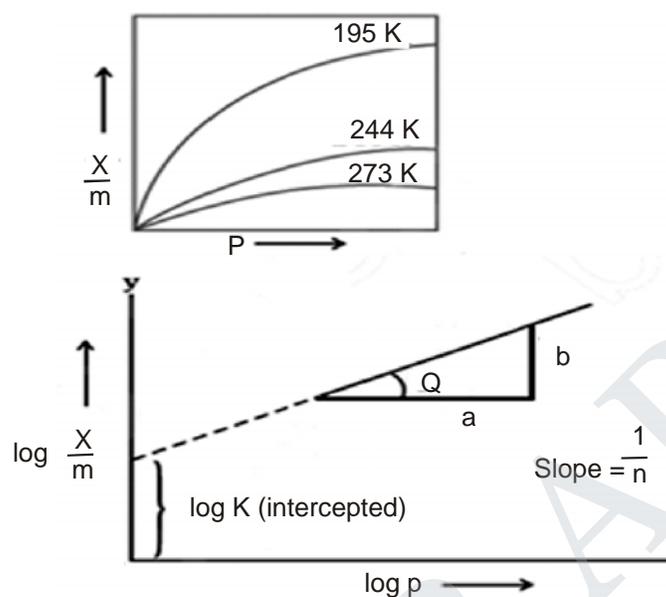
### **Plotting of Freundlich Adsorption Isotherm**

$$\frac{x}{m} = k \cdot p^{(1/n)}$$

Taking log both sides of equation, we get,

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log P$$

The equation is comparable with equation of straight line,  $y = mx + c$  where,  $m$  represents slope of the line and  $c$  represents intercept on  $y$  axis. Plotting a graph between  $\log(x/m)$  and  $\log p$ , we will get a straight line with value of slope equal to  $1/n$  and  $\log k$  as  $y$ -axis intercept.

Figure 2.9 :  $\log(x/m)$  vs.  $\log p$  graph

### Limitation of Freundlich Adsorption Isotherm

1. Freundlich equation is purely empirical and has no theoretical basis.
2. The equation is valid only upto a certain pressure and invalid at higher pressure.
3. The constants  $k$  and  $n$  are not temperature independent, they vary with temperature.
4. Freundlich's adsorption isotherm fails when the concentration of the adsorbate is very high.

### LANGMUIR ADSORPTION ISOTHERM

In 1916, Irving Langmuir proposed another adsorption Isotherm which explained the variation of adsorption with pressure

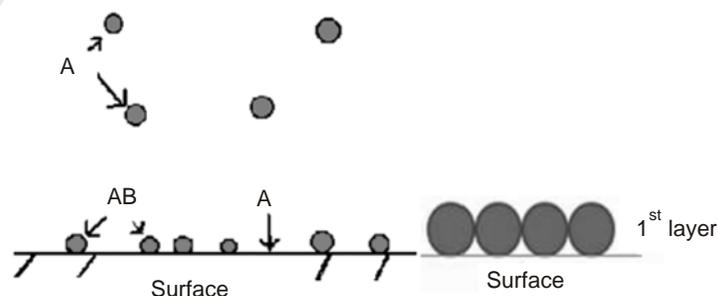


Figure 2.10 : Equilibrium between free molecule and adsorbed molecules

**Assumptions of Langmuir Isotherm**

Langmuir proposed his theory by making following assumptions.

- (i) Surface is energetically uniform. Fixed number of vacant or adsorption sites are available on the surface of the solid.
- (ii) All the vacant sites are of equal size and shape on the surface of adsorbent.  
Each site can hold maximum of one gaseous molecule and a constant amount of heat energy is released.
- (iii) Heat of adsorption is constant throughout the surface and it ranges from 0 to 1.
- (iv) Dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules.
- (v) Adsorption is monolayer or unilayer.

**Derivation**

Langmuir Equation depicts the relationship between the extent of adsorption and pressure. Langmuir proposed that dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules. Using the equilibrium equation, equilibrium constant can be calculated.



where  $A(g)$  – is unadsorbed gaseous molecule

$B(s)$  – is unoccupied metal surface and

$AB$  – is adsorbed gaseous molecule

According to Kinetic theory,

$$\text{Rate of forward reaction} = K_a [A] [B]$$

$$\text{Rate of backward reaction} = K_d [AB]$$

At equilibrium, Rate of forward reaction is equal to Rate of backward reaction

$$K_a [A] [B] = K_d [AB]$$

A new parameter ‘ $\theta$ ’ is introduced.

Let  $\theta$  be the number of sites of the surface which are covered with gaseous molecule and  $(1-\theta)$  be the fraction of surface unoccupied by gaseous molecule. Rate of forward direction depends upon two factors, number of sites available on the surface of adsorbent,  $(1 - \theta)$  and pressure,  $P$ .

$$\text{Rate of forward reaction} \propto P (1 - \theta)$$

$$\text{Rate of adsorption} \propto P (1 - \theta) \text{ or}$$

$$\text{Rate of adsorption} = K_a P (1 - \theta)$$

Rate of backward reaction or rate of desorption depends upon number of sites occupied by the gaseous molecules on the surface of adsorbent.

$$\text{Rate of desorption} \propto \theta \text{ (or)}$$

$$\text{Rate of desorption} = K_d \theta$$

At equilibrium, rate of adsorption is equal to rate of desorption.

$$K_a P (1 - \theta) = K_d \theta$$

The above equation can be written in terms  $\theta$ .

$$K_a P - K_a P \theta = K_d \theta$$

$$K_a P = K_a P \theta + K_d \theta$$

$$K_a P = (K_d + K_a P) \theta$$

$$\theta = \frac{K_a P}{(K_d + K_a P)}$$

Divide numerator and denominator on RHS by  $K_d$ , we get

$$\theta = \frac{\frac{K_a P}{K_d}}{\frac{K_d}{K_d} + \frac{K_a P}{K_d}}$$

$$\text{But } K = \frac{K_a}{K_d}$$

Substituting in the above equation we get

$$\theta = \frac{KP}{1 + KP}$$

This is known as **Langmuir Adsorption Equation**.

### Alternate form of Langmuir Adsorption Equation

Langmuir adsorption equation can be written in an alternate form in terms of volume of gas adsorbed. Let  $V$  be volume of gas adsorbed under given sets of conditions of temperature and pressure and  $V_{\text{mono}}$  be the adsorbed volume of gas at high pressure conditions so as to cover the surface with a unilayer of gaseous molecule.

$$\theta = \frac{V}{V_{\text{mono}}}$$

Substituting the value of  $\theta$  in Langmuir equation

$$\frac{V}{V_{\text{mono}}} = \frac{KP}{1 + KP}$$

$$(or) \quad V_{\text{mono}} = 1 + \frac{1}{kP}$$

in terms of pressure  $P$  we get, Langmuir Adsorption Equation in alternate form.

Thus, if we plot a graph between  $P/V$  vs  $P$ , we will obtain a straight line with Slope =  $1/V_{\text{mono}}$  and intercept =  $1/KV_{\text{mono}}$ .

### Limitations of Langmuir Adsorption Equation

- (i) The adsorbed gas has to behave ideally in the vapour phase. Langmuir equation is valid under low pressure only.
- (ii) Langmuir Equation assumes that adsorption is monolayer. But, monolayer formation is possible only under low pressure condition. Under high pressure condition the assumption breaks down as gas molecules attract more and more molecules towards each other.
- (iii) Another assumption is the surface of solid is homogeneous but in real solid surfaces is heterogeneous.

- (iv) Langmuir equation assumed that molecules do not interact with each other. This is impossible as weak force of attraction exists even between molecules of same type.
- (v) In adsorption liquefaction of gases taking place, which results in decrease in randomness but the value is not zero.

## 5. CONTACT THEORY (OR) MECHANISM OF HETEROGENEOUS CATALYSIS (OR) ADSORPTION THEORY

This theory postulated by Faraday in 1883. It explains the action of heterogeneous catalysis. Heterogeneous catalysis has five steps.

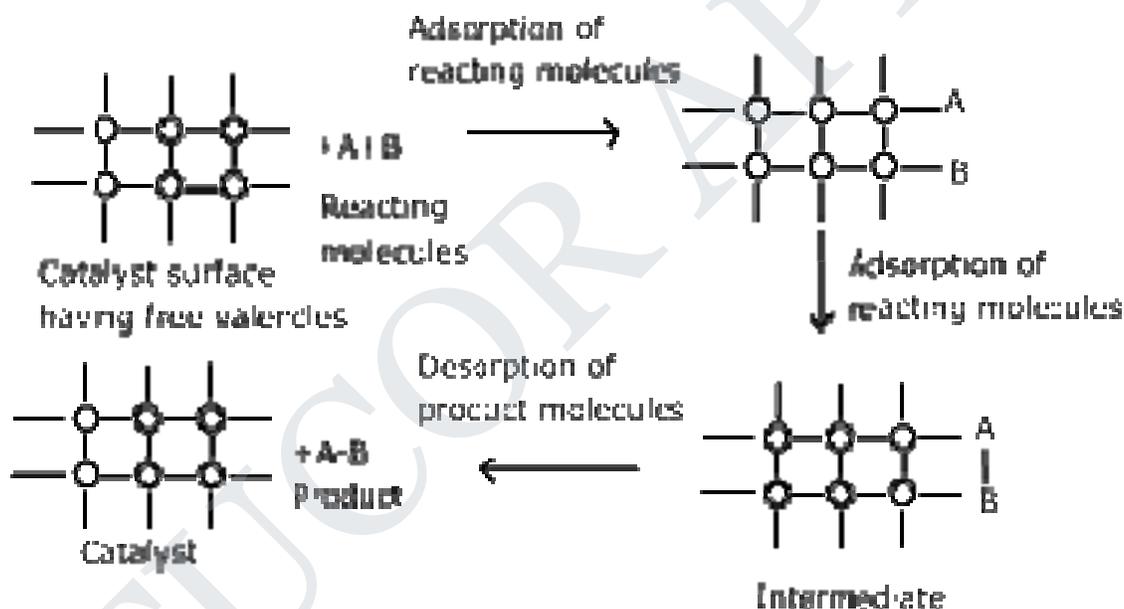


Figure 2.11 : Mechanism of heterogeneous catalysis

- (i) **Diffusion of Reactant(s) to the Surface:** The reactants diffuse to the surface of the catalysts. Some of the reactant cross the barrier and enter the interior exposed surface that includes paths and cracks on the external surface.
- (ii) **Adsorption of reactants:** Bonds are formed as the reactant(s) are adsorbed onto the surface of the catalyst. The ability for an atom or molecule to stick to the surface is known as the Sticking Co-efficient.
- (iii) **Reaction:** The reactants, when bound to the surface have a higher probability of reacting with each other, and after the reaction, they form an intermediate compound.
- (iv) **Desorption of products:** The intermediate compound gets desorbed from the surface, which again becomes available for adsorption for other molecules.
- (v) **Diffusion of Product(s):** The intermediate compound then disintegrates to form the final products and the products are then desorbed from the surface of the catalyst.

For example,

### 1. Conversion of ethylene to ethane

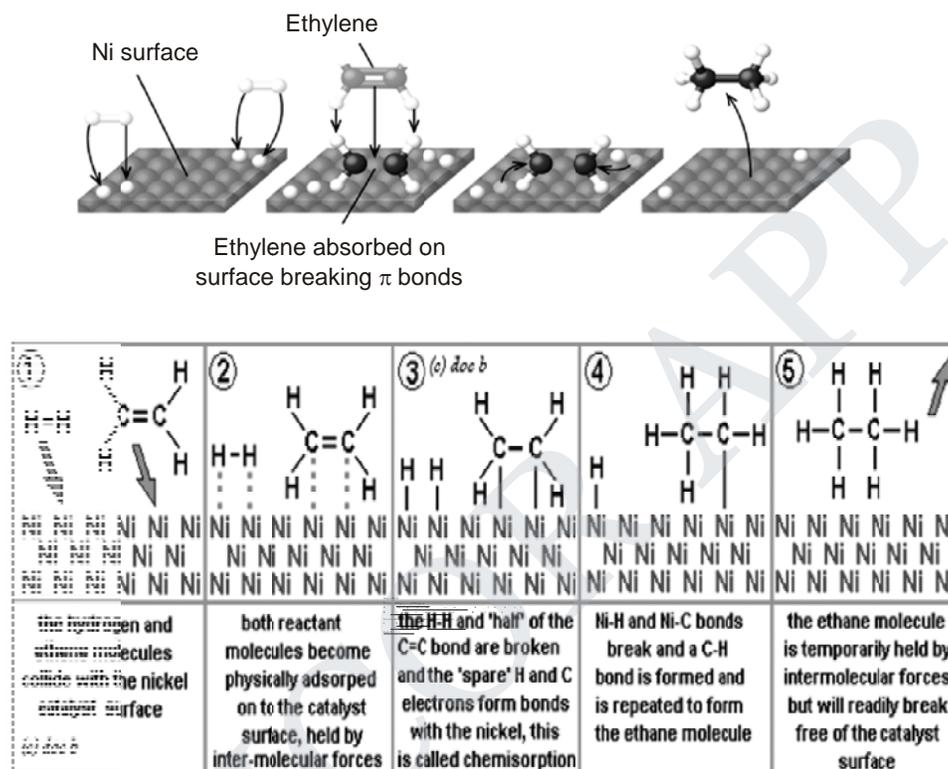
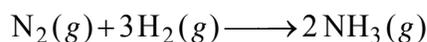


Figure 2.12 : Conversion of ethylene to ethane

### 2. Haber–Bosch reaction

The original Haber–Bosch reaction chambers used osmium as the catalyst, less expensive iron-based catalyst, which is still used today.



The reaction mechanism, involving the heterogeneous catalyst, is believed to involve the following steps:

1.  $\text{N}_2(\text{g}) \rightarrow \text{N}_2(\text{adsorbed})$
2.  $\text{N}_2(\text{adsorbed}) \rightarrow 2\text{N}(\text{adsorbed})$
3.  $\text{H}_2(\text{g}) \rightarrow \text{H}_2(\text{adsorbed})$

4.  $\text{H}_2$  (adsorbed)  $\rightarrow$  2 H (adsorbed)
5.  $\text{N}$  (adsorbed) + 3 H (adsorbed)  $\rightarrow$   $\text{NH}_3$  (adsorbed)
6.  $\text{NH}_3$  (adsorbed)  $\rightarrow$   $\text{NH}_3$  (g)

## 6. KINETICS OF SURFACE REACTION

The kinetics of heterogeneously-catalyzed reactions might vary with the partial pressures of the reactant gases above the catalyst surface which can be predicted by using the Langmuir isotherm.

### 6.1 KINETICS OF UNIMOLECULAR DECOMPOSITION

Examples of unimolecular decomposition

1. Decomposition of  $\text{NH}_3$  to  $\text{N}_2$  and  $\text{H}_2$  on metal surfaces,
2. Decomposition of Phosphine on glass,
3. Decomposition of Formic acid on glass, Pt, Ag, Au, or  $\text{TiO}_2$ .

Consider the surface decomposition of a molecule A, i.e. the process



#### *Assumption*

1. The decomposition reaction occurs uniformly across the surface sites. Molecule 'A' may be adsorbed and is not restricted to a limited number of specific sites.
2. The products are very weakly bound to the surface and, they can be easily deformed.
3. The rate determining step is the surface decomposition step.

According to Langmuir adsorption isotherm molecule 'A' adsorbed on the surface is in equilibrium with the gas phase and the surface concentration is represented as:

$$\theta = \frac{b \cdot P}{(1 + b \cdot P)}$$

The rate of the surface decomposition is given by an expression :

$$\text{Rate} = k \theta$$

Substituting,  $\theta$ , in the rate expression we get:

$$\text{Rate} = \frac{k b P}{(1 + b P)}$$

The reaction is expressed within two limits:

**a. Low pressure limit:**  $b \cdot P \ll 1$  (First order reaction with a first order constant  $k' = k \cdot b$ )

$$\text{Rate} = \frac{k' \cdot P}{(1 + bP)}$$

$$\text{Rate} = \frac{K' \cdot P + K'}{b}$$

So  $\text{Rate} \propto k \cdot b \cdot P$  as  $\frac{K'}{b}$  is constant.

Under low pressure ' $\theta$ ' is very small and rate is directly proportional to pressure

**b. High pressure limit:**  $b \cdot P \gg 1$  (Zero order reaction)

$$\text{Rate} = \frac{k \cdot b \cdot P}{(1 + bP)}$$

$$\text{Rate} = \frac{k}{(1 + bP)}$$

Therefore

$$(1 + b \cdot P) \sim b \cdot P \quad \text{and} \quad \text{Rate} \sim k$$

Under high pressure  $\theta$  is almost unity.

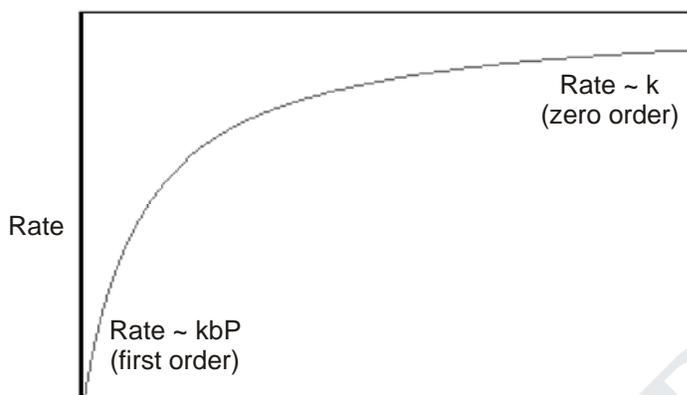


Figure 2.13 : Graphical representation of unimolecular surface decomposition

## 6.2 KINETICS OF BIMOLECULAR REACTION (Langmuir-Hinshelwood)

Between molecular adsorbates.

Consider the reaction:



**Assumption:**

The surface reaction between the two adsorbed species is the rate determining step. The rate of the reaction of the two adsorbed molecules for biomolecular surface will be given by:

$$\text{Rate} = k \theta_A \theta_B$$

According to Langmuir adsorption isotherm:

$$\theta = \frac{b \cdot P}{1 + b \cdot P}$$

where two molecules (A & B) are competing for the same adsorption sites then

$$\theta_A = \frac{b_A P_A}{1 + b_A P_A + b_B P_B} \quad \text{and} \quad \theta_B = \frac{b_B P_B}{1 + b_A P_A + b_B P_B}$$

Substituting these into the rate expression gives:

$$\text{Rate} = k \theta_A \theta_B = \frac{k b_A P_A \cdot b_B P_B}{(1 + b_A P_A + b_B P_B)^2}$$

**Condition**

1. Reactant A and B in first order then

$$b_A P_A \ll 1 \quad \text{and} \quad b_B P_B \ll 1$$

$\theta_A$  &  $\theta_B$  are very low.

$$\text{Hence, Rate} \rightarrow k b_A P_A b_B P_B = k' P_A P_B$$

2. First order in A, but negative first order in B then

$$b_A P_A \ll 1 \ll b_B P_B$$

$$\theta_A \rightarrow 0, \theta_B \rightarrow 1 \quad \text{so} \quad \text{Rate} = \frac{k b_A P_A}{(b_B P_B)} = \frac{k' P_A}{P_B}$$

**7. TYPES OF ADSORPTION ISOTHERM**

Adsorption process is usually studied through graphs known as adsorption isotherm. After saturation pressure  $P_s$ , adsorption does not occur anymore, as there are limited numbers of vacancies on the surface of the adsorbent. At high pressure when all the sites are occupied and further increase in pressure does not cause any difference in adsorption process. At high pressure, adsorption is independent of pressure. There are 5 different types of adsorption isotherms and each of them has specific characteristics.

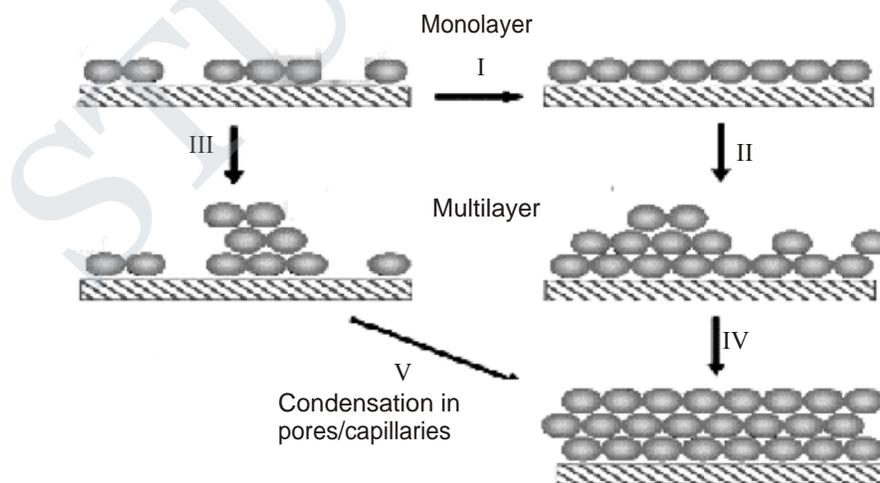


Figure 2.14 : Illustration of different types of Adsorption Isotherm

**Type I Adsorption isotherm** is for very small pores or microporous adsorbents. Adsorption occurs by filling of micropores and it mainly depicts Monolayer adsorption.

Eg. Adsorption of Nitrogen or Hydrogen on charcoal around  $-1800^{\circ}\text{C}$ .

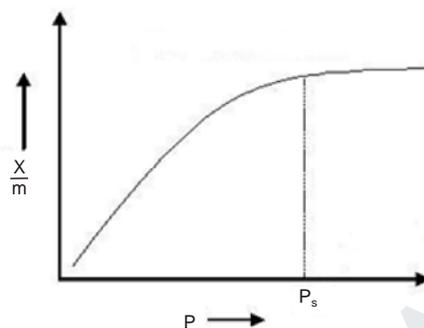


Figure 2.15 : Type I

**Type II Adsorption isotherm** shows large deviation from Langmuir model of adsorption. They are most frequently encountered when adsorption occurs on nonporous powders or macroporous adsorbents with unrestricted monolayer-multilayer adsorption.

The intermediate flat region in the isotherm corresponds to monolayer formation. When

the monolayer formation of the adsorbed molecules are complete, multilayer formation starts to

take place corresponding to the 'sharp knee' of the isotherms.

Eg: Iron (Fe) catalyst and Nitrogen ( $\text{N}_2(\text{g})$ ) adsorbed at  $-1950^{\circ}\text{C}$  on silica gel.

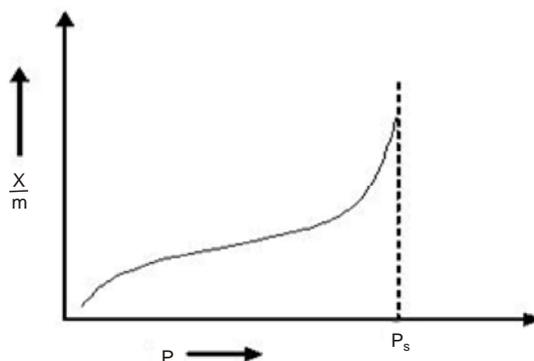


Figure 2.16 : Type II

**Type III Adsorption Isotherm** also shows large deviation from Langmuir model. This isotherm explains the formation of multilayer. They are characterized principally by heats of adsorption which are less than the adsorbate heat of liquefaction.

2.22

*Chemistry*

Eg: Bromine ( $\text{Br}_2$ ) at  $790^\circ\text{C}$  on silica gel or Iodine ( $\text{I}_2$ ) at  $790^\circ\text{C}$  on silica gel.

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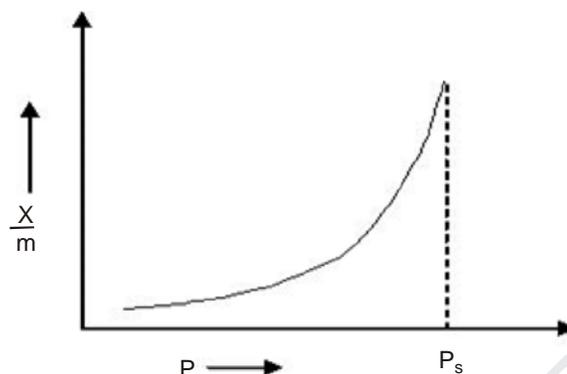


Figure 2.17 : Type III

**Type IV Adsorption Isotherm** occur on porous adsorbents possessing pores in the range of approximately 15-1000 angstroms (Å). At lower pressure region of graph is quite similar to Type II. This explains formation of monolayer followed by multilayer.

The intermediate flat region in the isotherm corresponds to monolayer formation.

The saturation level reaches at a pressure below the saturation vapor pressure. This can be explained on the basis of a possibility of gases getting condensed in the tiny capillary pores of adsorbent at pressure below the saturation pressure ( $P_s$ ) of the gas.

Eg. Adsorption of Benzene on Iron Oxide ( $Fe_2O_3$ ) at  $500^\circ C$  and adsorption of Benzene on silica gel at  $500^\circ C$ .

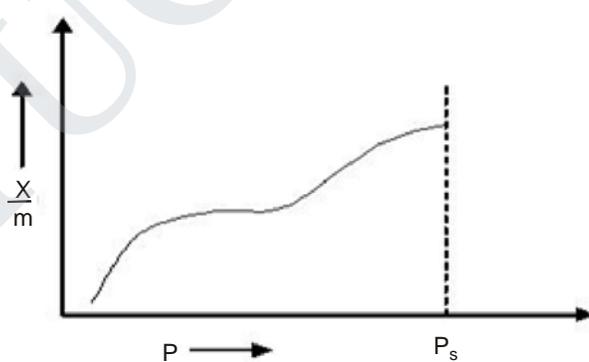


Figure 2.18 : Type IV

**Type V Adsorption Isotherm** results from small adsorbate-adsorbent interaction potentials similar to the Type III isotherms. However, Type V isotherms are also associated with pores in the same range as those of the Type IV isotherms.

Eg: Adsorption of Water (vapors) at  $1000^\circ C$  on charcoal.

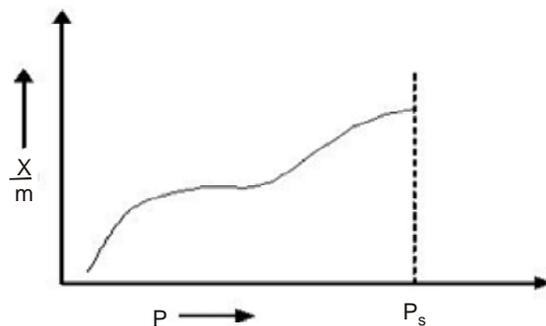


Figure 2.19 : Type V

**Type III and Type V** isotherms do not have the ‘sharp knee’ shape implying stronger adsorbate – adsorbate interactions than adsorbate-adsorbent interaction.

**Type IV and V** shows phenomenon of capillary condensation of gas.

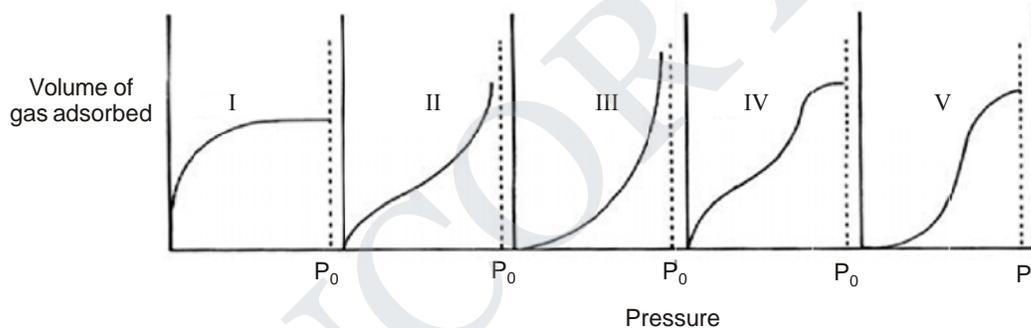


Figure 2.20 : Different types of adsorption isotherms

## 8. APPLICATION OF ADSORPTION

Extensive application of adsorption is been listed below

### (i) *Production of high vacuum*

In Dewar flasks activated charcoal is placed between the walls of the flask so that gas entering into the annular space gets adsorbed.

### (ii) *In Gas masks*

Activated carbon is used in gas masks to adsorb poisonous gases (e.g. oxide of sulphur, NO<sub>x</sub> etc.) and purifies air for breathing.

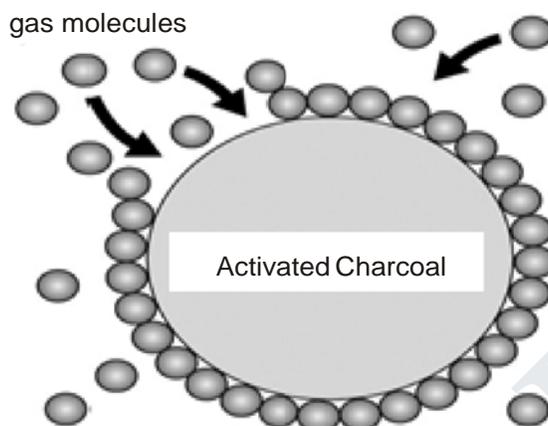


Figure 2.21 : Adsorption of poisonous gases using activated charcoal

**(iii) In desiccation or dehumidification**

Certain substances can be used to remove water vapour or moisture present in the air. Silica gel and alumina are used for dehumidification in electronic equipment.

**(iv) In clarification of sugar**

Sugar is decolorized by treating sugar solution with animal charcoal powder which removes the colour producing substances.

**(v) In paint industry**

The paint should not contain dissolved gases as it inhibits the adherence capacity of paint to the surface to be coated. The dissolved gases are therefore, removed by suitable adsorbents. This is done by adding suitable liquids which adsorb these films. Such liquids are called wetting agents. Eg. Use of spirit as wetting agent in furniture painting.

**(vi) Adsorption chromatography**

Analytical method, in which molecules are separated according to their adsorptive properties, where a mobile fluid phase is passed over an immobile solid adsorptive stationary phase.

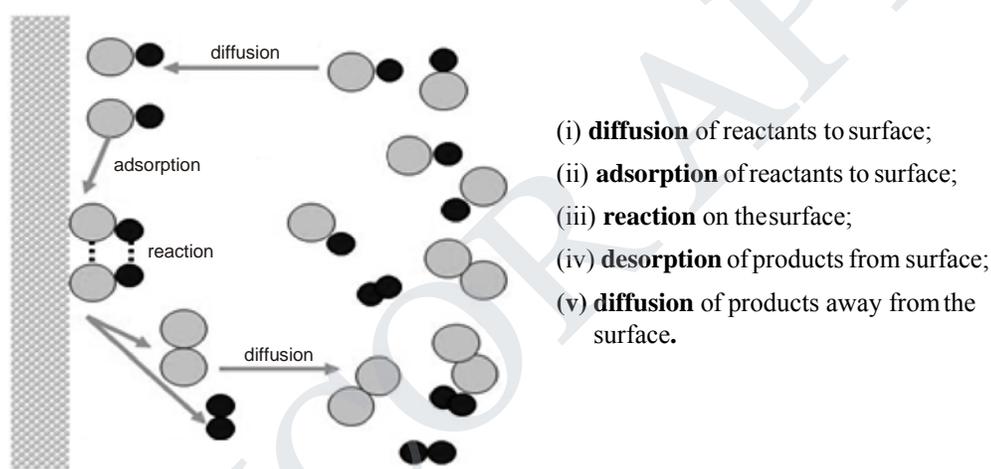
**(vii) In adsorption indicators**

Various dyes which possess adsorption property have been introduced as indicators mainly in precipitation titrations. For example KBr is titrated with  $\text{AgNO}_3$  using eosin as an indicator

**(viii) Heterogeneous Catalysis**

In heterogeneous catalytic reactions adsorption of gaseous reactants on solid catalyst occurs. The adsorption mechanism is responsible for the greater efficiency of the catalyst in the finely divided state and helps us to understand the action of catalyst promoters and poisons. eg,

1. Finely powdered nickel is used for the hydrogenation of oils.
2. In manufacture of sulphuric acid finely divided vanadium pentoxide ( $V_2O_5$ ) is used in the contact process.



- (i) **diffusion** of reactants to surface;
- (ii) **adsorption** of reactants to surface;
- (iii) **reaction** on the surface;
- (iv) **desorption** of products from surface;
- (v) **diffusion** of products away from the surface.

Figure 2.22 : Process of Heterogeneous Catalysis

**(ix) In adsorption indicators**

In many precipitation titrations many dyes are used as indicators which work on the principle of adsorption.

**(x) In curing diseases**

Some pharmaceutical drugs have the capacity to adsorb the germs on them and kill them and protect us from diseases.

**(xi) Lake test for aluminium**

It is based on adsorption of litmus paper by  $Al(OH)_3$  precipitate

**(xii) Separation of inert gases**

Due to the difference in degree of adsorption of gases by charcoal, a mixture of inert gases can be separated by adsorption on coconut charcoal at different low temperatures.

**(xiii) In softening of hardwater**

The use of ion exchangers for softening of hard water is based upon the principle of adsorption chromatography. The ion exchange resins helps to remove hardness causing ions from water and make it useful for industrial and domestic applications.

**(xiv) Arsenic Poisoning**

Colloidal ferric hydroxide is administered which adsorbs arsenic and removes it from body by vomiting

**(xv) Formation of stable emulsions in cosmetics and syrups etc.****(xvi) Froth floatation method**

Used for concentration of sulphide ores is based on adsorption.

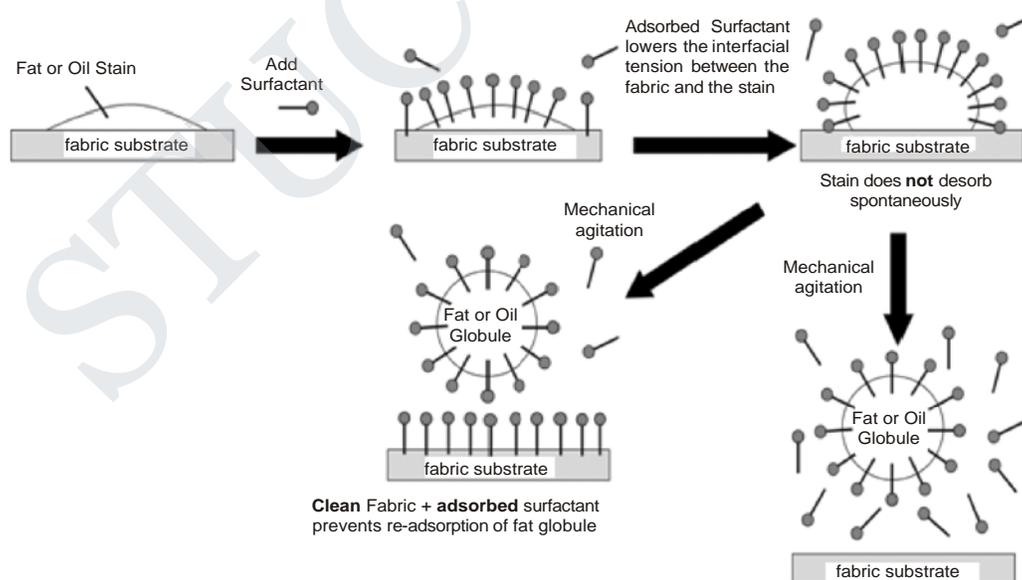
**(xvii) In cleaning action of soaps and detergents**

Figure 2.23 : Cleaning actions of soaps and detergents

**(xviii) Application of adsorbents on pollution abatement**

- o Many pollutants, both natural and synthetic, are gaseous in nature and it need to be effectively removed from the exhaust.
- o Gaseous industrial pollutants include  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{S}$ ,  $\text{SO}_x$ ,  $\text{NO}_x$ ,  $\text{NH}_3$ , Ethylene, Benzene, Ethanol, and HAP's. Adsorption is a mass transfer process in which a porous solid comes in contact with a liquid or gaseous stream to selectively remove pollutants or contaminates by adsorbing them onto the solid.
- o The most common adsorbents used in industry are activated carbon, silica gel, activated alumina (alumina oxide), and zeolite. Activated carbon is the most common non-polar adsorbent. Polar adsorbents have a great attraction to absorb moisture.
- o Most industrial exhaust streams contain moisture the use of polar adsorbents is significantly limited for air pollution control systems. There are two main types of adsorption systems; fixed bed or continuous.

**[1] Fixed Bed or Packed Bed Systems**

These are quite simple devices. The fixed bed or packed bed reactors are most commonly used for study of solid catalyst. A fixed bed reactor usually consists of a cylindrical vessel packed with the adsorbent material (eg. activated carbon) and it contains more surface area for adsorption. The contaminated or the polluted air enters the fixed bed system at the side, where there is an exhaust distributor. The exhausted air exits the fixed bed adsorber clean of pollutants or contaminates. Once the adsorbent is fully saturated with adsorbate the system requires change-out of the spent materials, which is then packed with new adsorbent material. The spent adsorbent will be thermally cleaned.

**Advantages**

1. Ideal plug flow behavior
2. Lower maintenance cost

**Disadvantage**

1. Plugging of bed due to coke deposition which results in high pressure drop.

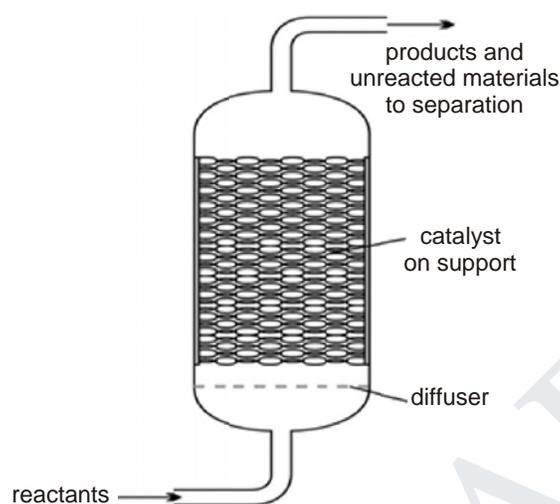


Figure 2.24 : Fixed Bed Reactor Device

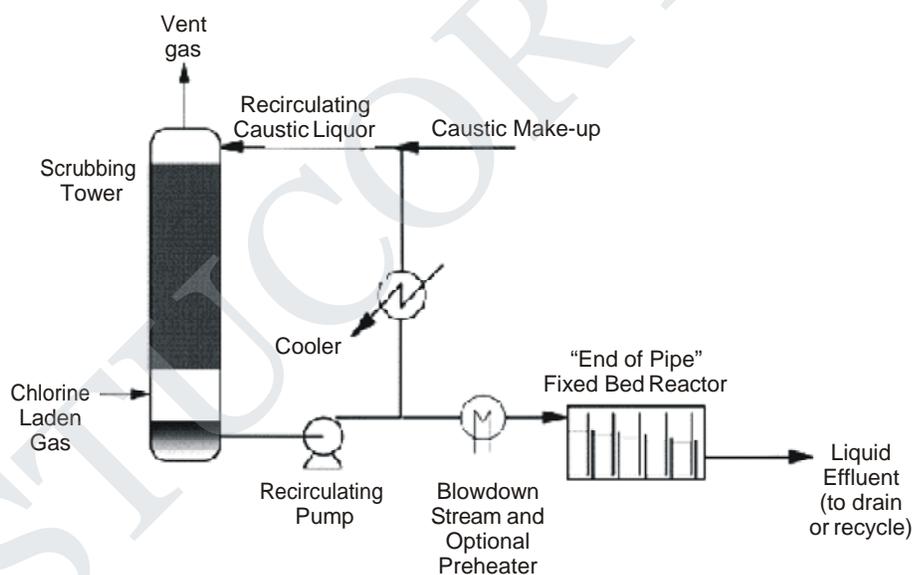


Figure 2.25 : Schematic representation of fixed bed reactor

## [2] Continuous Flow Reactor Systems

Continuous-flow reactors are almost always operated at steady state. These are more complex and provide continuous operations. These systems provide in-situ desorption of the adsorbates from the adsorbent. This can be done with superheated or saturated steam. The adsorbate can be condensed, collected, and re-used in the process. There are two adsorber

units in the system. The gases are being adsorbed in one unit as the other unit is being desorbed with steam. The exhaust from the desorbed bed can be condensed for solvent reuse or other beneficial purpose.

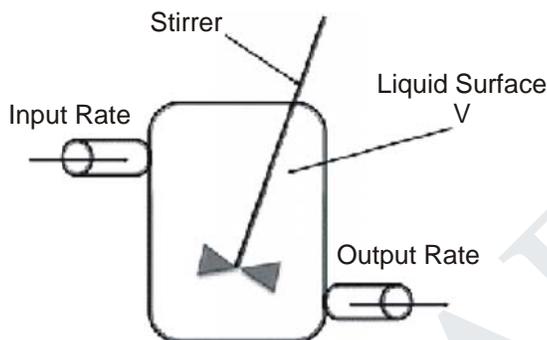


Figure 2.26 : Continuous Flow Reactor

### [3] Special Type of Continuous System (Zeolite Concentrator, or Rotary Concentrator)

A hydrophobic zeolite is designed in a monolithic rotor in which the contaminated air flows. An integrated thermal oxidizer is used to provide desorption of the solvents from the zeolite. They have wide acceptance in industrial air pollution control applications.

## CHAPTER 3: Catalysis

A catalyst is defined as a substance which alters the rate of a chemical reaction, itself remaining chemically unchanged at the end of the reaction. The process is called catalysis.

### 3.1 INTRODUCTION

The word “catalyst” was introduced into science by the great Swedish chemist Jons Jakob Berzelius (1779-1848) who also determined the atomic and molecular weights of thousands of substances, discovered several elements including selenium, first isolated silicon and titanium, and created the present system of writing chemical symbols and reactions.

Catalysts are of immense importance in chemistry and biology. All enzymes are catalysts that expedite the biochemical reactions necessary for life. (eg) Enzymes in saliva accelerate the conversion of starch to glucose.

#### 3.1.1 DEFINITION

*The process by which a substance speeds up a chemical reaction without being consumed or altered in the process.*

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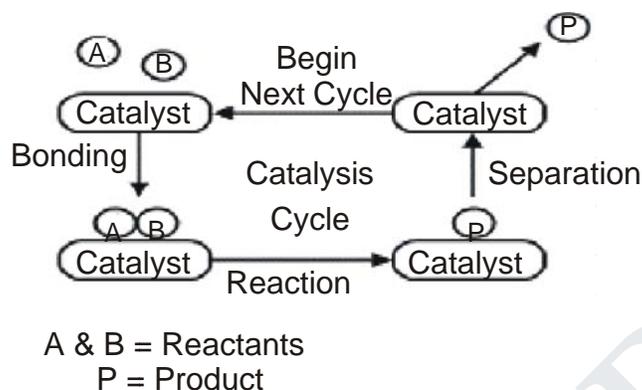


Figure 3.1 : Catalysis Cycle

## 1. TERMS

### 1. Catalyst

*A catalyst is a substance that decreases the activation energy of a chemical reaction without itself being changed at the end of the chemical reaction*

(or)

*It is the small amount of substance which alters the velocity of reaction without altering in any change in mass and composition at the end of the reaction.*

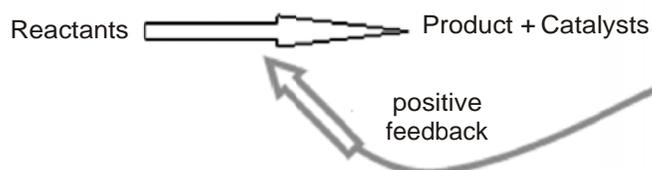
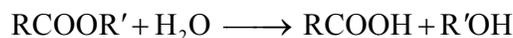
### 2. Positive and negative catalyst

Catalyst helps in altering the velocity of the reaction and the catalyst is called as positive catalyst. eg.  $MnO_2$  acts as catalyst in decomposition of  $KClO_3$  into  $KCl$  and  $O_2$ . Some catalyst have the capacity to retard the chemical reaction and they are called as negative catalyst. eg Alcohol retards the conversion of chloroform to phosgene.

### 3. Auto Catalysis

If the products of a reaction act as a catalyst for the reaction, it is referred to as autocatalysis

Eg.



## 2. MECHANISM OF CATALYTIC REACTION

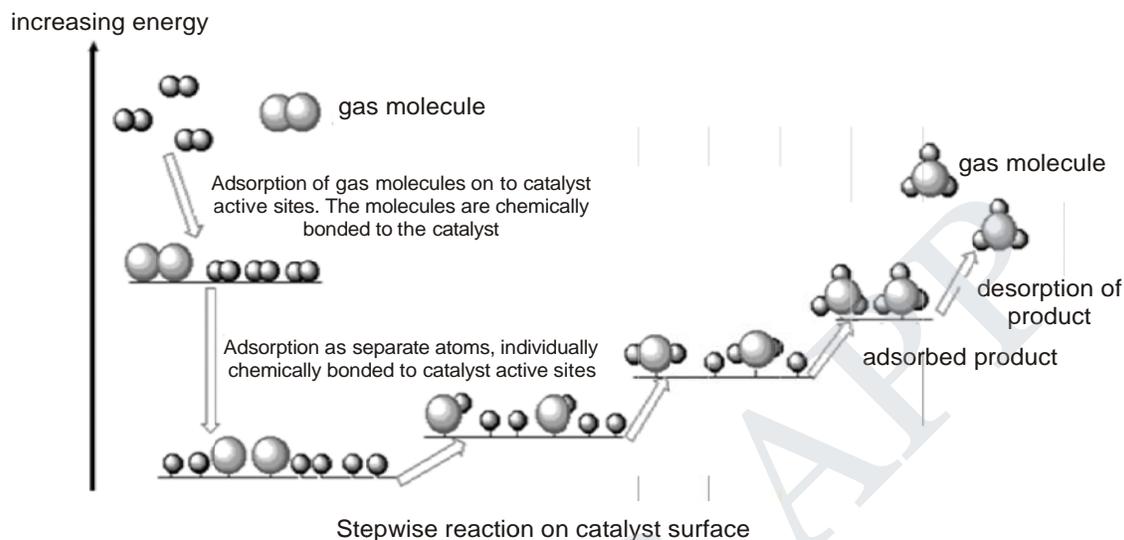
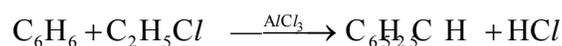


Figure 3.2 : Mechanism of catalytic reaction

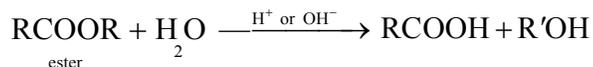
## 3. CRITERIA (OR) CHARACTERISTICS FOR CATALYST

- (i) A catalyst remains unchanged in mass and chemical composition at the end of the reaction. Qualitative and quantitative analysis show that a catalyst undergoes no change in mass or chemical nature. However, it may undergo a physical change. Thus granular manganese dioxide ( $MnO_2$ ) used as a catalyst in the thermal decomposition of potassium chlorate is left as a fine powder at the end of the reaction.
- (ii) A small quantity of catalyst is generally needed to produce almost unlimited reaction. Sometimes a trace of a metal catalyst is required to affect very large amounts of reactants. For example, one ten-millionth of its mass of finely divided platinum is all that is needed to catalyse the decomposition of hydrogen peroxide.

On the other hand, there are catalysts which need to be present in relatively large amount to be effective. Thus in Friedel-Crafts reaction,

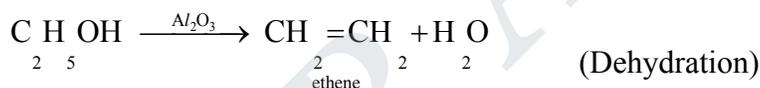


anhydrous aluminium chloride functions as a catalyst effectively when present to the extent of 30 per cent of the mass of benzene. For the acid and alkaline hydrolysis of an ester

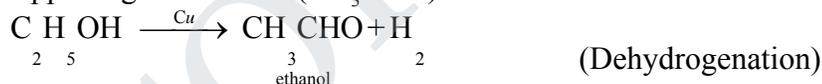


the rate of reaction is proportional to the concentration of the catalyst ( $\text{H}^+$  or  $\text{OH}^-$ )

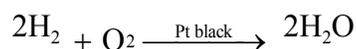
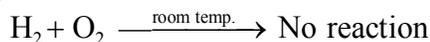
- (iii) A catalyst is more effective when finely divided In heterogeneous catalysis, the solid catalyst is more effective when in a state of fine subdivision than it is used in bulk. Thus a lump of platinum will have much less catalytic activity than colloidal or platinised asbestos. Finely divided nickel is a better catalyst than lumps of solid nickel.
- (iv) A catalyst is specific in its action While a particular catalyst works for one reaction, it will not necessarily work for another reaction. Different catalysts, moreover, can bring about completely different reactions for the same substance. For example, ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) gives ethene ( $\text{C}_2\text{H}_4$ ) when passed over hot aluminium oxide,



but with hot copper it gives ethanal ( $\text{CH}_3\text{CHO}$ )



- (v) A catalyst cannot, in general, initiate a reaction In most cases a catalyst speeds up a reaction already in progress and does not initiate (or start) the reaction. But there are certain reactions where the reactants do not combine for very long period (perhaps years). For example, a mixture of hydrogen and oxygen, which remains unchanged almost indefinitely at room temperature, can be brought to reaction by the catalyst platinum black in a few seconds.



Thus it is now considered that the catalyst can initiate a reaction. According to this view, the reacting molecules (in the absence of catalyst) do not possess minimum kinetic energies for successful collisions. The molecules rebound from collision without reacting at all

- (vi) A catalyst should remain unchanged in mass and chemical composition during end of the reaction.

- (vii) Catalyst can alter only the speed of the reaction but it should not affect the equilibrium of the reaction.
- (viii) Catalysts are more active at its optimum temperature. Change of temperature alters the rate of a catalytic reaction as it would do for the same reaction without a catalyst.
- (ix) The catalytic activity can be altered by adding a small amount of foreign substance. Such substances which catalyse the catalyst are called as **promoters** and the substance which inhibits the reaction are called as **catalytic poisons or anti-catalyst**.

#### 4. TYPES OF CATALYSIS

Catalytic reactions can be broadly divided into the following types,

##### HOMOGENEOUS CATALYSIS

When the reactants and the catalyst are in the same phase (i.e. solid, liquid or gas) it is said to be **homogeneous**.

##### *Examples of Homogenous Catalysis*

1. The depletion of ozone ( $O_3$ ) in the ozone layer of the Earth's atmosphere by chlorine free radicals ( $Cl^\bullet$ ) is an example where the reactant and product exist in gaseous phase. Slow breakdown of manmade chlorofluorohydrocarbons (CFCs), release chlorine free radical into the atmosphere, which converts gaseous ozone to gaseous oxygen ( $O_2$ ).
2. **Fischer esterification:** Reaction of carboxylic acid with an alcohol involves the use of sulfuric acid as the catalyst and is an example where everything is contained in a liquid phase.

##### HETEROGENEOUS CATALYSIS

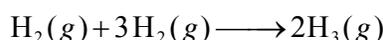
The catalytic process in which the reactants and the catalyst are in different phases is known as **heterogeneous catalysis**.

##### *Examples of Heterogeneous Catalysis*

1. The catalytic converters in automobiles convert exhaust gases such as carbon monoxide (CO) and nitrogen oxides ( $NO_x$ ) into more harmless gases like carbon dioxide ( $CO_2$ ) and nitrogen ( $N_2$ ). Metals (solids) like platinum (Pt), palladium (Pd) and rhodium (Rh) are used as the catalyst.

2. Manufacturing of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) involve solid vanadium pentoxide ( $\text{V}_2\text{O}_5$ ) as the catalyst to convert gaseous sulfur dioxide ( $\text{SO}_2$ ) into gaseous sulfur trioxide ( $\text{SO}_3$ ).
3. Catalytic hydrogenation of liquid Unsaturated hydrocarbons (alkenes) reacts with gaseous hydrogen ( $\text{H}_2$ ) to produce liquid saturated hydrocarbons (alkanes) where metals like platinum ( $\text{Pt}$ ) and palladium ( $\text{Pd}$ ) as the catalyst..

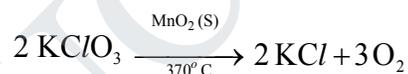
#### 4. Haber Process



The catalyst is porous iron prepared by reducing magnetite,  $\text{Fe}_3\text{O}_4$ , with potassium hydroxide ( $\text{KOH}$ ) added as a promoter.

**Positive Catalysis:** When the rate of the reaction is accelerated by the foreign substance, it is said to be a **positive catalyst** and phenomenon as **positive catalysis**. Examples of positive catalysis are given below.

- (i) Decomposition of  $\text{KClO}_3$



**Negative Catalysis:** There are certain, substance which, when added to the reaction mixture, retard the reaction rate instead of increasing it. These are called **negative catalyst** or **inhibitors** and the phenomenon is known as **negative catalysis**.

Some examples are as follows.

- (i) Oxidation of sodium sulphite



- (ii) Tetra Ethyl Lead (TEL) is added to petrol to retard the ignition of petrol vapours on compression in an internal combustion engine and thus minimize the **knocking effect**.

## 5. AUTOCATALYSIS

*When one of the products of reaction itself acts as a catalyst for that reaction the phenomenon is called Autocatalysis.*

In autocatalysis the initial rate of the reaction rises as the catalytic product is formed, instead of decreasing steadily (Figure). The curve plotted between reaction rate and time shows a maximum when the reaction is complete

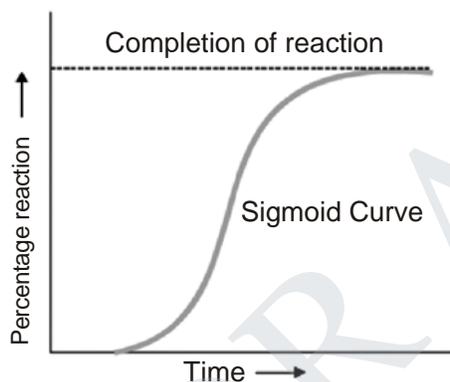
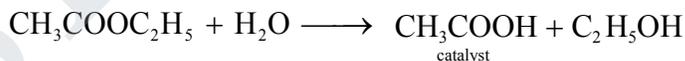


Figure 3.3 : Rate of autocatalytic reaction

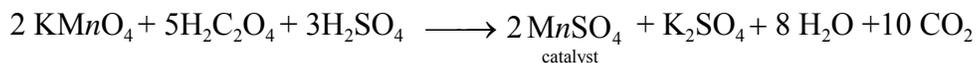
A chemical reaction is said to have undergone autocatalysis, or be autocatalytic, if the reaction product is itself the catalyst for that reaction.

*Examples of Autocatalysis*

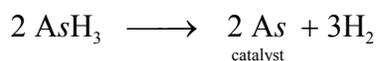
- (1) **Hydrolysis of an Ester.** The hydrolysis of ethyl acetate forms acetic acid ( $\text{CH}_3\text{COOH}$ ) and ethanol. Of these products, acetic acid acts as a catalyst for the reaction.



- (2) **Oxidation of Oxalic acid.** When oxalic acid is oxidised by acidified potassium permanganate, manganous sulphate produced during the reaction acts as a catalyst for the reaction.



- (3) **Decomposition of Arsine.** The free arsenic produced by the decomposition of arsine ( $\text{AsH}_3$ ) autocatalyses the reaction.



## 6. CATALYTIC POISONING AND PROMOTERS

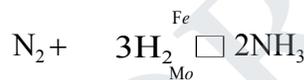
### Promoters

The activity of a catalyst can often be increased by addition of a small quantity of a second material. This second substance is either not a catalyst itself for the reaction or it may be a feeble catalyst.

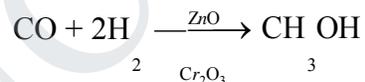
*A substance which, though itself not a catalyst, promotes the activity of a catalyst is called a promoter.* They are substances when added in small concentration can increase the activity of a catalyst.

### Example of Promoters

Molybdenum (Mo) or aluminium oxide ( $Al_2O_3$ ) promotes the activity of iron catalyst in the Haber synthesis for the manufacture of ammonia.



In some reactions, mixtures of catalysts are used to obtain the maximum catalytic efficiency. For example, in the synthesis of methanol ( $CH_3OH$ ) from carbon monoxide and hydrogen, a mixture of zinc and chromium oxide is used as a catalyst.



### Explanation of Promotion Action

The theory of promotion of a catalyst is not clearly understood. Presumably:

- (1) **Change of Lattice Spacing.** The lattice spacing of the catalyst is changed thus enhancing the spaces between the catalyst particles. The absorbed molecules of the reactant (say  $H_2$ ) are further weakened and cleaved. This makes a reaction go faster.
- (2) **Increase of Peaks and Cracks.** The presence of the promoter increases the peaks and cracks on the catalyst surface. This increases the concentration of the reactant molecules and hence the rate of reaction.

The phenomenon of promotion is a common feature of heterogeneous catalysis.

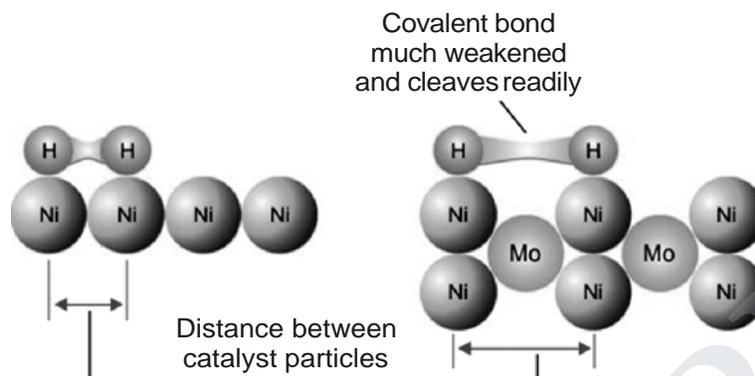


Figure 3.4 : How the change of crystal lattice spacing of catalyst makes the reaction go faster.

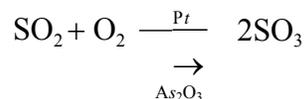
### CATALYTIC POISONS

Small amounts of substances can reduce the activity of catalyst. If the reduction in activity is reversible, the substances are called inhibitors. Inhibitors are sometimes used to increase the selectivity of a catalyst by retarding undesirable reactions.

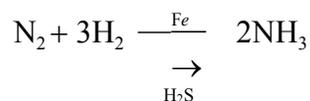
*A substance which destroys the activity of the catalyst to accelerate a reaction is called a poison and the process is called Catalytic Poisoning.*

#### Examples of Catalytic Poisoning

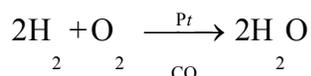
- (1) The platinum catalyst used in the oxidation of sulphur dioxide (Contact Process), is poisoned by arsenic oxide ( $As_2O_3$ )



- (2) The iron catalyst used in the synthesis of ammonia (Haber Process) is poisoned by  $H_2S$ .



- (3) The platinum catalyst used in the oxidation of hydrogen is poisoned by carbon monoxide



**Types of Catalytic Poison****(i) Temporary Poisoning**

Catalyst regains its activity when the poison is removed from the reaction

**(ii) Permanent Poisoning**

- a. Catalyst cannot regain its activity even if the catalytic poison is removed.
- b. Eg.  $\text{As}_2\text{O}_3$  poisons catalyst Pt permanently in manufacturing of  $\text{SO}_3$ .

**Explanation of Catalytic Poisoning**

- (1) The poison is adsorbed on the catalyst surface in preference to the reactants. Even a monomolecular layer renders the surface unavailable for further adsorption of the reactants. The poisoning by  $\text{As}_2\text{O}_3$  or CO appears to be of this kind.

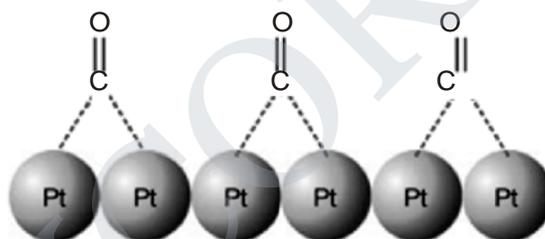
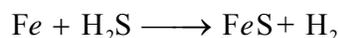


Figure 3.5 : Poisoning of platinum catalyst by carbon monoxide

- (2) The catalyst may combine chemically with the impurity. The poisoning of iron catalyst by  $\text{H}_2\text{S}$  falls in this class

**7. ACID AND BASE CATALYSIS**

**A number of homogeneous catalytic reactions are known which are catalysed by acids or bases, or both acids and bases. These are often referred to as Acid-Base catalysts.** Arrhenius pointed out that acid catalysis was, in fact, brought about by  $\text{H}^+$  ions supplied by strong acids, while base catalysis was caused by  $\text{OH}^-$  ions supplied by strong bases.

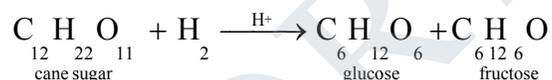
Many reactions are catalyzed by both acids and bases. Typical reactions catalysed by proton transfer are esterification and aldol reaction. Catalysis by either acid or base can be in two different ways (Specific catalysis and general catalysis).

### Example

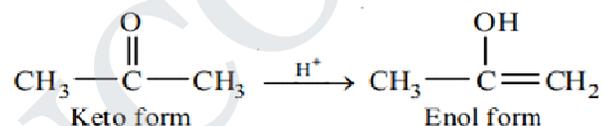
- Acid-specific (acid catalysis)— Decomposition of Sucrose into glucose and fructose occurs in presence of sulfuric acid
- Base-specific (base catalysis)— Addition of hydrogen cyanide to aldehydes and ketones in the presence of sodium hydroxide.

### Examples of Acid-Base Catalysis

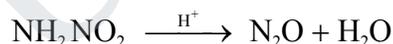
(1) Inversion of Cane Sugar:



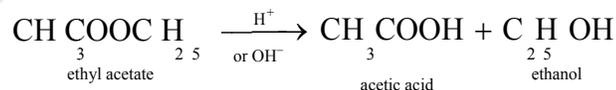
(2) Keto-Enol Tautomerism of Acetone :



(3) Decomposition of Nitramide :



(4) Hydrolysis of an Ester :



### Mechanism of Acid-Base Catalysis

(a) **In acid catalysis**, the  $\text{H}^+$  (or a proton donated by Bronsted acid) forms an intermediate complex with the reactant, which then reacts to give back the proton. For example, the mechanism of keto-enol tautomerism of acetone is:



Eg. Lead is a very good example for catalytic poisoning. It gets adsorbed to the honey comb of expensive metals and inhibits the function of catalyst. Catalytic converter has also forced the removal of lead from petrol.

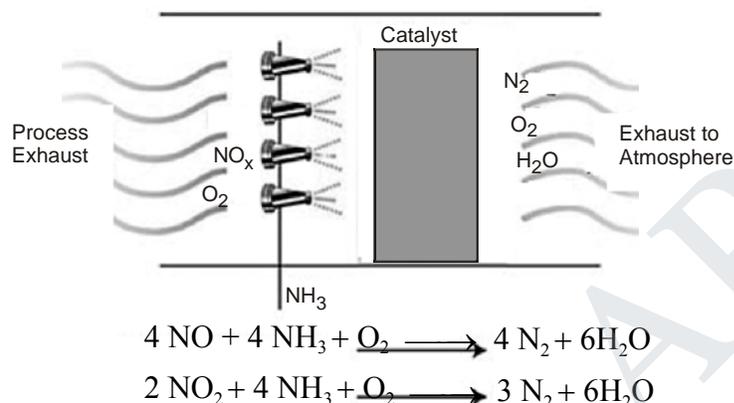


Figure 3.6 : Basic Catalytic Converter

## 2. Petroleum Refining

- (i) **Fluid catalytic cracking:** Breaking large hydrocarbon into smaller hydrocarbons.
- (ii) **Catalytic reforming:** Reforming crude oil to produce high quality gasoline component
- (iii) **Hydrodesulfurization:** Removing sulfur compounds from refinery intermediate products
- (iv) **Hydrocracking:** Breaking large hydrocarbon molecules into smaller ones
- (v) **Alkylation:** Converting isobutane and butylenes into a high-quality gasoline component
- (vi) **Isomerization:** Converting pentane into a high-quality gasoline component

## 3. Chemicals and petrochemicals

- (i) Haber process for ammonia production
- (ii) Styrene and Butadiene synthesis for use in producing synthetic rubber
- (iii) Contact process for production of sulfuric acid
- (iv) Ostwald process for production of nitric acid

- (v) Methanol synthesis
- (vi) Production of different plastics and synthetic fabrics

#### 4. Other

- (i) Fischer-Tropsch and Coal gasification processes for producing synthetic fuel gases and liquid fuels
- (ii) Various processes for producing many different medicine

### 9. BIOLOGICAL CATALYST—ENZYMES

Numerous organic reactions are taking place in the body of animals and plants to maintain the life process. These reactions being slow remarkably catalysed by the organic compounds known as **Enzymes**. All enzymes have been found to be complex protein molecules. Thus: Enzymes are protein molecules which act as catalysts to speed up organic reactions in living cells. The catalysis brought about by enzymes is known as Enzyme Catalysis.

Each enzyme is produced in a particular living cell to catalyse a reaction occurring in that cell. Many enzymes have been identified and obtained in pure crystalline state from the cells to which they belong. However the first enzyme as prepared by synthesis in the laboratory in 1969.

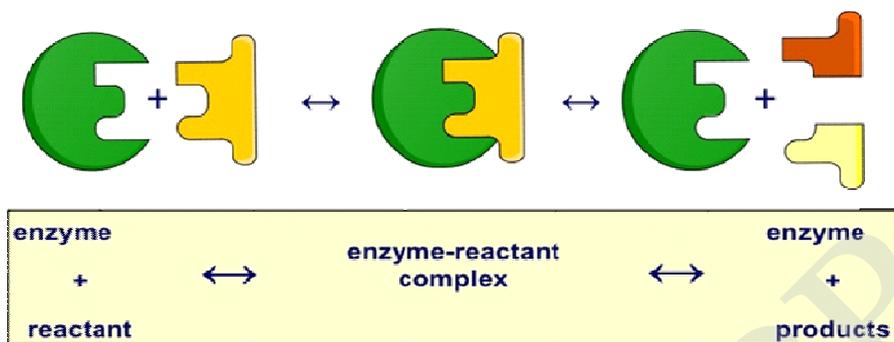
Enzymes are substances found in biological systems that act as catalyst for specific biochemical process. Enzymes are usually protein or steroid which is synthesized in the living cells of animals and plants. Enzymes catalyze reactions inside organism. Enzymes possess a incredible capacity to carry out complex chemical reactions like hydrolysis, oxidation, reduction etc.

Eg.(i) Amylase is an enzyme which breaks down starch into glucose.



(ii) Diastase converts starch to maltose and maltase converts maltose to glucose





Enzymes speed up reactions by lowering activation energy. Many enzymes change shape when substrates bind. This is termed as “*induced fit*”. Enzymes have active sites. The enzyme active site is the location on the enzyme surface where substrates bind, and where the chemical reaction catalyzed

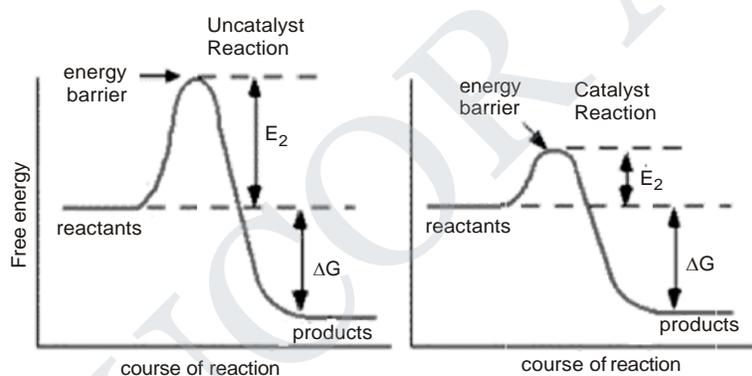


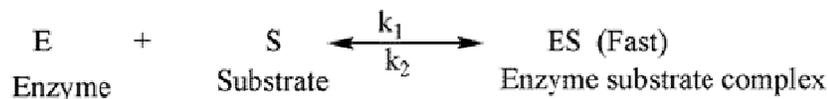
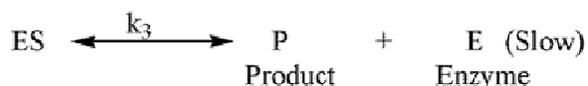
Figure 3.7 : Rate of free energy vs course of reaction

*Enzymes do not*

- Change the equilibrium constant for a reaction
- Change  $\Delta G$  for a reaction
- Convert a nonspontaneous reaction into a spontaneous reaction.

### KINETICS OF ENZYME CATALYSED REACTION OR MICHAELIS AND MENTENEQUATION

Consider the enzyme catalyzed reaction:

**Step 1: Formation of enzyme substrate complex****Step 2: Decomposition of enzyme substrate complex**

It can be expressed as follows:

$$V_0 = \frac{V_{\max} [S]}{K_m + [S]}$$

where the terms  $V_0$ ,  $V_{\max}$  and  $[S]$  and there is a constant  $K_m$ , which is known as **Michaelis constant**.

$$\text{Rate of formation of ES} = k_1 [E] \times [S]$$

$$\text{Rate of breakdown of ES} = (k_2 + k_3) \times [ES]$$

At steady state, the formation and the breakdown are equal. This steady state would only be temporary.

$$k_1 [E] \times [S] = (k_2 + k_3) \times [ES]$$

Rearranging the above equation :

$$[ES] = K_1 \frac{[E] \times [S]}{(K_2 + K_3)}$$

$$\text{(or)} \quad [ES] = \frac{[E] \times [S]}{(K_2 + K_3) / K_1}$$

But  $K_m = \frac{(K_2 + K_3)}{K_1}$  and substituting in above equation and we get

$$[ES] = [E] [S] / K_m$$

The total amount of enzyme equals the free and that bound to substrate

$$[E_T] = [E] + [ES]$$

$$[E] = [E_T] - [ES]$$

Substitute the value of E

$$[ES] = \frac{\{[E] \times [S]\}}{([S] + K_m)}$$

$$\text{Then } [ES] = \frac{\frac{\{[E_T][S]\}}{K}}{1 + [S] / K_m}$$

This simplifies to:

$$[ES] = \left\{ [E_T] \times [S] / ([S] + K_m) \right\}$$

Multiplying both sides by the kinetic constant  $k_3$  gives the velocity of the reaction

$$V = k_3 \times [ES] = k_3 \times [E_T] \times \left( \frac{[S]}{[S] + K_M} \right)$$

and substituting  $V_{\max}$  for  $k_3 \times [E_T]$  leads to the familiar form of the Michaelis Menten Equation:

$$V = V_{\max} \frac{X[S]}{[S] + K}$$

The above equation is called **Michaelis–Menton equation**. This equation is applicable to enzyme catalysed reaction having a single substrate. A quantitative estimation of initial rate of reaction, maximum velocity and substrate concentration is combined through a constant called Michaelis constant.

**Case 1:** First order reaction-When concentration of substrate is low.

If  $K_m \gg S$  then  $s$  is neglected and then the equation becomes

$$\text{Rate } (v) = V_{\max} \times [S] / (K_M)$$

**Case 2:** Zero order reaction-When concentration of substrate is high.

If  $K_m \ll S$  then  $K_m$  is neglected and equation becomes

$$\text{Rate } (v) = V_{\max} \times [S] / [S] \text{ so } V_{\max} = \text{Constant}$$

**Case 3:** If  $K_m = [S]$  then

$$\text{Rate } (V) = \frac{V_{\max} [S]}{[S] + [S]} = \frac{1}{2} V_{\max}$$

Reciprocating the above equation

$$\frac{1}{\text{Rate } (v)} = \frac{K_m}{V_{\max} [S]} + \frac{[S]}{V_{\max} [S]}$$

Rearranging the above equation:

$$\frac{1}{\text{Rate } (v)} = \frac{K_m}{V_{\max} [S]} + \frac{[S]}{V_{\max} [S]}$$

The above equation is similar to an equation of straight line  $y = mx + c$ . A graph is plotted between  $1/\text{rate}$  and  $1/[S]$  we get a straight line.

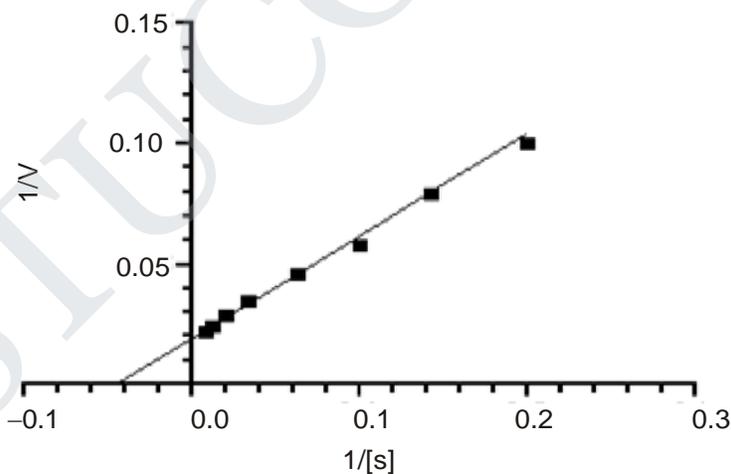


Figure 3.8

where slope =  $K_m/V_{\max}$  and Intercept =  $1/V_{\max}$

**FACTORS AFFECTING ENZYME ACTIVITY****a. Enzyme Concentration**

- If we keep the concentration of the substrate constant and increase the concentration of the enzyme, the rate of reaction increases linearly. (That is if the concentration of enzyme is doubled, the rate doubles.)
- This is because in practically all enzyme reactions the molar concentration of the enzyme is almost always lower than that of the substrate.

**b. Substrate Concentration**

- If we keep the concentration of the enzyme constant and increase the concentration of the substrate, initially, the rate increases with substrate concentration, but at a certain concentration, the rate levels out and remains constant.
- So at some point, increasing the substrate concentration does not increase the rate of reaction, *because the excess substrate cannot find any active sites to attach to.*

**c. Temperature**

- For enzyme-catalyzed reactions, like all chemical reactions, rate increases with temperature. However, enzymes are proteins, and at higher temperatures proteins become denatured and inactive. Thus, every enzyme has an optimum temperature.
- Optimum temperature - the temperature at which enzyme activity is highest-usually about 25°C–40°C.

**d. Effect of pH**

- Small changes in pH can result in enzyme denaturation and loss of catalytic activity.
- Because the charge on acidic and basic amino acid residues located at the active site depends on pH. Most enzymes only exhibit maximum activity over a very narrow pH range.
- Most enzymes have an optimum pH that falls within the physiological range of 7.0-7.5.
- Notable exceptions are the digestive enzymes pepsin and trypsin.
- pepsin (active in the stomach) - optimum pH of 1.5
- trypsin (active in the small intestine) - optimum pH of 8.0



## Unit III

# ALLOYS AND PHASE RULE

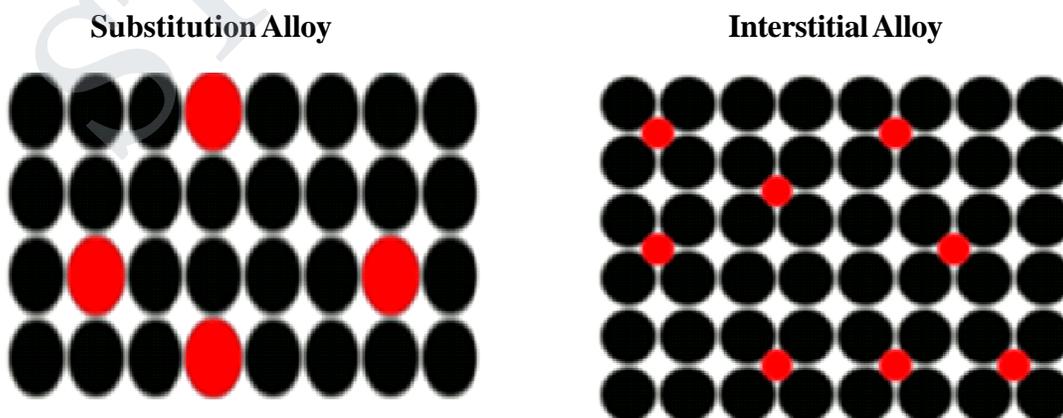
Purpose of Alloying - Effect of Alloying - Important Ores Its Properties and Uses - Various Methods in Heat Treatment of Alloys - Nichrome - Stainless Steel (or) Corrosion Resistant Steels - 18/8 stainless steel - Definition of Phase Rule - Terms involved in Phase Rule - Other Terms.

## CHAPTER 4: Alloys

### 4.1 INTRODUCTION

An alloy may be a solid solution of metal elements (a single phase) or a mixture of metallic phases (two or more solutions). Intermetallic compounds are alloys with a defined stoichiometry and crystal structure. Alloying elements are added to a base metal, to induce hardness, toughness, ductility. Combination of metals may reduce the overall cost of the material, imparts synergistic properties of the constituent metal elements such as corrosion resistance or mechanical strength. Alloys can be of two types.

- (a) **Substitution Alloy:** The atoms of the alloying agent replace atoms of the main metal,
- (b) **Interstitial Alloy:** The atoms slip in between the main metal atoms (in the gaps or “interstices”), Alloys are used in a wide variety of applications.



**DEFINITION**

*“A metallic solid or liquid that is composed of a homogenous mixture of two or more metals, metals and nonmetals or metalloid elements usually for the purpose of imparting specific characteristics”.*

(or)

*“A metallic material consisting of a mixture of two or more metals or metallic elements with non metallic elements”.*

(or)

*“An alloy is a partial or complete solid solution of one or more elements in a metallic matrix”.*

Eg. Brass is an alloy of copper and zinc, Steel is an alloy of iron and carbon

**PURPOSE OF ALLOYING**

Alloying of metals can be done to:

**(i) To prevent Rust (Corrosion)**

Pure metals have poor corrosion resistance. Alloying helps to reduce corrosion.

Eg. Chromium and nickel added to iron to form stainless steel.)

**(ii) To improve Hardness**

Pure metals are generally soft. Alloying of metals helps in increasing hardness.

Eg. Carbon is added to iron to form steel. Aluminium is very light and malleable but when added with copper and magnesium, it form duralumin which is very hard, withstand corrosion and light.

**(iii) To improve Appearance**

A normal metal usually gets dull when it exposed to air, water and UV light. Alloying is done to create an attractive surface and appearance.

Eg. Nickel were added to copper to form an alloy named cupro-nickel such alloy were used to make coins attractive and shiny.

**(iv) To increase tensile strength.**

Alloying increases tensile strength of metals.

Eg. Tensile strength of pure iron can be increased upto 10% by adding 1% carbon.

**(v) To impart colour**

Modification of colour can be done by alloying.

Eg. Cu is red in colour and Zn is silver white in colour. On alloying an yellow colour brass is formed.

**(vi) To decrease melting point**

Alloying lowers the melting point of pure metal.

Eg. Wood's metal (alloy of bismuth, lead, tin) possess m.pt=71°C which is lesser than constituent components.

**(vii) To impart castability**

To get good castings.

Eg. Tin and antimony are mixed with lead to provide good castability.

**EFFECT OF ALLOYING**

Different alloying elements have specific effects on the properties of a stainless steel. The property profile of steel depends on the nature of alloying element, heat treatment, and nature of impurities. The effect of the alloying elements differs to some extent.

<b>ALLOYING ELEMENT</b>	<b>EFFECTS OF ALLOYING</b>
<b>Aluminium</b>	Strong detoxifier, Refines grains, Improves oxidation resistance
<b>Chromium</b>	Increases tensile strength, hardness, wear resistance, increase resistance to oxidation
<b>Cobalt</b>	Retains strength, hardness. Increase thermal conductivity
<b>Copper</b>	Increase machineability, Corrosion resistance, Detrimental to surface quality.
<b>Manganese</b>	Improves strength, hardness. Eliminates the effects of sulphur, decrease ductility, machine ability.
<b>Molybdenum</b>	Enhance resistance to creep (at low temperature) and increase resistance to corrosion and mechanical strength
<b>Nickel</b>	Increases basic strength, ductility, toughness, Ferrite strength
<b>Neobium</b>	Increases high temperature strength, creep resistance
<b>Silicon</b>	Improves resistance to corrosion
<b>Titanium</b>	Stabilises steel and increase strength
<b>Vanadium</b>	Refines grains, increase toughness
<b>Boron</b>	Increases hardness
<b>Nitrogen</b>	Increase mechanical strength, increase corrosion resistance
<b>Sulphur</b>	Decreases ductility and weldability
<b>Tungsten</b>	Present as impurity in steel but improves pitting corrosion resistance
<b>Carbon</b>	Increase mechanical strength, reduce toughness and mechanical strength
<b>Cerium</b>	Increase resistance to oxidation at high temperature

**IMPORTANT ORES ITS PROPERTIES AND USES**

ALLOY	COMPOSITION	PROPERTIES	USES
Bronze	~ 90% copper ~ 10% tin	~ Hard and strong ~ Does not corrode easily Has shiny surfaces	~ to build statues and monuments ~ in the making of swords, medals and artistic materials
Brass	~ 70% copper ~ 30% zinc	~ Harder than copper	~ in the making of musical instruments and kitchenware
Steel	~ 99% iron ~ 1% carbon	~ Hard and strong	~ in the construction of building and bridges ~ in the building of cars and railway tracks
Stainless steel	~ 74% iron ~ 8% carbon ~ 18% chromium	~ shiny ~ strong ~ does not rust	~ to make surgical instruments
Duralumin	~ 93% aluminium ~ 3% copper ~ 3% magnesium ~ 1% manganese	~ light ~ strong	~ to make the body of aeroplanes and bullet trains
Pewter	~ 96% tin ~ 3% copper ~ 1% antimony	~ luster ~ shiny ~ strong	~ in the making of souvenirs

**2. HEAT TREATMENT OF STEEL**

**Heat Treatment** is the heating and cooling of metals to change their physical and mechanical properties, without letting it change its shape. Heat treatment is done to refine grain structure, remove imprisoned gas and to remove internal stress.

**DEFINITION:**

*“Process of heating and cooling of solid steel article under controlled condition to enhance certain physical properties without altering its chemical composition”.*

**VARIOUS METHODS IN HEAT TREATMENT OF ALLOYS****1. Annealing**

Annealing means softening. It is a process of heating the steel slightly above the critical temperature of steel (723°C) and allowing it to cool down very slowly.

### Types of Annealing

There are various types of annealing.

1. **Full Annealing** - The process involves heating the steel to 30 to 50°C above the critical temperature of steel then allowing steel to slowly cool down inside the furnace. Hot Worked sheets, forgings, and castings made from medium and high carbon steel need full annealing.
2. **Process Annealing** - The process involves heating the steel to a temperature just below the critical temperature of steel. This process is mainly suited for low carbon steel. Process annealing tends to improve hardness and decrease ductility. This is mainly carried in cold rolled steel.

### Advantages of Annealing

- a. Softens the steel.
- b. Enhances and improves the machinability
- c. Increases ductility
- d. Enhances toughness
- e. Improves homogeneity
- f. Refinement of grains

### 2. Hardening (or) Quenching

Heating steel, beyond critical temperature until all pearlite is transformed into austenite, and then quenching it rapidly in water or oil. Hardening steel causes the structure of carbon to crystallize. High carbon steel (0.6% C) is mainly used. Medium carbon steels, with a carbon content of 0.4 to 0.55%, can also be hardened, but these steels need to have other metals alloyed with them. Mild steels, with a carbon content of 0.4 % or less, cannot be hardened directly.

#### Advantages

- a. Resistance to wear
- b. Steel becomes extra brittle

### 3. Tempering

Heating already hardened steel to a temperature lower than its hardening temperature and cooling it slowly.

**Advantage**

- a. To decrease the hardness, strength (temperature should not exceed 400°C).
- b. To increase the toughness and ductility of hardened steels (temperature should not exceed 400-600°C).
- c. Removes the tensions.

**4. Normalising**

Heating the suitable steel to a temperature typically in the range 830-950°C (at or above the hardening temperature of hardening steels, or above the carburising temperature for carburising steels) and then cooling in air. It is a heat treatment of steel to change the grain size to improve the physical properties of the steel. When the steel is originally cast and rolled a lot of the steel consists of large ferritic grains. To reduce it normalizing is done.

**Advantage**

- a. Refinement of grains
- b. Increasing toughness
- c. Removes internal stress

**Application**

Normalization is mainly used on carbon and low alloyed steels to normalize the structure after forging, hot rolling or casting.

**5. Case Hardening**

Heating low carbon steel to red hot and forcing the carbon content into its surface so it becomes rich in carbon. Carbon is added to the outer surface of the steel, to a depth of approximately 0.03 mm. It is done by two ways

**a. Carburising**

Mild steel article is heated in a cast iron box containing charcoal powder and heated to 900-950°C and allowing it to cool slowly. The outer surface is converted to high carbon steel containing 0.8-1.2% within 3-4 hours.

**b. Hardening**

Carburized article is reheated to about 900°C and suddenly quenched in oil, so brittleness is removed and core becomes soft. Then article is reheated to 700°C and again quenched in water so that outer core is hardened again

Case Hardening is a process that is used to harden the outer layer of case hardening steel while maintaining a soft inner metal core. It is less complex than hardening and tempering.

**6. Flame Hardening**

Localized Heat Treatment on certain steels in order to increase surface hardness. Heating the surface to be hardened with a high temperature oxygen-acetylene flame through a nozzle and cooling done by spraying water. Flame hardening is fast and inexpensive. Carbon steels containing 0.35 -0.55% carbon and many low alloy steels can be hardened effectively.

**7. Nitriding**

Gas Nitriding develops a very hard case in a part at relatively low temperature, without the need for quenching metal alloy. The alloy is heated in presence of ammonia at a temperature of 550°C. The nitrogen combines with the surface constituent and form hard nitrides. It is time consuming.

**Advantage**

- a. To get super hard surface.

**8. Cyaniding**

It is a type of case hardening. Low carbon steel or mild carbon steel is immersed in metal in a molten state containing cyanide (KCN or NaCN) and heated to 870°C and cooling is done by quenching in oil or water.

**Advantage**

- a. To get super hard surface

**3. NICHROME AND STAINLESS STEEL****NICHROME**

Nichrome is a nickel-chromium alloy with non-magnetic properties. The alloy also sometimes includes some parts of iron as its constituents. Also known as nichrome 80/20.

---

Chemical Formula	:	NiCr
Composition	:	80% Ni and 20% Cr.

**Properties**

1. Color	:	Silvery gray colour.
2. Specific gravity	:	8.4.
3. Density	:	8400 kg/m <sup>3</sup> .
4. Melting point	:	1400°C.
5. Electrical resistivity	:	$1.0 \times 10^6$ to $1.5 \times 10^6 \Omega$
6. Specific heat	:	450 Jkg <sup>-1</sup> C <sup>-1</sup> .
7. Thermal conductivity	:	11.3 Wm <sup>-1</sup> C <sup>-1</sup> .
8. Modulus of elasticity	:	$2.2 \times 10^{11}$ Pa.
9. Thermal Expansion Coefficient	:	$14 \times 10^{-6}/^\circ\text{C}$ .
10. Operating temperature	:	900°C.
11. Temperature Coefficient of resistance:	:	Between 25°C and 100°C.
12. Corrosivity	:	Highly resistant to corrosion.
13. Oxidation	:	Resistant to oxidation at high temperatures.

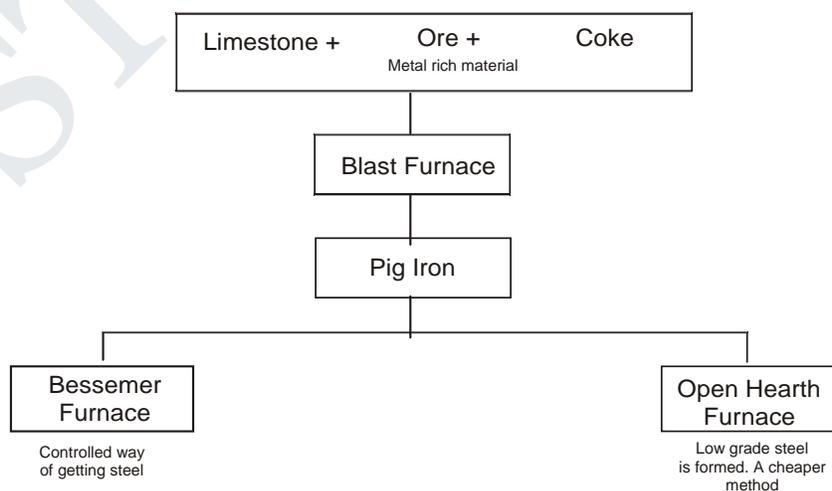
**Uses of Nichrome:**

- It is extensively used in the fireworks and explosives industry.
- It is used to prepare bridgewire for electric ignition systems like model rocket igniters, electric matches and electronic cigarettes.
- It is used in ceramic works.
- It is also used when clay pieces are fired in kilns.

- e. Nichrome wires are used to test the flame color in the non-illuminated cations like sodium, copper, potassium and calcium.
- f. It is also used in microbiological laboratories.
- g. It is used in the manufacturing of motorcycle silencers.
- h. It is also used to prepare Nichrome thin films. These thin films are frequently used in hybrid assemblies in integrated circuits which are used in the fields of telecommunications.
- i. Nichrome is used in building toasters, soldering iron, hair dryers and electric ovens..
- j. It is also used to build thermocouples.

### STAINLESS STEEL (OR) CORROSION RESISTANT STEELS

Steel is an alloy of iron. It is essentially a low carbon steel which contains chromium at 10% or more by weight. The addition of chromium to stainless steel only imparts corrosion resisting properties. The chromium content of the steel allows the formation of a rough, adherent, invisible, corrosion resisting chromium oxide film on the steel surface. If mechanical or chemical attack occurs, this film is self-healing. The corrosion resistance and other useful properties of the steel are enhanced by increased chromium content and the addition of other elements such as molybdenum, nickel and nitrogen. Steel has many other uses aside from building and road construction. It is used in the construction of everything from ships to railroad cars. It is a main component in the building of automobiles, home appliances and shipping containers such as the 50-gallon drum. Steel is even used to create cans for food storage.



### Properties of Stainless Steel

1. Corrosion resistance
2. Fire and heat resistance
3. Strength-to-weight advantage
4. Higher resistance to oxidation (rust)
5. Impervious to water and air

### Types of Stainless Steel

There are three major groups in the family of stainless steels: Austenitic, Ferritic, and Martensitic.

- 1. Austenitic steels** : 70% of total stainless steel production.  
 Composition : 16 to 26 % chromium and up to 35 % nickel.

#### Properties

1. Have high corrosion resistance.
2. They are not hardenable by heat treatment
3. They are nonmagnetic.

Most common type is the 18/8, or 304, grade, which contains 18 percent chromium and 8 percent nickel.

#### Applications

1. Used in aircraft and the dairy and food-processing industries.

### 2. Ferritic Steels

Composition : 10.5 to 27 % chromium and are nickel-free;

#### Properties

1. They have low carbon content (less than 0.2%)
2. They are not hardenable by heat treatment
3. They have less critical anticorrosion properties.

Common ferritic grades include 18 Cr-2 Mo, 26 Cr-1 Mo, 29 Cr-4 Mo, and 29 Cr-4 Mo-2 Ni.

**Applications**

1. Used in architectural and auto trim.

**3. Martensitic Steels**

Composition : 11.5 to 18% chromium and up to 1.2 %  
carbon with nickel

**Properties**

1. They are hardenable by heat treatment .
2. They have modest corrosion resistance.

**Application**

1. Employed in cutlery, surgical instruments, wrenches, and turbines.

**18/8 STAINLESS STEEL**

It is also known as 302 or 304 grade stainless steel. This grade of stainless is generally regarded as one of the “workhorses” in stainless steel as it is widely available and cheap.

**Composition :** 18% chromium and 8% nickel and the rest is iron.

**Properties**

1. Provides a great finish when electropolished.
2. It is usually soft and prone to surface damage.
3. Electro polishing damage its reflectivity and scratch the surface.
4. Better resistance to corrosion than the 400 series. It can be hardened by only cold working and isn't magnetic.
5. Susceptible to corrosion from chloride solutions,

**Application**

1. Used in kitchen and food applications.
2. It is also used in buildings, décor, and site furnishings.

## **CHAPTER 5: Phase Rule**

### **5.1 INTRODUCTION**

The phase rule is a generalization given by Willard Gibbs (1874), which explains the equilibrium existing in heterogeneous system. **Gibb's Phase Rule** provides the theoretical explanation for characterizing the chemical state of a system, and predicting the equilibrium relations of the phases present as a function of physical conditions such as pressure and temperature.

#### **DEFINITION OF PHASE RULE**

It may be stated as: "The equilibrium between any number of phases is not influenced by gravity, electrical, magnetic forces or by surface action and it is influenced only by temperature, pressure and concentration. The number of degrees of freedom (F) of the system is related to number of components (C) and phases (P) and is related by the phase rule equation for any system at equilibrium at a definite temperature and pressure

$$F = C - P + 2$$

#### **TERMS INVOLVED IN PHASE RULE**

##### **PHASE (P)**

*"Homogeneous, physically distinct and mechanically separable portion of system, which is separated from other such parts of the system by definite boundary surface".*

##### **Condition to identify phase**

##### **(i) Liquid Phase**

The number of liquid phase depends on the number of liquids present and their miscibility.

- (i) If two liquids are immiscible, they will form two separate liquid phases.

Eg : Benzene and water

- (ii) If two liquids are miscible they will form one liquid phase only.

Eg : Alcohol and water

##### **(ii) Solid Phase**

Each solid forms a separate phase. The number of solid phase depends on the number of solids present in it.

Eg : Many forms of sulphur exist and all these forms separate phases.

**(iii) Gaseous Phase**

Gaseous mixture are thoroughly miscible in all proportions and it will form one phase only.

Eg : Mixture of  $N_2$  and  $H_2$  forms one phase only.

4. A solution of a substance in a solvent consists of one phase only.

Eg. Glucose solution.

5. A heterogeneous mixture like:



It consists of three phases ( i.e., two solids and one gaseous).

6. In the equilibrium reaction,



There are two solid phases, Fe and FeO and one gaseous phase consisting of  $H_2O(g)$  and  $H_2(g)$ . Thus three phases exist in equilibrium.

7. At freezing point, water consists of three phases:



8. A homogeneous solid solution of a salt forms a single phase.

**Example :** Mohr's salt  $[FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O]$  solution has a single phase.

**COMPONENT (C)**

*“The smallest number of independent variable constituents, taking part in state of equilibrium, by means of which the composition of each phase can be expressed in the form of chemical equation”.*

(or)

*“Number of component of a system may alternatively be defined as the number of chemical constituents of the system minus the number of equations relating to these constituents in an equilibrium state”.*

Eg.

- i. In the water system, Ice (s)  $\square$  Water (l)  $\square$  Water vapour (g)

The chemical composition of all the three phases is  $H_2O$ . Hence, it is one component system.

- ii. Sulphur system consists of four phases, rhombic, monoclinic, liquid and vapour, the chemical composition of all phases is S. Hence, it is one component system.

- ii. In the dissociation of  $NH_4Cl$  in a closed vessel,



The proportions of  $NH_3$  and  $HCl$  are equivalent and hence, the composition of both phases (solid and gaseous) can be expressed in terms of  $NH_4Cl$  alone. Hence, the number of component is one. However, if  $NH_3$  or  $HCl$  is in excess, the system become a two component system

- iv. Saturated solution of  $NaCl$  consists of solid salt, salt solution and water vapour.. It is a two component system.

- v. In the thermal decomposition of  $CaCO_3$



The composition of each of the three phases can be expressed in terms of at least any two of the independently variable constituents,  $CaCO_3$ ,  $CaO$  and  $CO_2$ . Suppose  $CaCO_3$  and  $CaO$  are chosen as the two components, the composition of different phases is represented as follows:

$$\text{Phase: } CaCO_3 = CaCO_3 + 0 CaO$$

$$\text{Phase: } CaO = 0 CaCO_3 + CaO$$

$$\text{Phase: } CO_2 = CaCO_3 - CaO$$

Thus, it is two component systems.

- vi. In the equilibrium,  $Fe_{(s)} + H_2O_{(g)} \rightleftharpoons FeO_{(s)} + H_{2(g)}$  the minimum components required the composition phase is three. Evidently, it is a three component system.

### DEGREE OF FREEDOM (F) OR VARIANCE

*“The minimum number of independently variable factors, such as temperature, pressure and composition of the phases, which must be arbitrarily specified in order to represent perfectly the condition of a system”*

Eg:

- i.  $Ice_{(s)} \rightleftharpoons Water_{(l)} \rightleftharpoons Vapour_{(g)}$

All the three phases are present in equilibrium, then no condition need to be specified, as the three phases can be in equilibrium only at particular temperature and pressure. It is an unvariant system.

- ii. For a system consisting of water in contact with its vapour,



We must state either the temperature or pressure to define it completely. Hence, degree of freedom is one or system is univariant.

- iii. For a gaseous mixture of  $N_2$  and  $H_2$ , we must state both the pressure and temperature, because if pressure and temperature are fixed, the volume automatically becomes definite. Hence, for a gaseous system, two factors must be stated in order to define it completely and thus, it has two degree of freedom (or bivariant system).

### MERITS OF THE PHASE RULE

1. It is applicable to both physical and chemical equilibria.
2. It is applicable to macroscopic systems.
3. It is a convenient method of classifying equilibrium states in terms of phases, components and degrees of freedom.
5. It indicates that different systems with same degree of freedom behave similarly.

### LIMITATIONS OF PHASE RULE

1. It can be applied only for system in equilibrium.
2. All phases of the system must be present simultaneously under the identical conditions of

temperature and pressure.

- It conditions that solid and liquid phases must not be in finely-divided state; otherwise deviations occurs.

## OTHER TERMS

### 1. Interface

At equilibrium, there is a narrow space between two phases where the matter doesn't exhibit properties of either phase.

### 2. Homogenous System

A system consisting of only one phase is said to be homogeneous.

Eg. A mixture of two immiscible liquids such as water and benzene, will exist in two distinct liquid phases and in addition there will be a vapour phase.

### 3. Heterogenous System

A system consisting of more than one phase is said to be heterogeneous

### 4. Reduced Phase Rule or Condensed Phase Rule

The normal phase rule equation is  $F = C - P + 2$

Considering 2 component system ( $C = 2$ ) then equation becomes  $F = 4 - P$ . The minimum number of phase at equilibrium can be only one. Then  $F = 4 - 1 = 3$ . Hence the maximum number of degree of freedom is three. To define such system all the three degree of freedom (temperature, pressure and composition) are required. This leads to 3 dimensional figures which cannot be explained on a paper. So one of the three variable need to be kept constant.

So the phase rule is condensed to

“ $F = C - P + 1$ ” for two component system and this is called as **reduced phase rule**.

### 4. Eutectic System:

Binary system consisting of two components, which are “Completely miscible with one another in liquid state but on solidification they give rise to an intimate mixture known as Eutectic” (easy melting)

**5. Eutectic Point:**

Two solid substances capable of forming solid solutions having the properties of lowering each others freezing point. The minimum freezing point corresponding to eutectic mixture is eutectic point.

**6. Eutectic Mixture:**

It is a solid solution of two or more substances having the lowest freezing point .

**2. THERMAL ANALYSIS AND COOLING CURVES**

Thermal Analysis is a classical method of determining phase diagrams. By melting and cooling an alloy of known composition and plotting temperature-time curves, the final phase change temperature can be determined.

**2.1 Cooling Curve Method**

It is one of the oldest and simplest method to determine the phase diagram and phase transition. The freezing point, Eutectic point of a mixture can be determined easily.

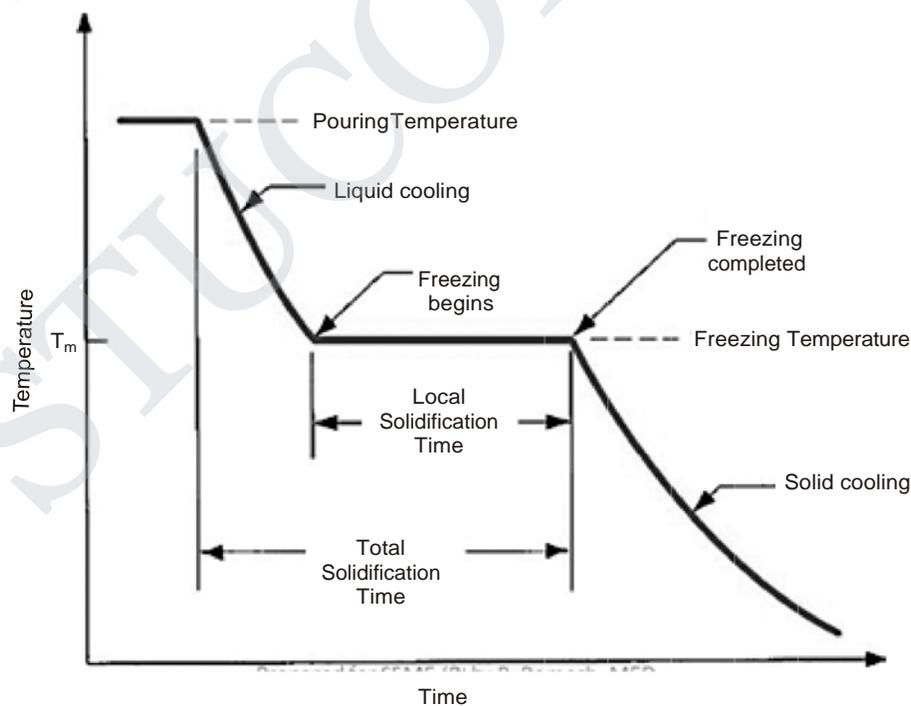
**a. Cooling Curve of Pure Metal**

Figure 5.1 : Cooling Curve of Pure Metal

A pure substance in the fused state is allowed to cool slowly and the temperature is noted at regular intervals. The rate of cooling is continuous until the freezing point is reached. Formation of solid occurs and there is a break in the continuity of the cooling curve and the temperature remains constant until the liquid is fully solidified. When complete solidification occurs there will be a continuous fall in temperature.

### b. Cooling Curve of Mixture

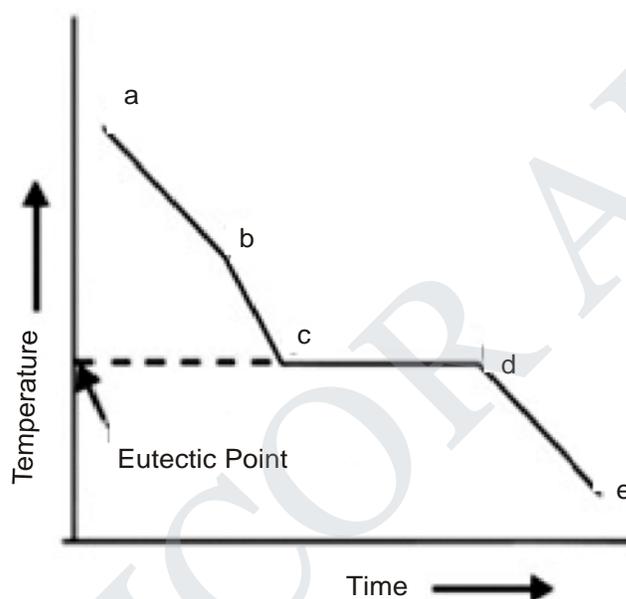


Figure 5.2 : Cooling Curve of a mixture a + b

When a mixture of two solids in the fused state are allowed to cool slowly and temperature is noted at different intervals. Initially the rate of cooling will be continuous. At point 'b' when a solid phase begins to form, the rate of cooling curve exhibits a break and the temperature does not remain constant. The temperature decreases continuously until the eutectic point 'c' is reached. Now the temperature remains constant until complete solidification occurs. There after, at the point 'd' the fall of temperature becomes uniform.

### c. Applications:

1. The melting point and eutectic temperature can be determined
2. The percentage of the compounds and its behaviour can be found out.
3. The behaviour of the compound can be understood from the cooling curve.
4. To derive the phase diagram of any two component system.

### 3. ONE COMPONENT SYSTEM OR WATER SYSTEM

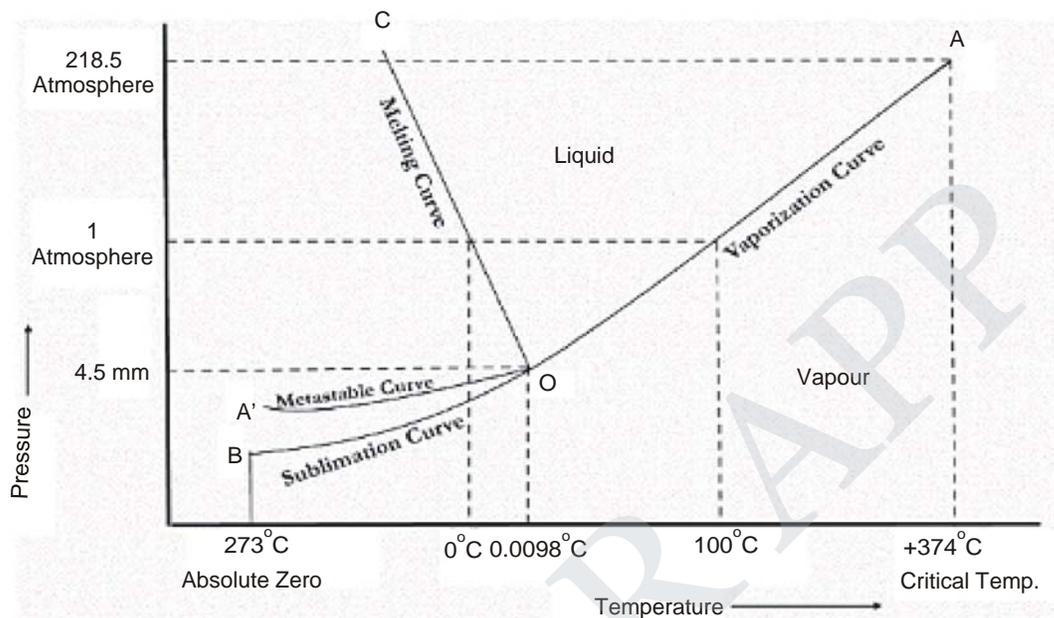


Figure 5.3 : Phase Diagram of Water System

#### Curve OA : Vapour pressure curve or Vapourisation curve

The equilibrium exists between water and water vapour along this curve. The curve OA extends upto the critical point of water (218 atm and temp 374°C) where the liquid and vapour are indistinguishable from each other only one phase will exist .

Water (l)  $\rightleftharpoons$  Water vapour (g)

$$F = C - P + 2, F = 1 - 2 + 2 \text{ so } F = 1 (\text{Univariant system})$$

#### Curve OB : Sublimation curve of ice.

The equilibrium exists between solid ice and water vapour along this curve. Curve OB extends upto absolute zero and further more no vapour phase can exist.

Water(s)  $\rightleftharpoons$  Water vapour (g)

$$F = C - P + 2, F = 1 - 2 + 2 \text{ so } F = 1 (\text{Univariant system})$$

**Curve OC : Melting curve or Fusion curve of ice.**

The Equilibrium exists between solid ice and water along this curve. Curve OC indicates that the melting point of ice decreases with increase of pressure.



$$F = C - P + 2, F = 1 - 2 + 2, \text{ So } F = 1 (\text{Univariant system})$$

**Curve OA: Metastable Curve**

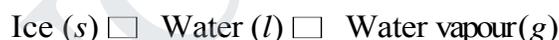
Equilibrium exists between Supercooled water and water vapour

The super-cooled water and vapour system is metastable because as soon as small particle of ice is brought in contact with the super-cooled liquid, the entire liquid solidifies. This is called **Seeding**.

$$F = C - P + 2, F = 1 - 2 + 2 \text{ so } F = 1 (\text{Univariant system})$$

**Point 'O': Triple point**

The curves OA, OB, and OC meet at the triple point 'O' where all the three phases are in equilibrium. This occurs at 0.0098°C and vapour pressure 4.58 mm Hg.



$$F = C - P + 2, F = 1 - 3 + 2 = 0 (\text{non variant})$$

If either pressure or temperature is changed, the three phases would not exist and one of the phases would disappear.

**Areas**

Area above AOC : Existence of water in liquid state.

Area below AOB : Existence of only water vapour.

Area above BOC : Existence of water as solid ice.

In all the three areas there exist one-phase and one-component,

$$\text{So } F = C - P + 2; 1 - 1 + 2 = 2 (\text{Bi variant})$$

#### 4. TWO COMPONENT SYSTEM (LEAD SILVER SYSTEM)

It is also called as **Simple Eutectic system**. This system has two components and four phases. The phases are

- Solid Ag
- Solid Pb
- Molten solution of Ag and Pb.

The boiling points of silver and lead being considerably high, the vapour phase is practically absent. As it is a two component system reduced phase rule need to be applied.

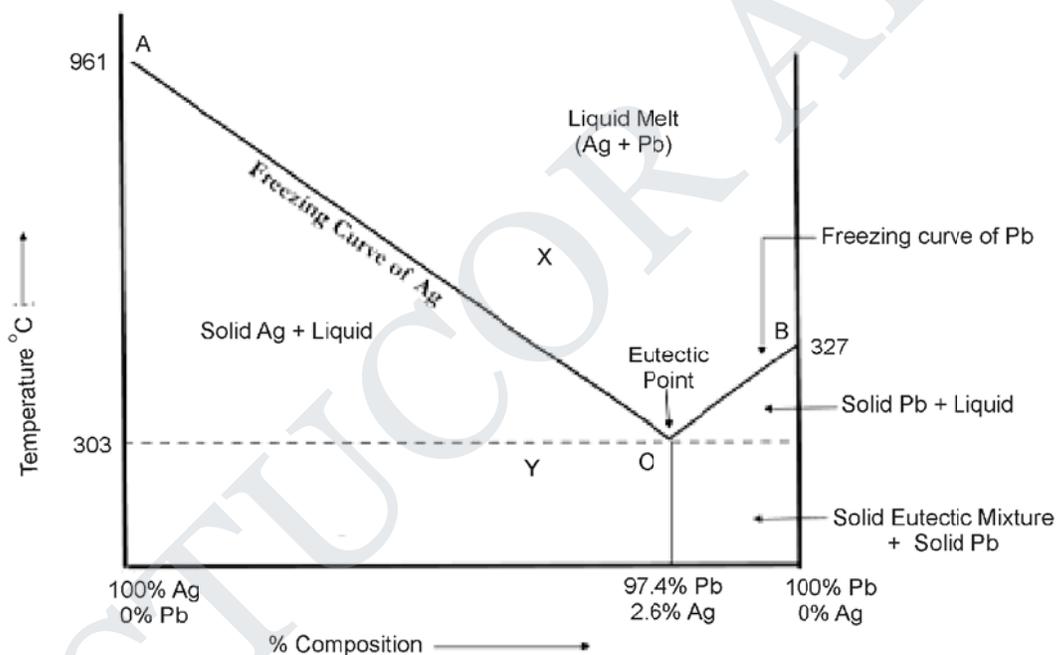


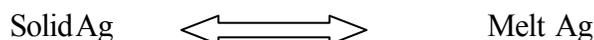
Figure 5.4 : Phase Diagram of Lead Silver System

**Point A:** Melting point of pure Ag (961°C)

**Point B:** Melting point of Pure Pb (327°C)

**Curve OA:** Freezing point curve of Ag.

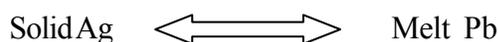
Along this curve Solid Ag and Liquid Ag are in equilibrium.



$$F = C - P + 1, F = 2 - 2 + 1 = 1 \text{ (monovariant system)}$$

**Curve OB:** Freezing point curve of Pb.

Along this curve Solid Pb and Liquid Pb are in equilibrium.



$$F = C - P + 1, F = 2 - 2 + 1 = 1 \text{ (monovariant system)}$$

For curve OA and OB one variable T or % C need to be specified and the other variable is fixed. Curve OA and OB meet at point O (303°C) where liquid melt gets saturated and on cooling further an eutectic composition (97.4% Pb and 2.6%) Ag crystallizes.

**Point O:** Eutectic point

Solid Pb, Solid Ag and their liquid melt are in equilibrium. It is the lowest temperature where the liquid melt of Ag and Pb will freeze.



$$F = C - P + 1, F = 2 - 3 + 1 = 0 \text{ (Non variant system)}$$

The variables temperature (303°C) and composition (97.4% Pb and 2.6% Ag) are fixed.

**Area ACB:**

This region represents the single phase system (**melt of Ag and Pb**).

Applying the reduced phase rule;

$$F = C - P + 1 = 2 - 1 + 1 = 2 \text{ (Bivariant)}$$

**Eutectic Mixture:**

A mixture containing two components which are not miscible in the solid state. The eutectic temperature is 303°C and eutectic composition is 97.4% Pb and 2.6% Ag.

Below the temperature line of eutectic, there are two regions:

- (i) The region marked eutectic + solid Ag, in which crystalline silver and solid eutectic are stable, and
- (ii) The region marked eutectic + solid Pb, in which crystalline lead and solid eutectic are stable.

### **Application of lead silver system**

#### **Pattinson's Process or Desilverisation of Argentiferous lead:**

The recovery of Ag from argentiferous lead is explained in the process with the help of phase diagram. Argentiferous lead contain 0.1 % Ag and 99.9 % Pb. This alloy on heating above 327°C, then it is allowed to cool. The melted alloy reaches "Y" on the curve BO, solid Pb separates out and solution having more Ag. On further cooling, more of Pb separated till the eutectic point reached. At "O" an alloy containing 2.6 % Ag and 97.5 % Pb is obtained.



## Unit IV

# FUELS AND COMBUSTION

**Fuels:** Introduction – Classification of fuels – Coal - Analysis of coal (proximate and ultimate) – Carbonization – Manufacture of metallurgical coke (Otto Hoffmann method) – Petroleum – Manufacture of synthetic petrol (Bergius process) – knocking – Octane Number – Diesel Oil – Cetane Number – Natural Gas – Compressed Natural Gas (CNG) – Liquefied Petroleum Gases (LPG) – Power Alcohol and Biodiesel. **Combustion of Fuels:** Introduction – Calorific Value – Higher and Lower Calorific Values – Theoretical calculation of Calorific Value – Ignition Temperature – Spontaneous Ignition Temperature – Explosive Range – Flue Gas Analysis (ORSAT Method).

## CHAPTER 6: Fuels

### INTRODUCTION

The various types of fuels like liquid, solid and gaseous fuels are available for firing in boilers, furnaces and other combustion equipments. The selection of right type of fuel depends on various factors such as availability, storage, handling, pollution and landed cost of fuel.

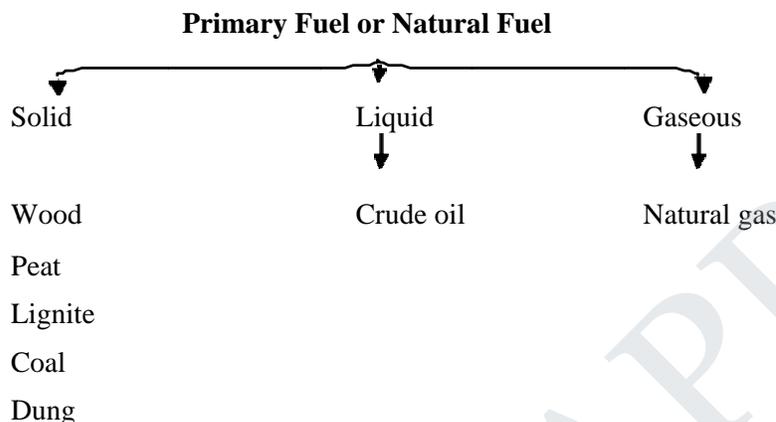
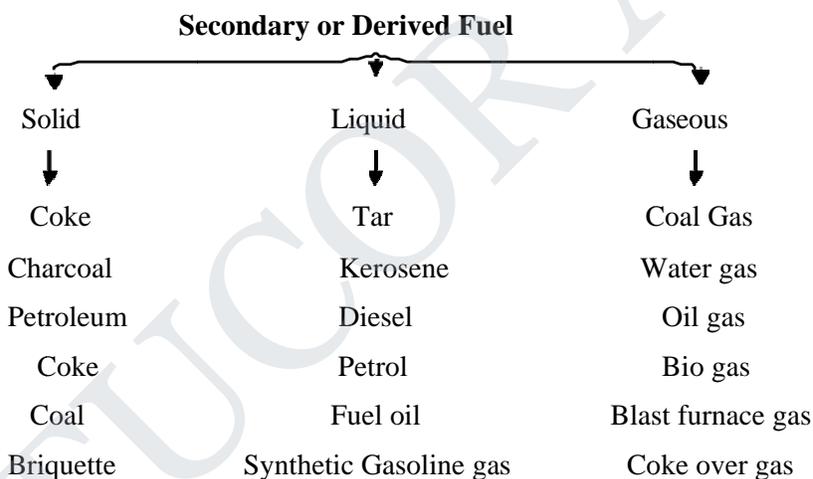
The knowledge of the fuel properties helps in selecting the right fuel for the right purpose and efficient use of the fuel.

The following characteristics, determined by laboratory tests, are generally used for assessing the nature and quality of fuels.

### CLASSIFICATION OF FUELS

**Chemical Fuels:** It is of two types.

- (i) **Primary Fuels :** It occurs in nature as such. ex. coal, petroleum, natural gas.
- (ii) **Secondary Fuels:** It is derived from primary fuels ex.: coke, gasoline, coal gas.

**Primary Fuel or Natural Fuel****Secondary or Derived Fuel****I. SOLID FUELS****COAL**

Coal is a highly carbonaceous matter that has been formed as a result of alteration of vegetable matter (eg., plants) under certain favourable conditions. It is chiefly composed of C, H, N and O besides non-combustible inorganic matter.

The successive stages in the transformation of vegetable matter into coal are— wood, peat, lignite, bituminous coal, steam coal and anthracite. Anthracite is probably the purest form of coal and contains 95 % carbon.

**CLASSIFICATION OF COAL****(a) Peat**

1. Peat is the first stage in the formation of coal.
2. Its calorific value is about 4000-5400 k cal/kg.
3. It is an uneconomical fuel due to its high proportion of (80 -90%) moisture and lower calorific value.
4. It is a brown fibrous mass.

**(b) Lignite**

1. Lignite is an intermediate stage in the process of coal formation.
2. Formation.
3. Its calorific value is about 6500-7100 kcal/kg
4. Due to the presence of high volatile content, it burns with long smoky flame.

**(c) Bituminous Coal**

Bituminous coal is further sub-classified on the basis of its carbon content into three types as:

1. Sub- bituminous coal,
2. Bituminous coal and
3. Semi-bituminous coal.

**(d) Anthracite**

1. Anthracite is the superior grade of coal.
2. Its volatile, moisture and ash contents are very less.
3. Its calorific value is about 8650 kcal/kg

**ANALYSIS OF COAL**

The quality of a coal is ascertained by the following two types of analysis are made.

**Proximate Analysis**

- *Proximate Analysis indicates the percentage by weight of the fixed carbon, volatiles, ash, and moisture content in coal.*

- The amounts of fixed carbon and volatile combustible matter directly contribute to the heating value of coal.
- Fixed carbon acts as a main heat generator during burning. High volatile matter content indicates easy ignition of fuel.
- The ash content is important in the design of the furnace grate, combustion volume, pollution control equipment and ash handling systems of a furnace.

### Significance of Various Parameters in Proximate Analysis

#### (a) Fixed Carbon

Fixed Carbon is the solid fuel left in the furnace after volatile matter is distilled off. It consists mostly of carbon but also contains some hydrogen, oxygen, sulphur and nitrogen not driven off with the gases. Fixed carbon gives a rough estimate of heating value of coal.

#### (b) Volatile Matter

Volatile Matters are the methane, hydrocarbons, hydrogen and carbon monoxide, and incombustible gases like carbon dioxide and nitrogen found in coal. Thus the volatile matter is an index of the gaseous fuels present. Typical range of volatile matter is 20 to 35%. The loss in weight of the sample is found out and the % of the volatile matter is calculated as:

$$\% \text{ of volatile matter in coal} = \frac{\text{loss in weight of the coal}}{\text{weight of air - dried coal}} \times 100$$

#### Volatile Matter

- Proportionately increases flame length, and helps in easier ignition of coal.
- Sets minimum limit on the furnace height and volume.
- Influences secondary air requirement and distribution aspects.
- Influences secondary oil support

#### (c) Ash Content

Ash is an impurity that will not burn. Typical range is 5 to 40%. After the analysis of volatile matter, the crucible with residual coal sample is heated without lid as  $700 \pm 50^\circ \text{C}$  for 1/2 an hour in a muffle furnace. The loss in weight of the sample is found out and the % of ash content is calculated as:

$$\% \text{ of ash content in coal} = \frac{\text{weight of ash formed}}{\text{weight of air - dried coal}} \times 100$$

**Ash**

- Reduces handling and burning capacity.
- Increases handling costs.
- Affects combustion efficiency and boiler efficiency
- Causes clinkering and slagging.

**(d) Moisture Content**

Moisture in coal must be transported, handled and stored. Since it replaces combustible matter, it decreases the heat content per kg of coal. Typical range is 0.5 to 10% . The loss in weight of the sample is found out and the % of moisture is calculated as:

$$\% \text{ of moisture in coal} = \frac{\text{loss in weight of the coal}}{\text{weight of air - dried coal}} \times 100$$

**Moisture**

- Increases heat loss, due to evaporation and superheating of vapour
- Helps, to a limit, in binding fines.
- Aids radiation heat transfer.

**(e) Sulphur Content**

Typical range is 0.5 to 0.8% normally.

**Sulphur**

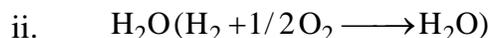
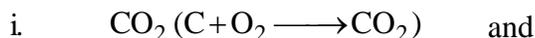
- Affects clinkering and slagging tendencies
- Corrodes chimney and other equipment such as air heaters and economizers
- Limits exit flue gas temperature

**Ultimate Analysis**

The ultimate analysis indicates the various elemental chemical constituents such as Carbon, Hydrogen, Oxygen, Sulphur, etc. It is useful in determining the quantity of air required for combustion and the volume and composition of the combustion gases. This information is required for the calculation of flame temperature and the flue duct design etc.

**(a) Determination of carbon and hydrogen in coal**

A known amount of coal is burnt in presence of oxygen thereby converting carbon and hydrogen of coal into –



respectively. The products of combustion  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are passing over weighed tubes of anhydrous  $\text{CaCl}_2$  and  $\text{KOH}$  which absorb  $\text{H}_2\text{O}$  and  $\text{CO}_2$  respectively.

The increase in the weight of  $\text{CaCl}_2$  tube represents the weight of water formed while the increase in the weight of  $\text{KOH}$  tube represents the weight of  $\text{CO}_2$  formed.

The percentage of carbon and hydrogen in coal can be calculated in the following way-

The weight of coal sample taken =  $x$  g

The increase in the weight of  $\text{KOH}$  tube =  $y$  g

The increase in the weight of  $\text{CaCl}_2$  tube =  $z$  g

Consider the following reaction:



44 g of  $\text{CO}_2$  contains 12 g of carbon

Therefore  $y$  g of  $\text{CO}_2$  contains  $= \frac{y \times 12}{44}$  g of carbon

$x$  g of coal contains  $= \frac{12 y}{44}$  g carbon

% of carbon in coal  $= \frac{12 y}{44 x} \times 100$  (or)

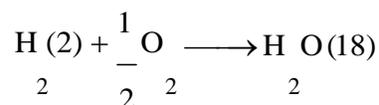
% of carbon in coal  $= \frac{\text{increase in weight of KOH tube}}{\text{weight of coal sample taken}} \times \frac{12}{44} \times 100$

**Significance**

It is the sum total of fixed carbon and the carbon present in the volatile matters like  $\text{CO}$ ,  $\text{CO}_2$ , hydrocarbons. Thus, total carbon is always more than fixed carbon in any coal. High total carbon containing coal will have higher calorific value.

**(b) Determination of hydrogen**

Consider the following reaction:



18 g of water contains 2 g of hydrogen.

$$z \text{ g of water contains } = \frac{2z}{18} \text{ of hydrogen}$$

$$x \text{ g of coal contains } = \frac{2z}{18} \text{ g of hydrogen}$$

$$\% \text{ of hydrogen in coal } = \frac{2z}{18x} \times 100 \quad (\text{or})$$

$$\% \text{ of hydrogen } = \frac{\text{increase in weight of } \text{CaCl}_2 \text{ tube}}{\text{weight of coal sample taken}} \times \frac{2}{18} \times 100$$

**Significance**

It increases the calorific value of the coal. It is associated with the volatile matter of the coal. When the coal containing more of hydrogen is heated, it combines with nitrogen present in coal forming ammonia. Ammonia is usually recovered as  $(\text{NH}_4)_2\text{SO}_4$ , a valuable fertilizer.

**(c) Determination of Nitrogen**

This is done by Kjeldhal's method: A known amount of powdered coal is heated with concentrated sulphuric acid in the presence of  $\text{K}_2\text{SO}_4$  and  $\text{CuSO}_4$  in a long necked Kjeldhal's flask. This converts nitrogen of coal to ammonium sulphate. When the clear solution is obtained (ie., the whole of nitrogen is converted into ammonium sulphate), it is heated with 50 % NaOH solution and the following reaction occurs:



The ammonia thus formed is distilled over and is absorbed in a known quantity of standard 0.1  $\text{NH}_2\text{SO}_4$  solution. The volume of unused 0.1  $\text{NH}_2\text{SO}_4$  is then determined by titrating against standard NaOH solution. Thus, the amount of acid neutralized by liberated ammonia from coal is determined using the formula.

$$\begin{aligned} \text{\% of Nitrogen in Coal} &= \frac{14 \times \text{volume of acid used} \times \text{normality}}{1000 x} \times 100 \\ &= \frac{1.4 \times \text{volume of acid used} \times \text{normality}}{x} \end{aligned}$$

**Significance**

Presence of nitrogen decreases the calorific value of the coal. However, when coal is carbonized, its  $N_2$  and  $H_2$  combine and form  $NH_3$ . Ammonia is recovered as  $(NH_4)_2SO_4$ , a valuable fertilizer.

**(d) Determination of sulphur in coal**

A known amount of coal is burnt completely in Bomb calorimeter in presence of oxygen.

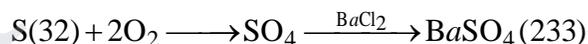
Ash thus obtained contains sulphur of coal as sulphate which is extracted with dil. HCl.

The acid extract is then treated with  $BaCl_2$  solution to precipitate sulphate as  $BaSO_4$ . The precipitate is filtered, washed, dried and weighed. From the weight of  $BaSO_4$ , the percentage of sulphur in coal is calculated in the following way.

The weight of coal sample taken =  $x$  g

The weight of  $BaSO_4$  precipitate =  $y$  g

Consider the following equations:



233 g of  $BaSO_4$  contains 32 g of sulphur

Therefore,  $y$  g of  $BaSO_4$  contains =  $\frac{32 y}{233}$  g sulphur

Therefore,  $x$  g of coal contains =  $\frac{32 y}{233}$  g sulphur

% of sulphur in the coal =  $\frac{32 y}{233} \times 100$

**Significance**

It increases the calorific value of the coal, yet it has the following undesirable effect.

The oxidation products of sulphur ( $\text{SO}_2$ ,  $\text{SO}_3$ ) especially in presence of moisture forms sulphuric acid which corrodes the equipment and pollutes the atmosphere.

**(e) Determination of oxygen in coal**

It is calculated indirectly in the following way-

$$\% \text{ of oxygen in coal} = 100 - \% (\text{C} + \text{H} + \text{N} + \text{S} + \text{ash}).$$

**Significance**

The less the oxygen content, the better is the coal. As the oxygen content increases, its moisture holding capacity also increases.

**CARBONIZATION**

Carbonization (or carbonisation) is the term for the conversion of an organic substance into carbon or a carbon-containing residue through pyrolysis or destructive distillation. It is often used in organic chemistry with reference to the generation of coal gas and coal tar from raw coal.

**Manufacture of Metallurgical Coke by Otto Hoffmann's Method**

When bituminous coal (coal containing about 90 % carbon) is heated strongly in absence of air, the volatile matter escapes out and a while, lustrous, dense, strong, porous and coherent mass is left which is called metallurgical coke.

In order to (i) save the fuel for heating purpose and (ii) recover valuable by-products like coal gas, ammonia, benzol oil, tar etc. Otto Hoffmann developed a modern by-product coke oven. Here, the heating is done externally by a portion of coal gas produced during the process itself. It also utilizes the waste flue gases for heating the checker work bricks.

The oven consists of a number of narrow silica chambers, each about 10-12 m long, 3-4m tall and 0.4-0.45 m wide, erected side by side with vertical flues between them to form a sort of battery. Each chamber has a hole at the top to introduce the charge, a gas off take and a refractory lined cast iron door at each end for coke discharge. The oven works on heat regenerative principle i.e. the waste gas produced during carbonization is utilized for heating. The ovens are charged from the top and closed to restrict the entry of air.

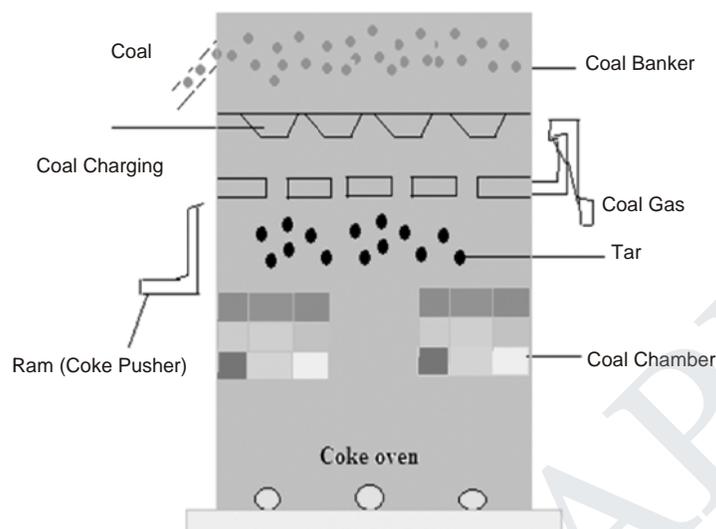


Figure 6.1 : Otto-Hoffmann's Coke Oven

Finely powdered, crushed coal is introduced through the charging hole at the top of the chambers which are then tightly closed at both ends to cut off the supply of air. The ovens are heated to  $1200^{\circ}\text{C}$  by burning producer gas. The air required for the combustion of the fuel is preheated in regenerators flanking the retorts, while the flue gases leave their acquired heat to one generator; the other generator is used for preheating the incoming air. The cycle goes on and the heating is continued until all the volatile matter has escaped.

It takes nearly 18 hours for carbonization of a charge. The heating of air-alone is required if the fuel gas is coal gas which has a high calorific value. If the fuel is producer gas or blast furnace gas, both air and fuel need to be preheated as they have low calorific value. When the carbonization is over, the red hot coke is pushed out into truck by a massive ram.

It is then quenched by spraying water (wet quenching). Alternatively, the red hot coke may be placed in a chamber and cooled by sending in inert gases from boilers. The inert gases are then circulated to boilers where they generate steam. This method is known as dry quenching. The dry quenched coke is cleaner, drier and stronger and contains lesser dust than the wet quenched. The yield is about 70%.

### Characteristics of Metallurgical Coke

The most important industrial fuel is the metallurgical coke. This is used in the metallurgical industry, especially in the blast furnace. A good metallurgical coke must have following requirements:

- **Purity:** Low moisture and ash content are desirable in metallurgical coke. It must contain minimum percentage of phosphorous and sulphur.
- **Porosity:** High porosity is desirable in furnace coke to obtain high rate of combustion.
- **Strength:** The coke should be hard and strong to withstand pressure of ore, flux etc. in the furnace.
- **Size:** Metallurgical coke must be uniform and medium size.
- **Calorific value:** This should be high.
- **Combustibility:** It should burn easily.
- **Reactivity:** It refers to its ability to react with  $O_2$ ,  $CO_2$ , steam and air. The metallurgical coke must have low reactivity.
- **Cost:** It must be cheap and readily available.

## II. LIQUID FUELS

### PETROLEUM

Petroleum or crude oil is a dark greenish -brown, viscous oil found deep in earth crust. It is composed mainly of various hydrocarbons (like straight-chain paraffins, cycloparaffins or naphthalenes, olefins and aromatics), together with small amounts of organic compounds containing oxygen, nitrogen and sulphur.

The average composition of crude oil is as follows:

<i>Constituents</i>	<i>Percentage (%)</i>
C	80-87
H	11-15
S	0.1-3.5
N + O	0.1-0.5

In countries like Germany and South Africa which do not have extensive petroleum deposits, motor fuels are derived from non-petroleum sources. Petroleum can be produced from coal by the following two methods.



## KNOCKING

In an internal combustion engine, a mixture of gasoline (petroleum) vapour and air is used as a fuel. After the initiation of the combustion reaction by spark in the cylinder, the flame should spread rapidly and smoothly through the gaseous mixture; thereby the expanding gas drives the piston down the cylinder. The ratio of the gaseous volume in the cylinder at the end of the suction stroke to the volume at the end of compression stroke of the piston is known as the compression ratio. The efficiency of an internal combustion engine increases with the compression ratio.

**“Knocking is a kind of explosion due to rapid pressure rise occurring in an IC engine”.**

However, successful high compression ratio is dependent on the nature of the constituents present in the gasoline used. In certain circumstances, due to the presence of some constituents in the gasoline used, the rate of oxidation becomes so great that the last portion of the fuel-air mixture gets ignited instantaneously producing an explosive violence known as knocking. The knocking results in loss of efficiency, since this ultimately decreases the compression ratio. The phenomenon of knocking is not yet fully understood. However, it is noted that the tendency of fuel constituents to knock is in the following order:

***Straight chain paraffins (n-paraffins) > branched chain paraffins (iso paraffins) > olefins > cycloparaffins (naphthalenes) > aromatics.***

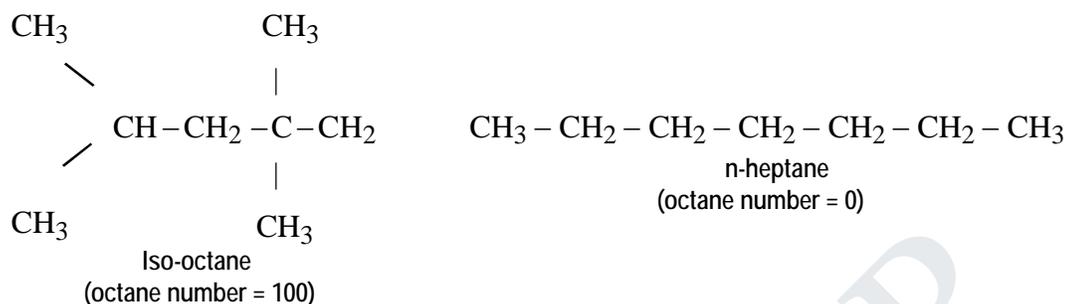
Thus, olefins of the same carbon chain length possess better antiknock properties than the corresponding paraffins and so on.

## OCTANE NUMBER

The most common way of expressing the knocking characteristics of a combustion engine fuel is by octane number introduced by Edger in 1972. It has been found that n-heptane,  $3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$ , knocks very badly and hence, its antiknock value has been arbitrarily given zero. On the other hand, iso-octane (2,2,4-trimethylpentane) gives very little knocking, so its antiknock value has been given as 100.

**“Thus, octane number (or rating) of a gasoline (or any other internal combustion engine fuel) is the percentage of iso-octane in a mixture of iso-octane and n-heptane”,** which matches the fuel under test in knocking characteristics.

Thus, if a sample of petrol gives as much of knocking as a mixture of 75 parts of iso-octane and 25 parts of n-heptane, then its octane number is taken as 75. The octane ratings of some common hydrocarbons are given in the table.



S.No	Hydrocarbon	Octane Number
1.	Benzene	100+
2.	Isopentane	90
3.	Cyclohexane	77
4.	2-methyl pentane	71
5.	n-pentane	62

Fuels with octane rating greater than 100 are quite common nowadays and they are rated by comparison with a blend of iso-octane with tetra ethyl lead (TEL) which greatly diminishes the knocking tendency of any hydrocarbon with which it is mixed. The value of octane number in such cases is determined by extrapolation.

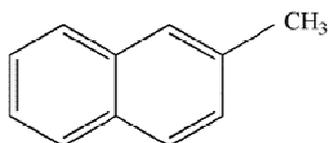
### DIESEL OIL

- It is relatively a high boiling point fraction of petroleum obtained between 250 - 320°C.
- It is a mixture of hydrocarbons in terms of carbon atoms  $C_{15}$ - $C_{18}$
- Its calorific value is about 11,000 kcal/kg. It is used as fuel for compression ignition engine.
- Its antiknock value can be improved by doping with isoamyl nitrate.

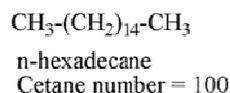
### CETANE NUMBER

In a diesel engine, the fuel is exploded not by a spark but by the application of heat and pressure. Diesel engine fuels consist of longer chain hydrocarbons than internal combustion engine fuels. In other words, hydrocarbon molecules in a diesel fuel should be as far as possible the straight chain ones, with a minimum admixture of aromatics and side chain hydrocarbon molecules.

The suitability of a diesel fuel is determined by its cetane value which is the percentage of hexadecane in a mixture of hexadecane and 2-methyl naphthalene, which has the same ignition characteristics as the diesel fuel in question.



2-methyl naphthalene  
Cetane number = 0



Thus, cetane number is defined as “the percentage of hexa decane present in a mixture of hexa decane and  $\alpha$ -methyl naphthalene, which has the same ignition lag as the fuel under test”.

The cetane number of a diesel fuel can be raised by the addition of small quantity of certain pre-ignition dopes like ethyl nitrite, isoamyl nitrite, and acetone peroxide. An oil of high octane number has a low cetane number and vice-versa.

Consequently, petroleum crude gives petrol of high octane number and diesel of low cetane number.

The cetane number decreases in the following order:

straight chain paraffins > cycloparaffins > olefins > branched paraffins > aromatics.

### III. GASEOUS FUELS

#### NATURAL GAS

Methane is the main constituent of Natural gas and accounting for about 95% of the total volume. Other components are: Ethane, Propane, Butane, Pentane, Nitrogen, Carbon Dioxide, and traces of other gases. Very small amounts of sulphur compounds are also present. Since methane is the largest component of natural gas, generally properties of methane are used when comparing the properties of natural gas to other fuels.

Natural Gas is a high calorific value fuel requiring no storage facilities. It mixes with air readily and does not produce smoke or soot. It has no sulphur content. It is lighter than air and disperses into air easily in case of leak. A typical comparison of carbon contents in oil, coal and gas is given in the Table.

Content	Fuel oil	Coal	Natural gas
Carbon	84	41.11	74
Hydrogen	12	2.76	25
Sulphur	3	0.41	-
Oxygen	1	9.89	Trace
Nitrogen	Trace	1.22	0.75
ash	Trace	38.63	-
water	Trace	5.98	-

### Compressed Natural Gas (CNG)

CNG is natural gas compressed to a high pressure of about 1000 atmospheres. A steel cylinder containing 15 kg of CNG contains about  $2 \times 10^4$  L or  $20 \text{ m}^3$  of natural gas at 1 atmospheric pressure. It is derived from natural gas and the main constituent of CNG is methane.

The average composition of CNG is as follows:

Constituents	Percentage %
Methane	88.5
Ethane	5.5
Propane	3.7
Butane	1.8
Pentane	0.5

### Properties

- (i) CNG is comparatively much less pollution causing fuel as it produces less CO, ozone and hydrocarbons during combustion.
- (ii) During its combustion, no sulphur and nitrogen gases are evolved.
- (iii) No carbon particles are ejected during combustion.
- (iv) It is less expensive than petrol and diesel.

- (v) The ignition temperature of CNG is 550
- (vi) CNG is a better fuel than petrol/diesel for automobiles.
- (vii) CNG requires more air for ignition.

### Uses

As CNG is the cheapest, cleanest and least environmentally impacting alternative fuel. In Delhi, it is mandatory for all buses, taxis and auto to use CNG as a fuel.

### Liquified Petroleum Gas (LPG)

LPG or bottled gas or refinery gas is obtained as a by-product during the cracking of heavy oils or from natural gas. LPG is dehydrated, desulphurised and traces of odorous organic sulphides (mercaptans) are added to give warning of gas leak. LPG is supplied under pressure in containers under the trade name like Indane, Bharat gas, etc. Its calorific value is about 27,800kcal/m<sup>3</sup>.

It consists of hydrocarbons of such volatility that they can exist as gas under atmospheric pressure, but can be readily liquefied under pressure. The main constituents of LPG are n-butane, isobutene, butylenes and propane, with little or no propylene and ethane.

The average composition of LPG is as follows:

Constituents	Percentage %
n-Butane	38.5
Iso Butane	37.0
Propane	24.5

### Power Alcohol

When ethyl alcohol is used as fuel in internal combustion engine, it is called as "power alcohol". Generally ethyl alcohol is used as its 5-25% mixture with petrol.

#### Advantages of Power Alcohol:

- Ethyl alcohol has good antiknocking property and its octane number is 90, while the octane number of petrol is about 65. Therefore, addition of ethyl alcohol increases the octane number of petrol.

- Alcohol has property of absorbing any traces of water if present in petrol.
- If specially designed engine with higher compression ratio is used, then disadvantage of lower Calorific value of ethyl alcohol can be overcome.
- Ethyl alcohol contains 'O' atoms, which helps for complete combustion of power alcohol and the polluting emissions of CO, hydrocarbon, particulates are reduced largely.
- Use of ethyl alcohol in petrol reduces our dependence on foreign countries for petrol and saves foreign considerably.
- Power alcohol is cheaper than petrol.

***Disadvantages of Power Alcohol:***

- Ethyl alcohol has calorific value 7000cal/gm much lower than calorific value of petrol 11500cal/gm. Use of power alcohol reduces power output upto 35%.
- Ethyl alcohol has high surface tension and its atomisation, especially at lower temperature, is difficult causing starting trouble.
- Ethyl alcohol may undergo oxidation reaction to form acetic acid, which corrodes engine parts.
- As ethyl alcohol contains 'O' atoms, the amount of air required for complete combustion of power alcohol is lesser and therefore carburettor and engine need to be modified, when only ethyl alcohol is used as fuel.

**Biodiesel**

A fuel derived from organic oils, such as vegetable oil, rather than petroleum. Biodiesel's use and production are increasing. It's typically used for aircraft, vehicles and as heating oil.

Vegetable oils comprise of 90–95% triglycerides with small amount of diglycerides, free fatty acids, phospholipids, etc. The viscosity of vegetable oils are higher and their molecular weights are in the range of 600 to 900, which are about 3 times higher than those of the diesel fuels.

**Problems in using Vegetable Oils directly**

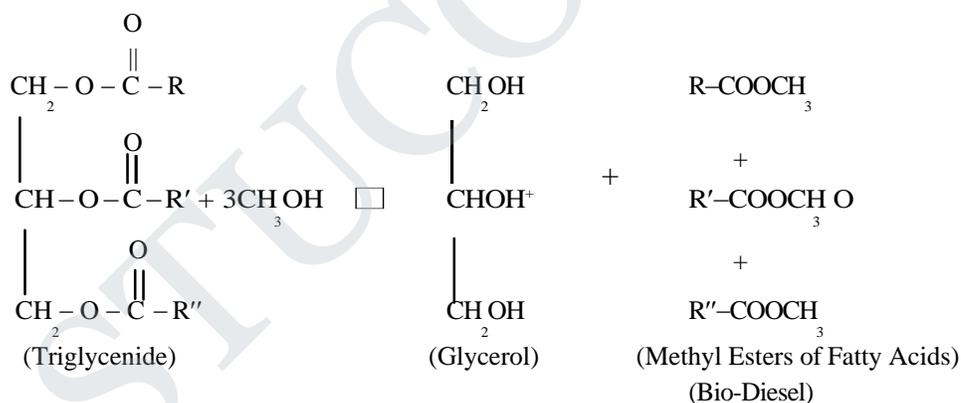
- (i) As the viscosity of vegetable oils are high, atomization is very poor and hence inefficient mixing of oil with air leads to incomplete combustion.
- (ii) Oxidation and Thermal polymerization of vegetable oils cause deposit formation.
- (iii) Their high velocity and consequent high flash point lead to more deposit formation.

**Manufacture: Trans-Esterification (or) Alcoholysis**

The above problems are overcome by reducing the viscosity of the vegetable oils by the process known as **trans-esterification or alcoholysis**. Alcoholysis is nothing but displacement of alcohol from an ester by another alcohol.

It involves treatment of vegetable oil (sunflower oil, palm oil, soyabean oil, mustard oil, etc.) with excess of methanol in the presence of catalyst to give mono ethyl esters of long chain fatty acid and glycerine. It is allowed to stand for some time and glycerine is separated.

Alcoholysis reaction is represented as  $0.0941 \times 587 \text{ kcal / kg}$



Methyl esters of fatty acids, thus formed, are called "Bio-diesel". **Bio diesel is defined as mono-alkyl esters of long chain fatty acids derived from vegetable oils or fats.**

*Advantages*

1. It can be produced from renewable, domestic resources.
2. Biodiesel is energy efficient (The total fossil fuel energy efficiency of biodiesel is 320% vs. 83% for petroleum diesel) (National Biodiesel Board, 1998)
3. It can be used directly in most diesel engine applications.
4. It can reduce global warming and tailpipe emissions (−41%)
5. It is nontoxic and biodegradable.
6. It is a good solvent and may clean out fuel line and tank sediments. (Note that this may result in fuel filter clogging during initial use)

*Limitations*

1. It contains approximately 8% less energy per gallon.
2. It generally has a higher cloud and pour point (will freeze at a higher temp) than conventional diesel.
3. It is not compatible with some hose and gasket materials, which may cause them to soften, degrade, and rupture.
4. It is not compatible with some metals and plastics.
5. It may increase nitrogen oxide emissions

## CHAPTER 7: Combustion of Fuels

### COMBUSTION OF FUELS

Fuel is a combustible substance, containing carbon as main constituent, which on proper burning gives large amount of heat, which can be used economically for domestic and industrial purposes. Eg., Wood, Charcoal, Coal, Kerosene, Petrol, Producer gas, Oilgas, LPG etc., During the process of combustion of a fuel (like coal), the atoms of carbon, hydrogen, etc. combine with oxygen with the simultaneous liberation of heat at a rapid rate.



#### Calorific Value

**Calorific Value of a Fuel** is “*the total quantity of heat liberated, when a unit mass (or volume) of the fuel is burnt completely*”.

#### Units of Heat:

- (1) **Calorie** □ is the amount of heat required to raise the temperature of one gram of water through one degree centigrade (15-16 °C).
- (2) **Kilocalorie** □ is equal to 1,000 calories. This is the unit of metric system and may be defined as “the quantity of heat required to raise the temperature of one kilogram of water through one degree centigrade. Thus, 1 kcal = 1,000 calories.
- (3) **British Thermal Unit (BTU)** □ is defined as “the quantity of heat required to raise the temperature of one pound of water through one degree Fahrenheit (60-61 °F). This is the English system unit. 1 BTU = 252 cal = 0.252 kcal and 1 kcal = 3.968 BTU
- (4) **Centigrade Heat Unit (CHU)** □ is “the quantity of heat required to raise the temperature of 1 pound of water through one degree centigrade”.

Thus, 1 kcal = 3.968 BTU = 2.2 CHU.

### Higher or Gross Calorific Value (GCV)

*It is the total amount of heat produced, when unit mass/volume of the fuel has been burnt completely and the products of combustion have been cooled to room temperature (15°C or 60°F).*

It is explained that all fuels contain some hydrogen and when the calorific value of hydrogen containing fuel is determined experimentally, the hydrogen is converted into steam. If the products of combustion are condensed to the room temperature, the latent heat of condensation of steam also gets included in the measured heat which is then called GCV.

### Lower or Net Calorific Value (NCV)

*It is the net heat produced, when unit mass/volume of the fuel is burnt completely and the products are permitted to escape.*

In actual practice of any fuel, the water vapour and moisture, etc., are not condensed and escape as such along with hot combustion gases. Hence, a lesser amount of heat is available.

$$\begin{aligned} \therefore \text{NCV} &= \text{GCV} - \text{Latent heat of condensation of water vapour produced} \\ &= \text{GCV} - \text{Mass of hydrogen} \times 9 \times \text{Latent heat of condensation of water vapour} \end{aligned}$$

### Theoretical Calculation of Calorific Value

The calorific value of fuel can be *approximately* computed by noting the amounts of the constituents of the fuel. The higher calorific value of some of the chief combustible constituents of fuel are tabulated below:

*Table : Calorific values of fuel constituents*

<i>Constituent</i>	<i>Hydrogen</i>	<i>Carbon</i>	<i>Sulphur</i>
HCV (kcal/kg)	34,500	8,080	2,240

The oxygen, if present in the fuel, is assumed to be present in combined form with hydrogen, i.e., in the form of *fixed hydrogen* (H<sub>2</sub>O). so, the amount of hydrogen available for combustion

$$= \text{Total mass of hydrogen in fuel} - \text{Fixed hydrogen}$$

$$= \text{Total mass of hydrogen in fuel} - \left(\frac{1}{8}\right) \text{Mass of oxygen in the fuel}$$

(ie., 8 parts of oxygen combine with one part of hydrogen to form H<sub>2</sub>O)

**Dulong's Formula** for calorific value from the chemical composition of fuel is:

$$\text{HCV} = \frac{1}{100} \left[ 8,080 C + 34,500 \left( \frac{\% H}{8} \right) + 2240 S \right] \text{ kcal / kg}$$

where C,H,O and S are the percentages of carbon, hydrogen, oxygen and sulphur in the fuel respectively. In this formula, oxygen is assumed to be present in combination with hydrogen as water, and

$$\text{LCV} = \left[ \text{HCV} - \frac{9}{100} H \times 587 \right] \text{ kcal / kg} = [\text{HCV} - 0.09H \times 587] \text{ kcal / kg}$$

This is based on the fact that 1 part of H by mass gives 9 parts of H<sub>2</sub>O, and latent heat of steam is 587 kcal/kg.

**PROBLEMS BASED ON CALORIFIC VALUE**

**Problem 1: Calculate the gross and net calorific values of coal having the following compositions, carbon = 85%, hydrogen = 8%, sulphur = 1%, nitrogen = 2%, ash = 4%, latent heat of steam = 587 cal/gm.**

**Solution:**

**(i) Gross Calorific Value (GCV)**

$$= \frac{1}{100} \left[ 8080 \times \% C + 34500 \left( \frac{\% H}{8} \right) + 2240 \times \% S \right] \text{ kcal / kg}$$

$$= \frac{1}{100} \left[ 8080 \times 85 + 34500 \left( \frac{8}{8} \right) + 2240 \times 1 \right] \text{ kcal / kg}$$

$$= \frac{1}{100} [6,86,800 + 2,76,000 + 2240] \text{ kcal / kg}$$

$$= \frac{1}{100} [9, 65, 040] \text{ kcal / kg}$$

$$= 9650.4 \text{ kcal/kg.}$$

**(ii) Net Calorific Value (NCV)**

$$= \text{GCV} - \frac{9}{100} \text{H} \times 587 \text{ kcal / kg}$$

$$= 9650.4 - \frac{9}{100} \times 8 \times 587 \text{ kcal / kg}$$

$$= 9650.4 - 422.64$$

$$= 9227.76 \text{ kcal / kg.}$$

**Problem 2: Calculate the net and gross calorific value of a coal sample having following composition. C = 82%, H = 8%, O = 5%, N = 1.4% and ash = 3.6%.**

**Solution:**

**(i) GCV**

$$= \frac{1}{100} \left[ 8080 \times \% C + 34500 \left( \frac{\% H}{8} \right) + 2240 \times \% S \right] \text{ kcal / kg}$$

$$= \frac{1}{100} \left[ 8080 \times 82 + 34500 \left( \frac{8}{8} \right) + 0 \right] \text{ kcal / kg}$$

$$= \frac{1}{100} [662560 + 254437.3]$$

$$= 9169.8 \text{ kcal / kg .}$$

**(ii) NCV**

$$= \text{GCV} - \frac{9}{100} \text{H} \times 587 \text{ kcal / kg}$$

$$= 9169.98 - \frac{9}{100} \times 8 \times 587$$

$$= 8747.34 \text{ kcal/kg.}$$

**Problem 3:** Calculate the gross and net calorific value of a fuel having following composition 82% C, 8% H, 5% O, 2.5% S, 1.4% N and 2.1% ash.

**Solution:** We know that,

$$\begin{aligned} \text{GCV} &= \frac{1}{100} [8080 c + 34500 (H - O / 8) + 22405] \text{ kcal / kg} \\ &= \frac{1}{100} [8080 \times 82 + 34500 (8 - 5 / 8) + 2240 \times 2.5] \\ &= 9225.97 \text{ kcal/kg} \end{aligned}$$

$$\text{NCV} = \text{GCV} - 0.09 H \times 587 \text{ kcal / kg}$$

$$\text{NCV} = 9225.97 - 0.09 \times 8 \times 587$$

$$= 8803.3 \text{ kcal/kg.}$$

### IGNITION TEMPERATURE (IT)

It is defined as “*the lowest temperature to which the fuel must be heated, so that it starts burning smoothly*”.

The ignition temperature of coal is about 300°C. In the case of liquid fuels, the ignition temperature is called the flash point, which ranges from 200–400°C. For gaseous fuels, the ignition temperature is in the order of 800°C.

### Spontaneous Ignition Temperature (SIT)

When a gaseous mixture of fuel and oxidant is maintained at ambient temperature, reaction rates are extremely slow. Increasing the mixture temperature, the reaction rate suddenly increases, giving rise to rapid combustion reactions. This condition is referred to as spontaneous ignition and the minimum temperature at which rapid combustion reactions are initiated is called **the spontaneous ignition temperature** [ $T_{sit}$ ].

The factors influencing the spontaneous ignition temperature of given mixture are the balance between heat release and heat loss, as well as the supply of reactants.

For liquid fuels, this parameter is determined using standardized tests, where liquid fuel is dropped into an open air container heated to a known temperature.

The spontaneous ignition temperature is defined as the lowest temperature at which visible or audible evidence of combustion is observed.

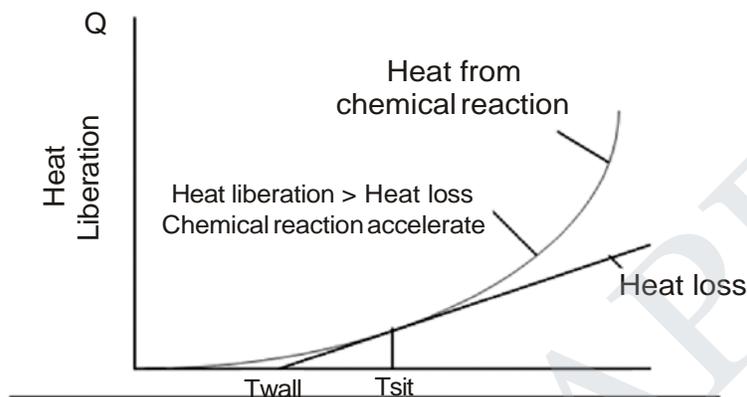


Figure 7.1 : Spontaneous Ignition Temperature

### Explosive Range (or) Limits of Inflammability

*Most of the gaseous fuels have two percentage limits called upper limit and lower limit. Those limits represent percentage by volume of fuel present in fuel-air mixture. The range covered by these limits is termed as explosive range of the fuel.*

For continuous burning the amount of fuel present in the fuel-air mixture should not go below the lower limit or above the upper limit.

For example, the explosive range of petrol is 2-4.5. This means that when the concentration of petrol vapour in petrol-air mixture is between 2 and 4.5 by volume, the mixture will burn on ignition. When the concentration of petrol vapour in petrol-air mixture is below 2% (lower limit) or above 4.5% (upper limit) by volume, the mixture will not burn on ignition.

### FLUE GAS ANALYSIS (ORSAT METHOD)

The mixture of gases like  $\text{SO}_2$ ,  $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{CO}$  etc. coming out from the combustion chamber is called flue gas.

#### *Analysis:*

The flue gas analysis is carried out by using Orsat's apparatus. The analysis of flue gas generally deals with the determination of  $\text{CO}_2$ ,  $\text{O}_2$  and  $\text{CO}$  by absorbing them in the respective solution of  $\text{KOH}$ , alkaline pyrogallol and ammonium cuprous chloride.

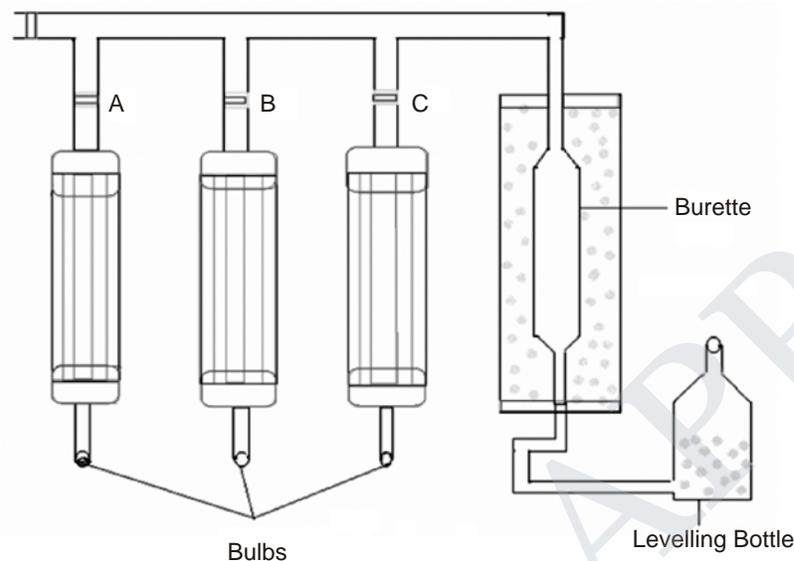


Figure 7.2 : Orsat's Apparatus

### ***Description of Orsat's Apparatus:***

Orsat's apparatus consists of a horizontal tube having 3 way stopcock at one end and a water jacketed measuring burette at the other end. The horizontal tube is connected to three different absorption bulbs for the absorption of  $\text{CO}_2$ ,  $\text{O}_2$  and  $\text{CO}$  respectively. The lower end of the burette is connected to the leveling bottle by means of rubber tube.

The level of water in the leveling bottle (water reservoir) can be raised or lowered by raising or lowering the water reservoir. By changing the level of water, the flue gas can be moved into various parts of the apparatus during analysis.

It is essential to follow the order of absorbing the gases-  $\text{CO}_2$  first;  $\text{O}_2$  second and  $\text{CO}$  last. This is because the absorbent used for  $\text{O}_2$  (ie., alkaline pyrogallol) can also absorb some amount of  $\text{CO}_2$  and the percentage of  $\text{CO}_2$  left would be less.

### ***Importance of Flue Gas Analysis:***

- (i) The analysis gives the idea of whether a combustion process is complete or not.
- (ii) The C and H present in a fuel undergo combustion forming  $\text{CO}_2$  and  $\text{H}_2\text{O}$  respectively. Any N present is not at all involved in the combustion. ie., the products of combustion are  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{N}_2$ .

- (iii) If analysis of a flue gas indicates the presence of CO; it is suggestive of incomplete combustion (Wastage of heat is inferred)
- (iv) If there is considerable amount of oxygen, it shows that there is excess supply of  $O_2$  although combustion would have been complete.

**(a) Absorption of  $CO_2$**

Flue gas is passed into the bulb A via its stopcock by raising the water reservoir.  $CO_2$  present in the flue gas is absorbed by KOH (usually 250 g KOH in 500 mL distilled water). The gas is again sent to the burette and then again sent to bulb A. This process is repeated several times, by raising or lowering of water reservoir so as to ensure complete absorption of  $CO_2$  in KOH. Now, the stopcock of bulb A is closed. The volume of residual gases in the burette is taken by equalizing the water level both in the burette and in the water reservoir. The difference between original volume and the volume of the gases after  $CO_2$  absorption gives the volume of  $CO_2$  absorbed.

**(b) Absorption of  $O_2$**

Stopcock of bulb A is closed and bulb B is opened. Oxygen present in the flue gas is absorbed by alkaline pyrogallol (25 g pyrogallol + 200g KOH in 500 mL distilled water). The absorption process is same as in bulb A.

**(c) Absorption of CO**

Now the stopcock of bulb B is closed and stopcock of bulb C is opened. Carbon monoxide present in the flue gas is absorbed by ammoniacal cuprous chloride (100 g  $Cu_2Cl_2$  + 125 mL liquid  $NH_3$  + 375 mL water). Here also absorption process is same as in bulb A.

Since the total volume of the gas taken for analysis is 100 mL, the volume of the constituents are their percentage.

The residual gas after the above three determinations is taken as nitrogen.

Further, as the content of CO in the flue gas would be very low, it should be measured quite carefully.



Unit V

# ENERGY SOURCES AND STORAGE DEVICES

Nuclear Fission – controlled nuclear fission – nuclear fusion – differences between nuclear fission and fusion – nuclear chain reactions – nuclear energy – light water nuclear power plant – breeder reactor – solar energy conversion – solar cells - wind energy. Batteries, fuel cells and supercapacitors: Types of batteries – primary battery (dry cell) secondary battery (lead acid battery, lithium-ion-battery) fuel cells H<sub>2</sub>-O<sub>2</sub> fuel cell, methanol oxygen fuel cell, SOFC and supercapacitors.

## CHAPTER 8: ENERGY SOURCES

### INTRODUCTION

*The only clean, safe energy source capable of ensuring the continuation of our industrial civilization while protecting the environment.*

*by Bruno Comby*

Nuclear energy is the energy that binds the protons and neutrons together in the nucleus (core) of an atom. Sometimes, a big nucleus splits into two smaller ones, releasing energy in the process. This process is called nuclear fission. The energy released is converted into heat, which can be used to drive a turbine and generate electricity.

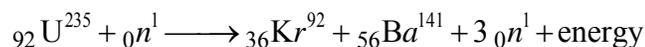
Nuclear energy is a clean, safe, reliable and competitive energy source. It is the only source of energy that can replace a significant part of the fossil fuels (coal, oil and gas) which massively pollute the atmosphere and contribute to the greenhouse effect.

In burning fossil fuels, we inject 23 billion tons of carbon dioxide every year into the atmosphere – 730 tons per second. Half of it is absorbed in the seas and vegetation, but half remains in the atmosphere. This is significantly altering the composition of the atmosphere and seriously affecting the climate of our planet.

## TYPES OF NUCLEAR REACTIONS

### Nuclear Fission

*It is the nuclear reaction in which heavy isotopes are split into lighter nuclei on bombardment by neutrons.* Fission reaction of  $U^{235}$  is given below:



- Fission is not a spontaneous process. It can only occur when a slow moving neutron strikes an unstable nucleus.
- In this decay process, the nucleus will split into two nearly equal nuclei and release several free neutrons and huge amounts of energy.
- These nuclei are isotopes of more stable elements. If left alone, they decay radioactively by emitting alpha or beta particles.
- On average, three neutrons are released. These can go on to be absorbed by other nuclei if they are slowed down by a moderator (a medium, such as graphite, heavy water, and beryllium that causes the neutrons to travel more slowly).
- If these neutrons are absorbed by other nuclei, this causes a chain reaction.
- For the chain reaction to occur there has to be a critical mass.
- For uranium, this is about the size of a tennis ball. The critical mass has a mass of about 15 kg (uranium has a very high density,  $19 \text{ g/cm}^3$ ). Anything less, the neutrons escape without setting off a chain reaction.
- If the chain reaction is not controlled, a nuclear explosion will occur.

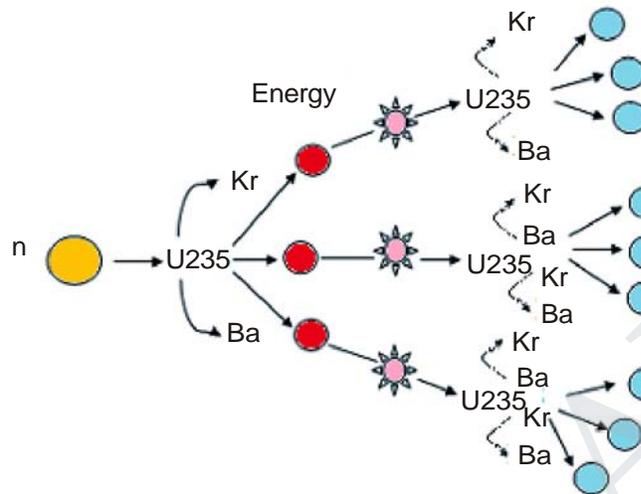
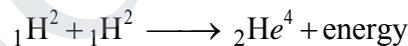


Figure 8.1 : Structure of fission reaction

### Nuclear Fusion

*Process of combination of lighter nuclei into heavier nucleus with simultaneous liberation of large amount of energy. (e.g) solar system.*



- Nuclear fusion reaction occurs in sun.
- When fusion happens, the products have a larger binding energy than the reactants. The mass defect results in the release of huge amounts of energy.
- Actually produces more energy per gram of products than fission and produces no by-products

***Why isn't it used yet then for energy production?***

- It currently requires more energy to initiate the reaction than it produces.
- Heat produced is so intense that containment vessels melt.

**Why does fusion require energy?**

- To combine, two nuclei must be close enough for the strong nuclear force to join them. But when the positive nuclei approach, the electrostatic force of repulsion is greater than the nuclear force. This means that the nuclei must be HIGHLY energetic to overcome the repulsion force.
- This means HIGH temperatures (millions of degrees Celsius), which is difficult to achieve while containing the atoms.
- Nuclear fusion is the energy-producing process taking place in the core of the Sun and stars.
- The core temperature of the Sun is about 15 million °C. At these temperatures, four hydrogen atoms fuse in a series of reactions to form a single helium atom and give off huge amounts of energy.

**DIFFERENCES BETWEEN FISSION AND FUSION REACTION**

S.No	Nuclear fission	Nuclear fusion
1.	It is a process of breaking a heavier nucleous.	It is a process of combination of lighter nuclei.
2.	It emits radioactive rays	It does not emit any kind of radioactive rays
3.	The mass number and atomic number of new elements are lower than	The mass number and atomic number of product is higher than that of starting elements
4.	It occurs at ordinary temperature	It occurs at high temperature
5.	It gives rise to chain reaction	It does not give rise to chain reaction
6.	It emits neutrons	It emits positrons
7.	It can be controlled	It cannot be controlled

**NUCLEAR CHAIN REACTIONS**

A nuclear chain reaction occurs when one nuclear reaction causes on the average one or more nuclear reactions, thus leading to a self-propagating number of these reactions. The specific nuclear reaction may be: the *fission of heavy isotopes* (e.g.  $^{235}\text{U}$ ) or the *fusion of light isotopes* (e.g.  $^2\text{H}$  and  $^3\text{H}$ )

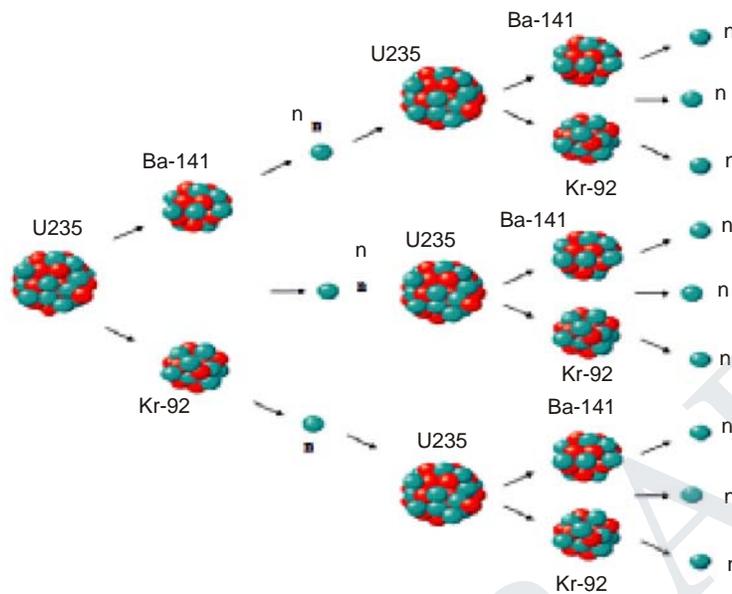


Figure 8.2 : Fission of heavy isotopes

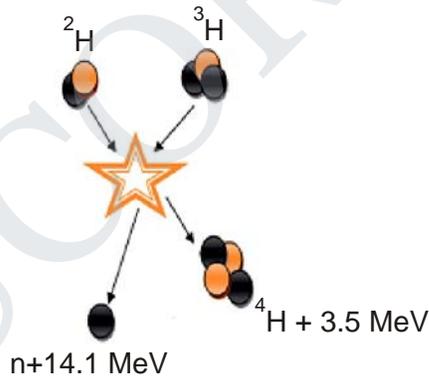


Figure 8.3 : Fusion of light isotopes

The production of 2-3 neutrons in each fission event makes it possible to use fission chain reactions for the production of energy

**A schematic nuclear fission chain reaction**

1. A uranium-235 atom absorbs a neutron and fissions into two new atoms (fission fragments), releasing three new neutrons and some binding energy.
2. One of these neutrons is absorbed by an atom of uranium-238 and does not continue the reaction. Another neutron is simply lost and does not collide with anything, also not continuing

the reaction. However one neutron does collide with an atom of uranium-235, which then fissions and releases two neutrons and some binding energy.

- Both of these neutrons collide with uranium-235 atoms, each of which fissions and releases between one and three neutrons, which can then continue the reaction.

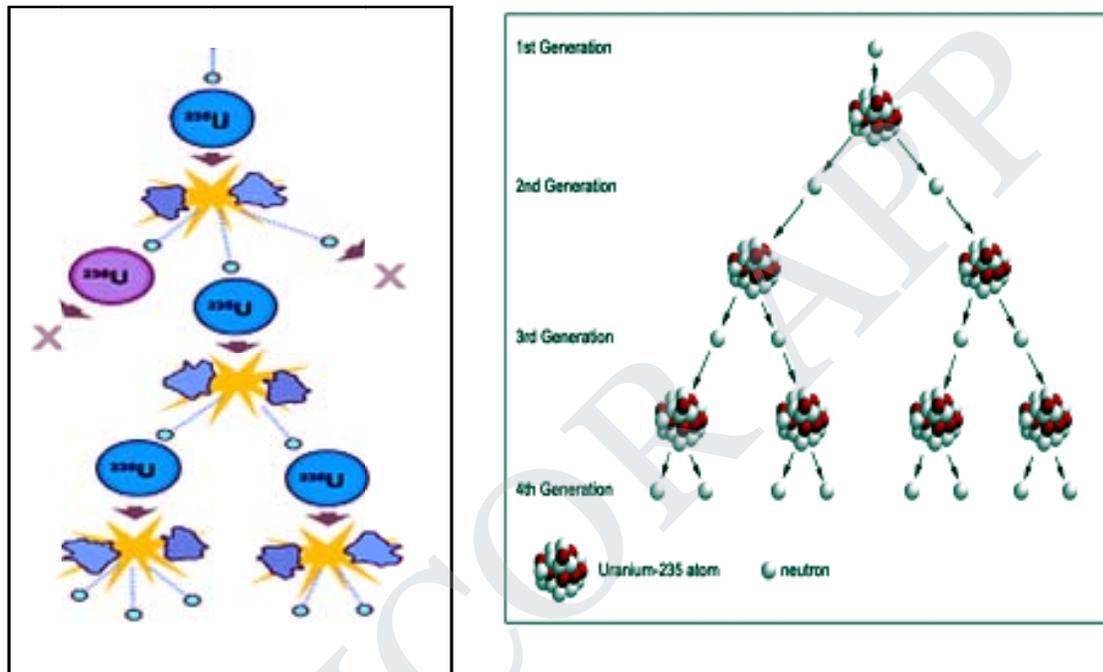


Figure 8.4 : Fission Chain Reaction

1st Generation: on average 2 neutrons

....

$k^{\text{th}}$  Generation:  $2k$  neutrons

**Mean Generation Time  $\Lambda$**  is the average time from a neutron emission to a capture that results in a fission  $\Lambda = 10^{-7} - 10^{-8}$  c

80<sup>th</sup> generation in  $10^{-5} - 10^{-6}$  c: during this time  $2^{80} = 10^{24}$  neutrons are produced which lead to

- the fission of  $10^{24}$  nuclei (140 g) of  $^{235}\text{U}$
- = release of  **$3 \cdot 10^{13}$  Watt of energy** ( $1\text{W} = 1\text{J/c}$ ,  $1\text{eV} = 1.602 \cdot 10^{-19}\text{J}$ )
- which is equivalent to 1000 tonnes of oil.

- Controlled chain reactions are possible with the isotopes  $^{235}\text{U}$ ,  $^{233}\text{U}$  and  $^{239}\text{Pu}$ .
- *The chemical element isotopes that can sustain a fission chain reaction are called nuclear fuels, and are said to be fissile.*
- The most common nuclear fuels are  $^{235}\text{U}$  (the isotope of uranium with an atomic mass of 235 and of use in nuclear reactors) and  $^{239}\text{Pu}$  (the isotope of plutonium with an atomic mass of 239).

The effective neutron multiplication factor,  $k$ , is the average number of neutrons from one fission that causes another fission.

$$k = \frac{\text{number of neutrons in one generation}}{\text{number of neutrons in preceding generation}}$$

#### **Fission chain reaction chain reactions are used**

- **Nuclear power plants** operate by precisely controlling the rate at which nuclear reactions occur, and that control is maintained through the use of several redundant layers of safety measures. Moreover, the materials in a nuclear reactor core and the uranium enrichment level make a nuclear explosion impossible, even if all safety measures failed.
- **Nuclear weapons** are specifically engineered to produce a reaction that is so fast and intense that it cannot be controlled after it has started. When properly designed, this uncontrolled reaction can lead to an explosive energy release.

#### **NUCLEAR ENERGY**

The enormous amount of energy released during the nuclear fission is due to the loss in some mass. During nuclear fission, the sum of the masses of the products formed is slightly less than the sum of masses of target species and bombarding neutron. The loss in mass gets converted into energy according to Einsteins equation

$$E = mc^2$$

where,  $C$  = velocity

$m$  = mass lose

$E$  = energy

## NUCLEAR REACTOR

### Light Water Nuclear Power plant

Light water nuclear power plant is one in which  $U^{235}$  fuel rods are submerged in water. Here the water acts as coolant and moderator.

- The fission reaction is controlled by inserting or removing the control rods of  $B^{10}$  automatically from the spaces between the fuel rods
- The heat emitted by  $U^{235}$  in the fuel core is absorbed by the coolant
- Heat is transferred to sea water and then converted into steam.
- The steam then drives the turbines, generating electricity.

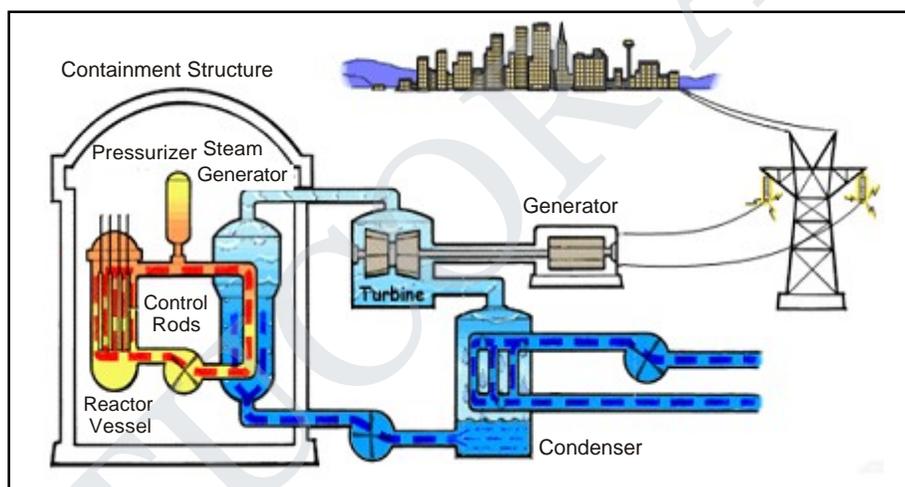
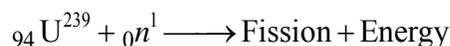
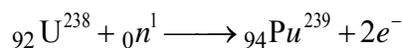


Figure 8.5 : Structure of light water nuclear power plant

### Breeder Reactor

A nuclear reactor with conversion or multiplication factor greater than one is a breeder reactor. A breeder reactor generates fissionable nuclei from fertile nuclei. E.g., the fertile material like uranium-238 is converted into fissile  ${}_{94}\text{Pu}^{239}$  by using slow neutrons.  ${}_{94}\text{Pu}^{239}$  undergoes fission and produces energy.



- A breeder reactor is a nuclear reactor that generates new fissile or fissionable material at a greater rate than it consumes such material. These reactors were initially (1940s and 1960s) considered appealing due to their superior fuel economy; a normal reactor is able to consume less than 1% of the natural uranium that begins the fuel cycle, whereas a breeder can utilize a much greater percentage of the initial fissionable material, and with re-processing, can use almost all of the initial fissionable material.
- Breeders can be designed to utilize thorium, which is more abundant than uranium. Currently, there is renewed interest in breeders because they would consume less natural uranium (less than 3% compared to conventional light-water reactors), and generate less waste, for equal amounts of energy, by converting non-fissile isotopes of uranium into nuclear fuel.
- Production of fissile material in a reactor occurs by neutron irradiation of fertile material, particularly uranium-238 and thorium-232.
- In a breeder reactor, these materials are deliberately provided, either in the fuel or in a breeder blanket surrounding the core, or most commonly in both.
- Production of fissile material takes place to some extent in the fuel of all current commercial nuclear power reactors. Towards the end of its life, a uranium PWR fuel element is producing more power from the fissioning of plutonium than from the remaining uranium-235. Historically, in order to be called a breeder, a reactor must be specifically designed to create more fissile material than it consumes.

### **SOLAR ENERGY CONVERSION**

In ancient times, wood was the most common source of heat energy. The energy of flowing water and wind was also used for limited activities. *Can you think of some of these uses?* The exploitation of coal as a source of energy made the industrial revolution possible. Increasing industrialization has led to a better quality of life all over the world. It has also caused the global demand for energy to grow at a tremendous rate. The growing demand for energy was largely met by the fossil fuels – coal and petroleum.

Our technologies were also developed for using these energy sources. But these fuels were formed over millions of years ago and there are only limited reserves. The fossil fuels are non-renewable sources of energy, so we need to conserve them. If we were to continue consuming these sources at such alarming rates, we would soon run out of energy! In order to avoid this,

alternate sources of energy were explored. But we continue to be largely dependent on fossil fuels for most of our energy requirements.

Energy development is increasingly dominated by major global concerns of over-population, air pollution, fresh water pollution, coastal pollution, deforestation, biodiversity loss, and global climate deterioration. To prevent disastrous global consequences, it would increasingly be impossible to engage in large-scale energy-related activities without insuring their sustainability, even for developing countries in which there is a perceived priority of energy development and use and power generation over their impact on the environment, society, and indeed on the energy sources themselves.

### Solar Cells

*A device which converts the solar energy (energy obtained from the sun) directly into electrical energy is called 'Solar cell'. This is also called as 'Photovoltaic cell'.*

#### Principle

The basic principle involved in the solar cells is based on the photovoltaic (PV) effect. When sun rays fall on the two layers of semiconductor devices, potential difference between the two layers is produced. This potential difference causes flow of electrons and thus produces electricity.

*Example:* Silicon solar cell

#### Construction

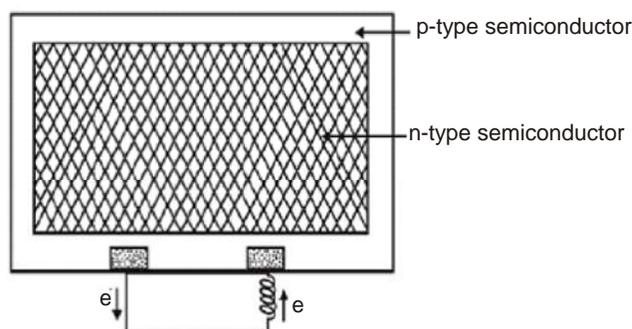


Figure 5.5 : Solar Cell

Solar cell consists of a p-type (such as Si doped with boron) and an n-type (such as Si doped with phosphorous) semiconductor plates. They are in close contact with each other.

### **Working**

When the solar rays fall on the top layer of p-type semiconductor, the electrons from the valence band get promoted to the conduction band and cross the p-n junction into n-type semiconductor. Thereby potential difference between two layers is created, which causes flow of electrons (i.e. electric current). The potential difference and hence current increases as more solar rays falls on the surface of the top layer.

Thus, when this p- and n- layers are connected to an external circuit, electrons flow from n-layer to p-layer and hence current is generated.

### **Applications of Solar Cells**

- (i) Solar cells are used in street lights.
- (ii) Water pumps are operated by using solar batteries.
- (iii) They are used in calculators, watches, radios and TVs.
- (iv) They are used for eco-friendly driving vehicles.
- (v) Silicon Solar cells are used as power source in space crafts and satellites.
- (vi) Solar cells can even be used in remote places and in forests to get electrical energy without affecting the atmosphere.

### **Wind Energy**

*Moving air is called wind. Energy recovered from the forces of wind is called wind energy.*

- Wind power is the conversion of wind energy into a useful form, such as electricity, using wind turbines. At the end of 2008, worldwide nameplate capacity of wind-powered generators was 121.2 gigawatts (GW).
- Wind turbines produce electricity by using the natural power of the wind to drive a generator.

- The wind is a clean and sustainable fuel source, it does not create emissions and it will never run out as it is constantly replenished by energy from the sun.
- In many ways, wind turbines are the natural evolution of traditional windmills, but now typically have three blades, which rotate around a horizontal hub at the top of a steel tower.
- Most wind turbines start generating electricity at wind speeds of around 3–4 metres per second (m/s), (8 miles per hour); generate maximum ‘rated’ power at around 15 m/s (30mph); and shut down to prevent storm damage at 25 m/s or above (50mph).

### Working

- Generating electricity from the wind is simple: Wind passes over the blades exerting a turning force. The rotating blades turn a shaft inside the nacelle, which goes into a gearbox.
- The gearbox increases the rotation speed for the generator, which uses magnetic fields to convert the rotational energy into electrical energy.
- The power output goes to a transformer, which converts the electricity from the generator at around 700 Volts (V) to the right voltage for the distribution system, typically between 11 kV and 132 kV.
- The regional electricity distribution networks or National Grid transmit the electricity around the country, and on into homes and businesses.

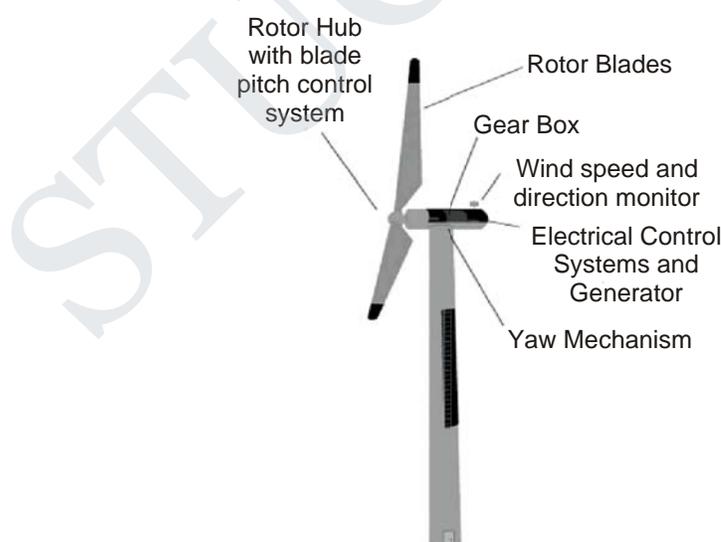


Figure 8.6 : Components of a typical wind turbine

**Advantages**

- (i) It is cheap and economical.
- (ii) It is renewable and
- (iii) It does not cause pollution.

**Disadvantages**

- (i) They produce noise.
- (ii) Wind farms erected on the migratory routes of birds create problems.
- (iii) Wind turbines interfere with electromagnetic signals.

## **CHAPTER 9: STORAGE DEVICES**

### **BATTERIES**

Battery is a device that stores chemical energy and releases it as electrical energy. Hence a device which converts chemical energy into electrical energy is called battery, cell, or storage battery.

A battery is an electrochemical cell which is often connected in series in electrical devices as a source of direct electric current at a constant voltage. A cell contains one anode and one cathode. The emf of a single cell is around 2 volt. A battery contains several anode and cathode. The emf of a battery which contains six anodes and six cathodes is around 12 V.

***Batteries are classified as follows:***

- (i) Primary battery
- (ii) Secondary battery and
- (iii) Fuel battery or Flow battery

#### **Primary Battery**

Primary battery is a cell in which the cell reaction is not reversible. Thus, once the chemical reaction takes place to release the electrical energy, the cell gets exhausted. They are use and throw type.

*Example:* Dry cell, Leclanche cell etc.

### Dry Cell or Leclanche's Cell

A cell without fluid component is called as dry cell.

*Example:* Daniel Cell, Alkaline Battery.

#### Construction and Working

The anode of the cell is zinc container containing an electrolyte consisting of  $\text{NH}_4\text{Cl}$ ,  $\text{ZnCl}_2$  and  $\text{MnO}_2$  to which starch is added to make it thick paste-like so that is less likely to leak. A graphite rod serves as the cathode, which is immersed in the electrolyte in the centre of the cell.

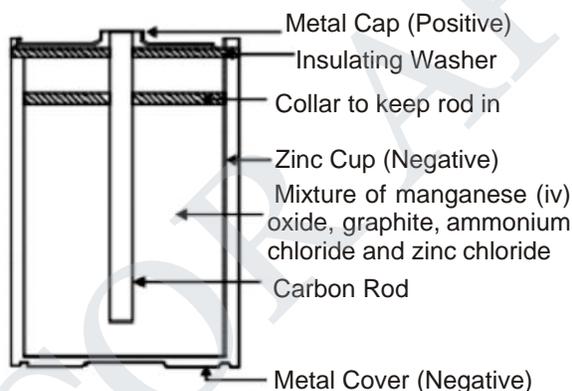


Figure 9.1 : Leclanche's Cell

The electrode reactions are given below.

#### Anodic Reaction

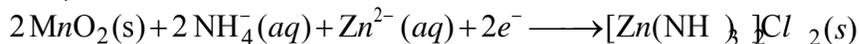
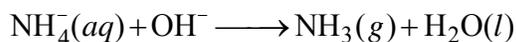


(Oxidation)

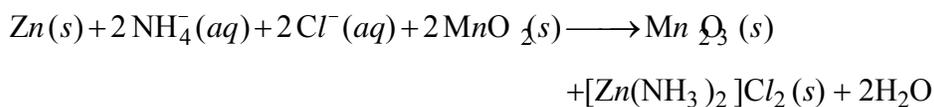
#### Cathodic Reaction



(Reduction)



#### Overall Reaction



The dry cell is a primary battery, since no reaction is reversible by supplying electricity. Dry cell is very cheap to make. It gives voltage of about 1.5 V.

### Advantages

- (i) When current is drawn rapidly, drop in voltage occurs.
- (ii) Since the electrolyte is acidic, Zn dissolves slowly even if it is not in use.

### Uses

- Dry cells are used in flash-lights, transistor radios, calculators, etc

### Secondary Battery

Secondary battery is a cell in which the cell reaction is reversible. They are rechargeable cells. Once the battery gets exhausted, it can be recharged.

*Example:* Nickel-Cadmium cell, Lead-acid cell (storage cell), etc.

### Lead–Acid Storage Cell

The typical example for storage cell is Lead-acid storage cell. A secondary battery can operate as a voltaic cell and as an electrolytic cell. When it acts as a voltaic cell, it supplies electrical energy and becomes run down. When it is recharged, the cell operates as an electrochemical cell.

### Construction and Working

A lead – acid storage cell consists of a number of voltaic cells (3 to 6) connected in series to get 6 to 12 V battery. In each cell, a number of Pb plates, used as anodes are connected in parallel and a number of PbO<sub>2</sub> plates, used as cathodes are connected in parallel. The plates are separated by insulators like rubber or glass fibre. The entire combination is immersed in 20% dil. H<sub>2</sub>SO<sub>4</sub>.

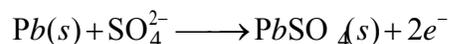
The cell is represented as:



When the lead-acid storage battery operates, the following cell reactions occur.

**Anodic Reaction**

Oxidation reaction takes place at anode. The electrons are released from anode. Hence the anode is called as negative anode and is represented as (-). Lead is oxidized to  $Pb^{2+}$  ions and gives two electron, which further combines with  $SO_4^{2-}$  to form insoluble  $PbSO_4$ .

**Cathodic Reaction**

Reduction takes place at cathode. Hence the cathode is called as positive cathode and is represented as (+).  $PbO_2$  is reduced to  $Pb^{2+}$  ions, which further combines with  $SO_4^{2-}$  to form insoluble  $PbSO_4$ .

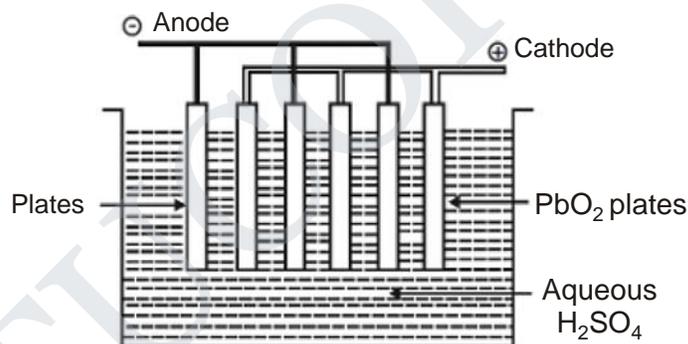
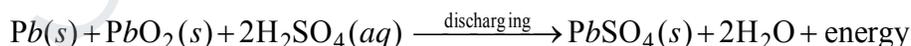


Figure 9.2 : Lead Storage Cell

**Overall cell reaction during discharging**

From the above cell reactions, it is clear that  $PbSO_4$  is precipitated at both the electrodes and the concentration of  $H_2SO_4$  decreases. So, the battery needs recharging.

**Overall cell reaction during recharging**

The cell can be recharged by passing electric current in the opposite direction. The electrode reaction gets reversed. As a result,  $Pb$  is deposited on anode and  $PbO_2$  on the cathode. The concentration of  $H_2SO_4$  also increases.

**Advantages of Lead–Acid batteries**

1. It is made easily.
2. It produces very high current.
3. The self-discharging rate is low.
4. It works effectively even at low temperatures.

**Uses**

1. Lead – acid batteries are used in cars, buses, trucks etc.
2. It is used in gas engine ignition, telephone exchanges, and power stations hospitals.
3. IT industry, educational institutions, laboratories etc.

**Li–Ion Batteries**

Li-Ion Batteries consist of a three primary functional components. The main components of a Li-ion battery device are the positive electrode, negative electrode and the electrolyte, for which a variety of materials may be used.

Generally, the most useful material for the positive electrode is one of three materials: lithium cobalt oxide, lithium iron phosphate, or a spinel such as lithium  $MnO_2$ .

On the other hand, the most common materials for the negative electrode are carbon based compounds and lithium- containing alloys.

Upon charging, lithium ions are extracted from the positive electrode material and inserted into the negative electrode material. Upon discharging, the reverse process takes place. Common batteries should exhibit three characteristics:

- (a) high energy and power capacity,
- (b) high charging rate, and
- (c) long lifetime (cycling stability).

Although Li-ion batteries are available commercially, the performance of Li-ion batteries is limited by the current electrode and electrolyte materials. For future generations of rechargeable Li-ion batteries, not only for applications in portable electronic devices but especially for clean energy storage and use in hybrid electric vehicles, further improvements of materials are essential.

We need to find new, efficient and effective ways to improve the physical and chemical characteristics of the materials for use in electrochemical Li-ion batteries.

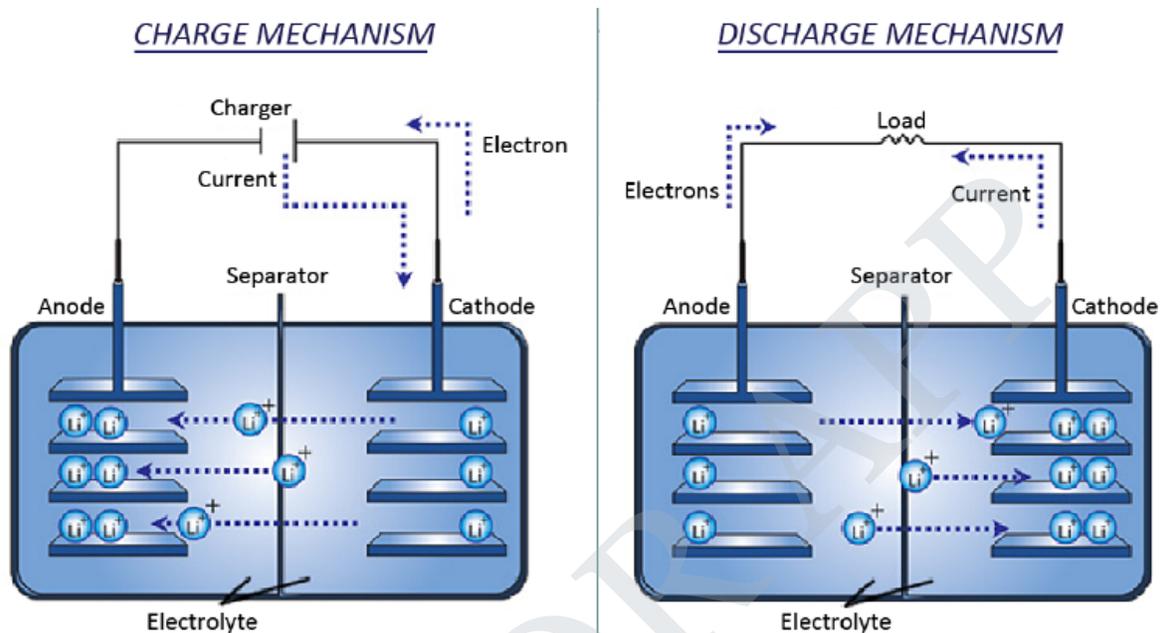


Figure 9.3 : Lithium ion cell during charging and discharging

### Fuel Battery or Flow Battery

Flow battery is an electrochemical cell that converts the chemical reaction into electrical energy. When the reactants are exhausted, new chemicals replace them.

*Example:* Hydrogen-oxygen cell, Aluminium-air cell, etc.

In Aluminium-air cell, when the cell is exhausted, a new aluminium rod is used and the solution is diluted with more water as the electrochemical reaction involves aluminium and water.

### FUEL CELLS

First developed by William Grove In 1839, Grove was experimenting on electrolysis (the process by which water is split into hydrogen and oxygen by an electric current), when he observed that combining the same elements could also produce an electric current.

*A fuel cell is an electrochemical conversion device. It produces electricity from fuel (on the anode side) and an oxidant (on the cathode side), which react in the presence of an electrolyte. The reactants flow into the cell, and the reaction products flow out of it, while the*

electrolyte remains within it. Fuel cells can operate virtually continuously as long as the necessary flows are maintained.

Fuel Cells are different from electrochemical cell batteries in that they consume reactant from an external source, which must be replenished – a thermodynamically open system. By contrast, batteries store electrical energy chemically and hence represent a thermodynamically closed system.

Many combinations of fuels and oxidants are possible. A hydrogen fuel cell uses hydrogen as its fuel and oxygen (usually from air) as its oxidant. Other fuels include hydrocarbons and alcohols. Other oxidants include chlorine and chlorine dioxide.

### ***Classification of Fuel Cells***

*Based on the type of Electrolyte*

1. Polymer Electrolytic Membrane Fuel Cell (PEMFC)
2. Direct Methanol Fuel Cell (DMFC)
3. Alkaline Fuel cell (AFC)
4. Phosphoric Acid Fuel cell (PAFC)
5. Molten Carbonate Fuel Cell (MCFC)
6. Solid Oxide Fuel Cell (SOFC)

### **Hydrogen Oxygen Fuel Cells**

- In Polymer Electrolyte Membrane (PEM) fuel cells, protons move through the electrolyte to the cathode to combine with oxygen and electrons, producing water and heat.
- Polymer Electrolyte Membrane (PEM) fuel cell uses a polymeric membrane as the electrolyte, with platinum electrodes.
- These cells operate at relatively low temperatures.
- These cells are the best candidates for cars, for buildings and smaller applications. Polymer Electrolyte Membrane (PEM) fuel cells—also called proton exchange membrane fuel cells—deliver high power density and offer the advantages of low weight and volume, compared to other fuel cells.

- PEM fuel cells use a solid polymer as an electrolyte and porous carbon electrodes containing a platinum catalyst.
- They only hydrogen, oxygen from the air, and water to operate and do not require corrosive fluids like some fuel cells. They are typically fueled with pure hydrogen supplied from storage tanks or onboard reformers.
- The platinum catalyst is also extremely sensitive to CO poisoning, making it necessary to employ an additional reactor to reduce CO in the fuel gas if the hydrogen is derived from an alcohol or hydrocarbon fuel. This also adds cost.
- Developers are currently exploring platinum/ruthenium catalysts that are more resistant to CO.

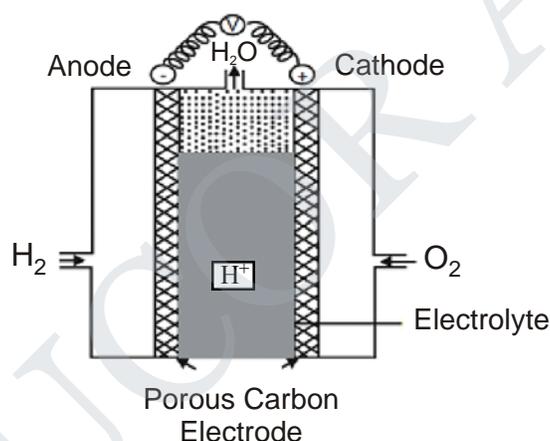
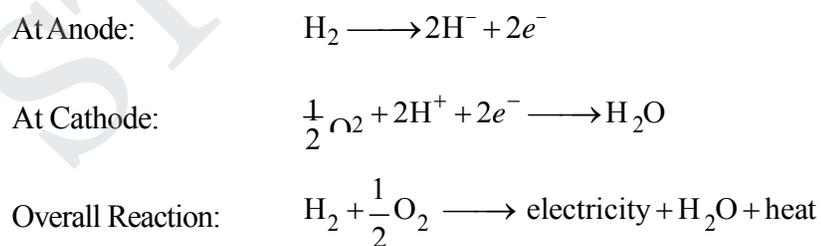


Figure 9.4 : Hydrogen-Oxygen Fuel Cells



### Advantages

1. They are efficient and instant in operation.
2. They are pollution free.

3. They produce electric current directly from the reaction of a fuel and an oxidizer.
4. They are light in weight

**Disadvantages**

1. Fuel cells cannot store electric energy.
2. Electrodes are expensive and short lived.
3. H<sub>2</sub> should be pure.

**Applications**

1. H<sub>2</sub>-O<sub>2</sub> fuel cells are used in space crafts, submarines to get electricity
2. In H<sub>2</sub>-O<sub>2</sub> fuel cell, the product water is a valuable source of fresh water for astronauts.

**SUPERCAPACITORS**

Supercapacitors represent an important component for energy storage devices, particularly for short-acting high power batteries. Batteries suffer from a relatively slow power delivery or uptake, faster and higher-power energy storage systems are needed in a number of applications, and this role has been given to the supercapacitors.

- The highest performance supercapacitors are currently based on NSMs, given that increased electrode surface area improves the capacitance. It is the reason why so many researchers have been involved in working on different kinds of NSMs.
- In brief, supercapacitors are formed by two polarizable electrodes, a separator and an electrolyte. They utilize double layer capacitance where the ions of the electrolyte are adsorbed on the charged electrode, resulting in a Helmholtz layer.
- The Helmholtz double layer thickness is defined as half the diameter of the adsorbed solvated ions at the electrode/solution interface. The power density of supercapacitors is lower than that of batteries.

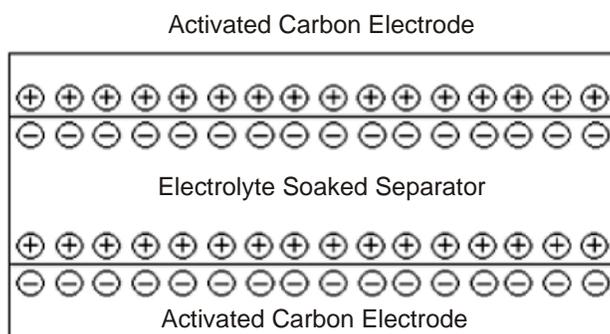


Figure 9.5 : Typical construction of a super capacitor

Therefore, the development of supercapacitors aims to improve the power density and significantly reduce cost. These electrochemical devices are also known as *ultracapacitors*, *pseudo capacitors*, and *Electric Double Layer Capacitors (EDLC)*.

